

## Full Length Research Paper

# Distribution and ecological risk assessment of pesticide residues in surface water, sediment and fish from Ogbesse River, Edo State, Nigeria

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The contamination of pesticides in water, sediments, *Clarias gariepinus*, and *Tilapia zilli* from Ogbesse River was investigated to evaluate the pollution status and potential hazard in river system. A total of sixteen pesticides were analyzed using Gas Chromatography (GC) equipped with Electron Capture Detector (GC-ECD). The concentration of pesticide residues ranged from ND to 0.43 µg/l for water samples, 0.82 to 2.14 µg/kg dw for sediment, 0.04 to 2.34 µg/kg/ww for *C. gariepinus* and 0.02 to 1.73 µg/kg/ww for *T. zilli*. There was a clear dominance of the organochlorine; Hexachlorocyclohexane ( $\alpha$  HCH,  $\gamma$  - HCH (lindane),  $\beta$ - HCH) in all matrixes. Ecological risk assessment of pesticide residues in water samples using the Risk Quotient deterministic method showed the likelihood of cause adverse effects for each fish species ( $RQ \geq 1$ ). Human health risk assessment indicated that the consumption of contaminated fishes (*C. gariepinus* and *T. zilli*) could have potential health implications.

**Key words:** Pesticides, chromatography, risk quotient, estimated daily intake, hazard quotient, environmental exposure.

## INTRODUCTION

In a quest to increase agricultural productivity there has been an increase in the use of pesticides. Pesticides include insecticides, herbicides, rodenticides, and fungicides (Chopra et al., 2010). These persistent organic pollutants (POPs) have become an integral part of the Nigerian society and are being used for diverse activities ranging from crop protection from insect pests, weeds, rodents and fungal diseases to animal husbandry and public health applications (Zhou et al., 2006). Despite these overwhelming benefits, chemical pesticides are usually not target-specific and may cause harm to non-

target organisms. Most pesticides are very persistent, remaining in the environment for long periods (Chopra et al., 2010). Due to their stable structure and lipophilic character, pesticides, especially organochlorine pesticides (OCPs), tend to bioconcentrate and biomagnify in the food chains particularly those associated with fatty tissues, leading to vertebrate and non-vertebrate toxicity in non-target organisms and even humans (Okoya et al., 2013; Masia et al., 2013; Ize-Iyamu et al., 2007). Upadhi and Wokoma (2012), Williams (2013), Ezemonye et al. (2008a, b, 2009),

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Ize-Iyamu et al. (2007), Adeboyejo et al. (2011), Okeniyia et al. (2009) and Adeyemi et al. (2011) are few studies that have provided evidence of pesticide contamination in various environmental compartments in some rivers in Nigeria. Protecting Nigeria's fresh water bodies from pesticides and other pollutants is of utmost importance due to their prevailing toxicity even at trace levels. Thus, data pertaining to pesticide concentration in rivers are very critical.

The purpose of this research is to determine the presence of selected pesticides in water, sediment and biota of the Ogbesse River. To our knowledge, few studies have assessed the risk of pesticide occurrence to non-target organisms and humans in Nigeria. Therefore this study assesses the ecotoxicological risk to non-target organisms accrued by the presence of these pesticides and also establishes the risk of exposure to humans as a result of the eventual consumption of pesticide contaminated fishes.

## MATERIALS AND METHODS

### Site description and sampling

Ogbesse River is located in Ogbesse town (N 06° 45' 40", E 005° 46' 07.4") within the forest belt ecological zone of Edo State, Figure 1. It is prominent for cocoa, plantain and pepper production. The river separates Ondo and Edo States. The surrounding area of this river is typified by the presence of commercial cocoa farms, which constantly make use of agrochemicals to enhance their production. Water samples (n=216) were collected from three sites along the stretch of the river, 0.3 m below the water surface with a pre-cleaned glass bottle using hydrobios sample based on the method by Ezemonye et al. (2008a,b).

Sediment samples (n=216) were also collected using methods described by Ezemonye et al. (2008a,b). Samples were taken from the positions where an accumulation of fine-texture substrate took place. The upper 2 cm of bed sediment at each site were collected with a Teflon-coated spoon and wrapped in aluminum foil. Samples of *Clarias gariepinus* and *Tilapia zilli* were captured randomly and/or bought from fishermen around each river (Ize-Iyamu et al., 2007). Samples were collected monthly for 18 months.

### Extraction and analysis

Sediment samples were extracted and cleaned up according to the method described by USEPA (2004). Edible portions of *C. gariepinus* and *T. zilli* samples were extracted and cleaned up according to Steinwandter (1992), while water samples were extracted and cleaned up based on Osibanjo and Adeyeye (1997) and USEPA (2004). The cleaned up extracts were analyzed for pesticides ( $\alpha$  HCH,  $\gamma$  - HCH,  $\beta$  - HCH, Heptachlor, Heptachlor Epoxide, Aldrin, Dieldrin, Endrin, p,p DDT, Endosulfan I, Endosulfan II, Endosulfan aldehyde, Endosulfan sulfate, Atrazine, Glyphosate and Carbofuran).

Results were obtained using a Hewlett-Packard (hp) 5890 Series II equipped with 63Ni Electron Capture Detector (ECD) of activity 15 mCi with an auto sampler. The efficiency of the analytical method (the extraction and clean-up methods) was determined by recoveries of an internal standard. Peak identifications were conducted by comparing the retention time of standards and those obtained from the extracts. Concentrations were calculated using a

four-point calibration curve. Method detection limits (MDLs) ranged from 0.005  $\mu\text{g/l}$  for pesticides in water and 0.01  $\mu\text{g/g/dw}$  for pesticides in sediment and biota. A simple, rapid solvent extraction method was used to determine total lipids in each fish tissue based on the method described by Randall et al. (1998) and lipid normalized concentrations were obtained using the ratio between pesticide concentration in tissue and lipid fraction in the tissue.

### Risk assessment

Risk Quotient Method (RQ) was used to determine the risk of pesticide exposure in aquatic organisms. RQ is the ratio of the Measured Environmental Concentration (MEC) to the Predicted No Effect Concentration (PNEC). The predicted no effect concentration (PNEC) was obtained by multiplying the  $\text{LC}_{50}$  with an assessment factor (AF) of 100.  $\text{LC}_{50}$  was obtained from Munn et al. (2006). The assessment factor takes into account the uncertainty in extrapolation from laboratory toxicity tests for a limited number of species to the real environment (Sangchan et al., 2012).

### PCA analysis

Residues obtained from water, sediment and fish analysis was subjected to Principal Component Analysis (PCA) using SPSS 20 statistical software to infer the hypothetical sources of pesticides. PCA was performed by varimax rotation because it minimizes the number of variables with a high loading on each component, facilitating the interpretation of PCA results (Frimpong et al., 2013).

### Health risk estimation

To assess the risk of pesticide contained in each fish species on consumers, the guidelines for potential risk assessment drawn up by the US EPA were used. Estimated Average Daily Intake (EADI) was obtained by multiplying the residual pesticide concentration ( $\mu\text{g/kg}$ ) in each fish species by the consumption rate in Nigeria ( $\text{kg/day}$ ) and dividing the product by the body weight ( $\text{kg}$ ) (WHO 1997; Fianko et al., 2011). The food and agricultural organization (FAO, 2011) quotes the per capita consumption of fishes in Nigeria as 9 kg per year.

## RESULTS AND DISCUSSION

### Concentration of pesticides in water

Concentrations of pesticides in water are shown in Table 1 and Figure 2, with Heptachlor Epoxide having the highest mean concentration (0.4  $\mu\text{g/l}$ ). Overall, HCHs (31%) were the most dominant pesticide recorded in water samples. The concentration of pesticide residues was significantly higher ( $p \geq 0.05$ ,  $t = 0.41$ ) during the wet season when compared with the dry season.

The presence of these pesticides residues in water samples from Ogbesse River is indicative of the possible contamination of the river through various anthropogenic sources within the region especially agriculture. It was also observed that concentrations of pesticide residues in this study were higher than recommended guideline value for pesticides residues in fresh water bodies set by European Union (EU) (0.1  $\mu\text{g/l}$ ) (Hamilton et al., 2003).

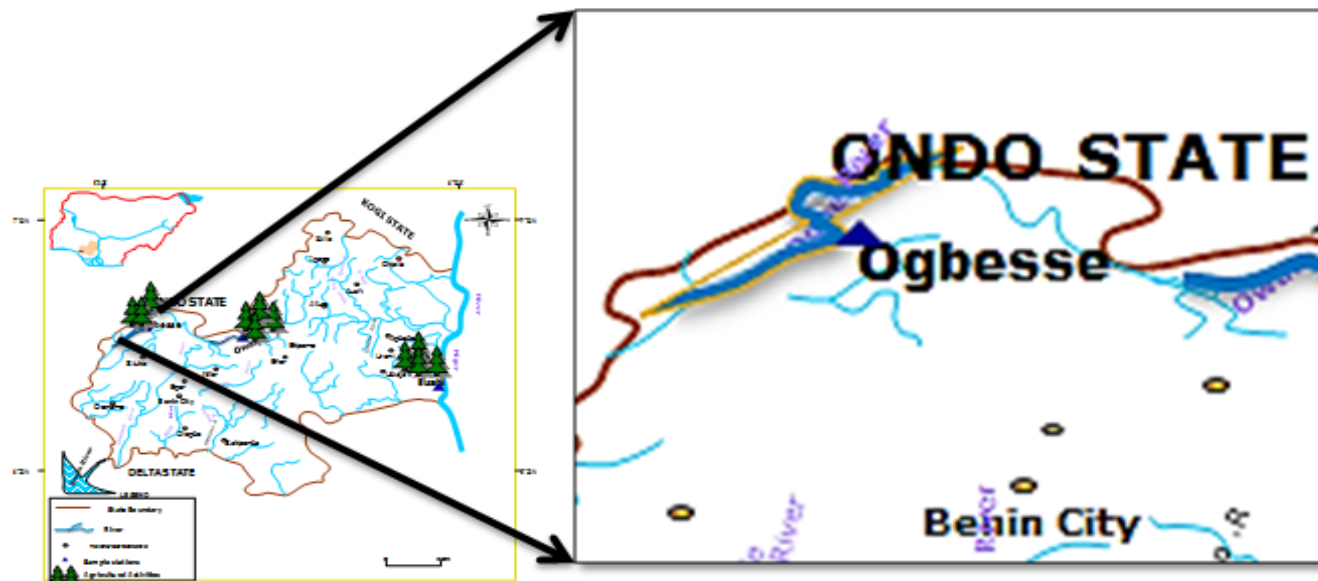


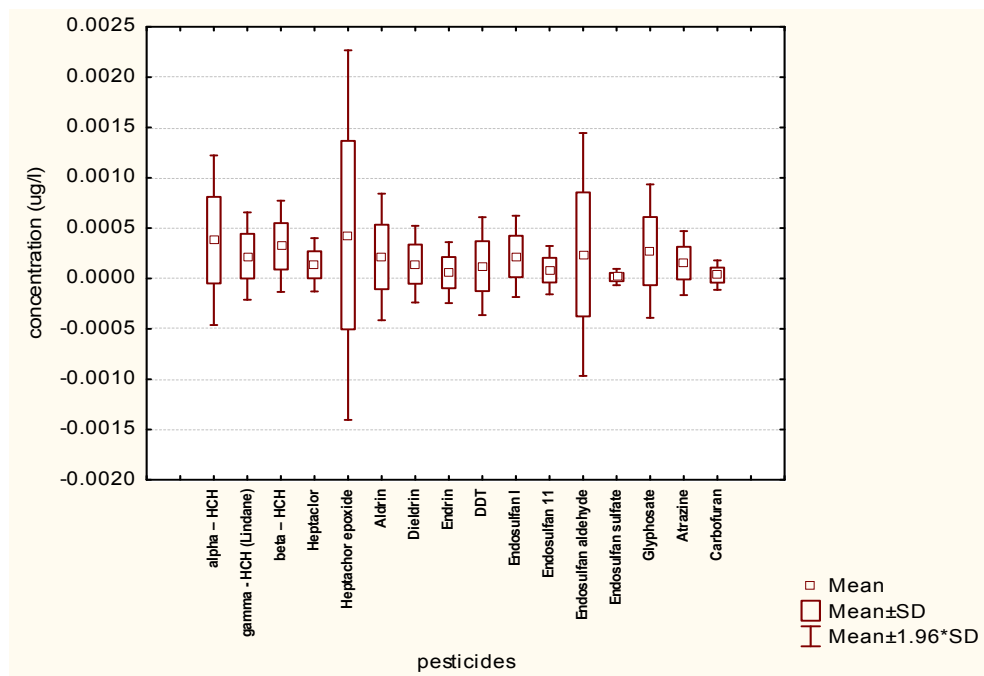
Figure 1. Map showing the study area and sampling points.

Table 1. Concentration of pesticide residues in surface water, sediment and fish for Ogbesse River.

Pesticide residues	Water ( $\mu\text{g/l}$ )	Sediment ( $\mu\text{g/gdw}$ )	<i>Clarias gariepinus</i> ( $\mu\text{g/gdw}$ )	<i>Tilapia zilli</i> ( $\mu\text{g/gww}$ )
	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD
Alpha – HCH	0.38 $\pm$ 0.10	2.14 $\pm$ 0.32	1.86 $\pm$ 0.44	0.88 $\pm$ 0.32
Gamma - HCH (Lindane)	0.22 $\pm$ 0.05	1.26 $\pm$ 0.37	0.66 $\pm$ 0.15	0.13 $\pm$ 0.05
Beta – HCH	0.32 $\pm$ 0.05	1.81 $\pm$ 0.42	2.34 $\pm$ 0.68	1.73 $\pm$ 0.60
Heptaclor	0.14 $\pm$ 0.03	1.35 $\pm$ 0.47	0.43 $\pm$ 0.19	0.74 $\pm$ 0.36
Heptachlor epoxide	0.43 $\pm$ 0.22	1.07 $\pm$ 0.31	0.25 $\pm$ 0.10	0.17 $\pm$ 0.06
Aldrin	0.21 $\pm$ 0.08	1.30 $\pm$ 0.40	0.63 $\pm$ 0.19	0.12 $\pm$ 0.06
Dieldrin	0.14 $\pm$ 0.05	0.94 $\pm$ 0.46	0.53 $\pm$ 0.21	0.08 $\pm$ 0.03
Endrin	0.06 $\pm$ 0.04	0.66 $\pm$ 0.28	0.45 $\pm$ 0.27	0.07 $\pm$ 0.04
DDT	0.12 $\pm$ 0.06	0.85 $\pm$ 0.34	0.04 $\pm$ 0.03	0.08 $\pm$ 0.05
Endosulfan I	0.22 $\pm$ 0.05	1.06 $\pm$ 0.31	0.13 $\pm$ 0.10	0.22 $\pm$ 0.08
Endosulfan 11	0.08 $\pm$ 0.03	0.81 $\pm$ 0.28	0.38 $\pm$ 0.30	0.03 $\pm$ 0.03
Endosulfan aldehyde	0.23 $\pm$ 0.15	1.03 $\pm$ 0.34	0.27 $\pm$ 0.12	0.02 $\pm$ 0.02
Endosulfan sulfate	0.01 $\pm$ 0.01	0.25 $\pm$ 0.12	0.26 $\pm$ 0.23	0.16 $\pm$ 0.10
Glyphosate	0.27 $\pm$ 0.08	1.20 $\pm$ 0.35	0.86 $\pm$ 0.51	0.42 $\pm$ 0.21
Atrazine	0.15 $\pm$ 0.04	0.94 $\pm$ 0.26	0.63 $\pm$ 0.28	0.09 $\pm$ 0.03
Carbofuran	0.03 $\pm$ 0.02	0.82 $\pm$ 0.35	0.22 $\pm$ 0.22	0.02 $\pm$ 0.02

While HCH, Endosulfan, Endrin, DDT, Dieldrin and Carbofuran, were above Canadian EPA and WHO guideline values for domestic and drinking purposes, concentrations observed in water samples were also higher than the allowable residual limit of individual and total concentration of pesticides residues in drinking water at 0.1 and 0.5  $\mu\text{g/l}$ , respectively set by NISERA (Adeyemi et al., 2008). Further comparison with previous

studies showed that concentrations observed in this study were lower than concentrations of pesticides residues observed in Lagos lagoon (Adeyemi et al., 2011), Benin rivers (Ogba, Okoro and Ovia) (Ize-Iyamu et al., 2007) and Warri rivers (Ezemonye et al., 2008a) in a study in Warri rivers. However concentrations observed in this study were higher than those observed in the Niger Delta (Upadhi and Wokoma, 2012), Lagos Lagoon



**Figure 2.** Profile of pesticide residues in water samples from Ogbesse River.

(Williams, 2013; Adeboyejo et al., 2011); Rivers in the South West Nigeria (Okeniyia et al., 2009); Northern River (Darko and Babayo, 2013), and Ondo Rivers (Okoya et al., 2013).

### Concentration of pesticides in sediment

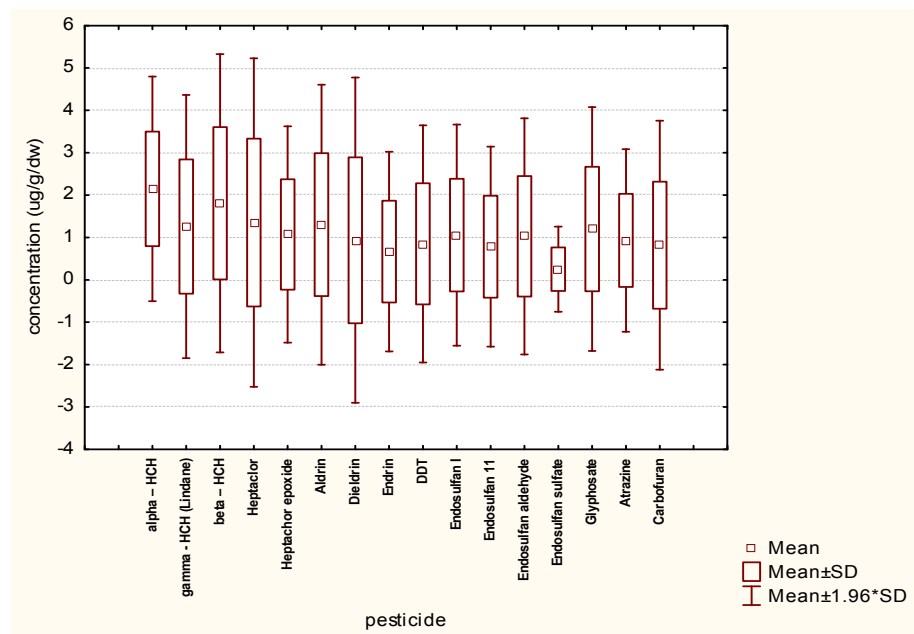
All the selected pesticides were detected in sediment samples obtained from Ogbesse River (Table 1, Figure 3). It was observed that alpha HCH had the highest mean concentration (2.4  $\mu\text{g}/\text{kgdw}$ ) while overall HCHs (29%) was the predominant pesticide. It was also observed that the concentration of pesticide residues in sediment samples were relatively higher during the dry season compared with the wet season. However, there was no significant difference ( $p \geq 0.05$ ,  $t = 0.83$ ) between the concentrations of pesticides residues observed during the dry season and the wet season. There was a higher concentration of pesticide residues in sediment samples compared to water samples, which indicates the hydrophobic nature of the pesticides detected (Ezemonye et al., 2008b; Ezemonye et al., 2009; Williams, 2013).

Hexachlorocyclohexane (HCH) showed predominance in this river, indicating the introduction of HCH to sediments via runoffs from surrounding agricultural areas, where HCH pesticides have been used or are currently being used (Olatunbosun et al., 2011). Furthermore, the half-life of HCH and its isomers in the environment ranges from 15 months, 50 days and 20 days for alpha HCH, gamma HCH and beta HCH respectively (FAO,

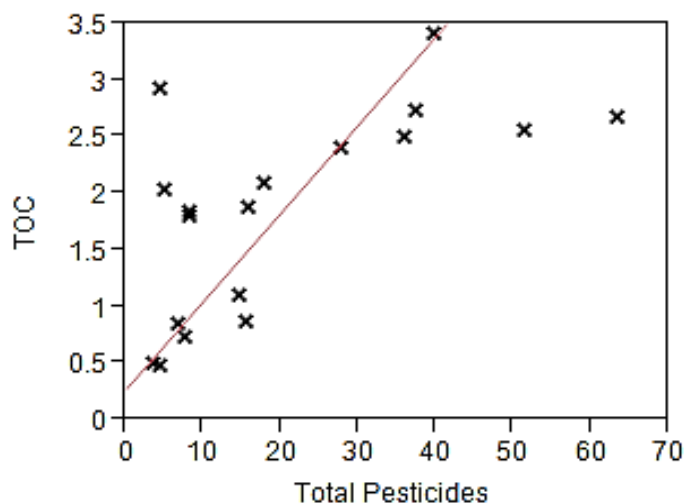
1997); hence, the detection of these pesticides is indicative of the fact that they were recently applied. This is further confirmed by the ratio of  $\alpha$ -HCH and  $\gamma$ -HCH. In the entire river sampled,  $\alpha$ -HCH /  $\gamma$ -HCH ratio in sediment samples were below 3, indicating that the source of HCH in the environment is a fresh input of technical HCH (Chen et al., 2009). There was also a positive correlation between the total organic carbon content and pesticide concentration in sediments, which indicates that the sediment organic carbon could enhance adsorption and deposition of these pesticides compounds (Figure 4). This finding is similar to Devi et al. (2013), who reported significant correlations between organochlorines and TOC in India, but does not agree with the studies by Olatunbosun et al. (2011) and Liu et al. (2008), who reported that there was no correlation between OCPs and TOC in sediment from water bodies in Niger Delta and China respectively, suggesting that TOC has no influence on the distribution of OCPs in the sediments.

### Concentration of pesticide in biota

Lipid normalized concentrations of pesticides in the two fish species collected from Ogbesse River is presented in Table 1 and Figures 5 and 6. In *C. gariepinus*, Beta HCH had the highest mean concentration (2.34  $\mu\text{g}/\text{gdw}$ ) while p,p DDT had the lowest mean concentration (0.04  $\mu\text{g}/\text{gdw}$ ). Seasonal distributions indicate that each pesticide residue in *C. gariepinus* had high concentrations during the wet season. However, there



**Figure 3.** Profile of pesticide residues in sediment samples from Ogbesse River.



**Figure 4.** Correlation between total organic carbon and total pesticide concentration in sediment sample from Ogbesse River ( $r^2 = 0.6$ ).

was no significant difference ( $p \geq 0.05$ ,  $t=0.09$ ) between the concentrations of pesticides residues during the dry season and the wet season.

On the other hand, beta HCH had the highest mean concentration ( $1.73 \mu\text{g/gww}$ ) in *T. zilli* samples and seasonal distribution showed higher concentrations of each pesticide during the wet season. However, there was no significant difference ( $p \geq 0.05$ ,  $t=0.61$ ) between the concentrations of pesticides residues observed during the dry season and the wet season. Overall, HCHs were

predominant in *C. gariepinus* and *T. zilli*. The presence of pesticides in *C. gariepinus* and *T. zilli* could be attributed to uptake either through bioconcentration from water through gills or epithelial tissues and through bioaccumulation through water and through food leading to eventual biomagnification in different organisms, occupying successive trophic levels (Murty, 1986). Hence, the presence of pesticide residues implies that there is clear evidence of the bioconcentration and bioaccumulation of pesticides from the surrounding

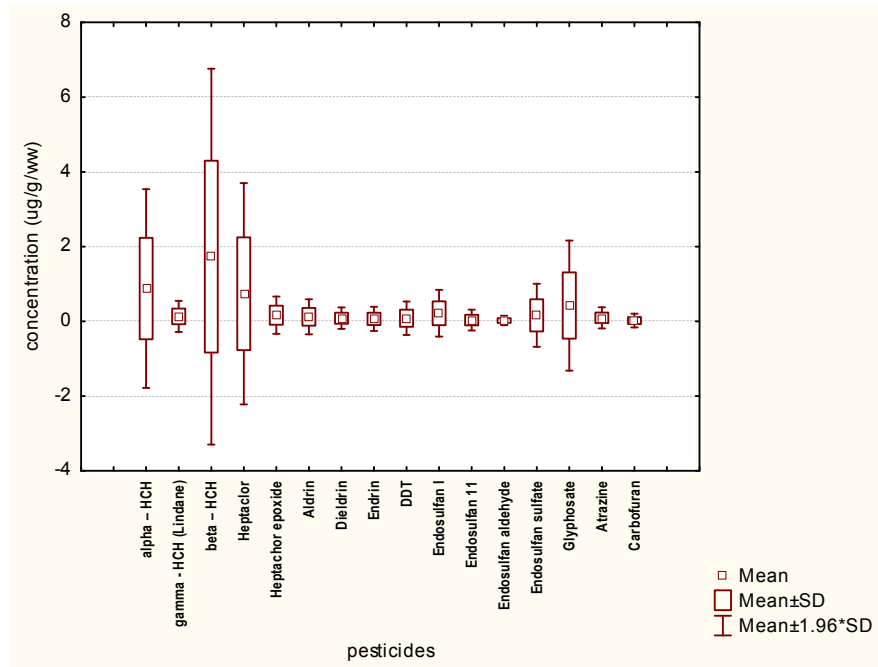


Figure 5. Profile of pesticide residues in *Tilapia zilli* samples from Ogbesse River.

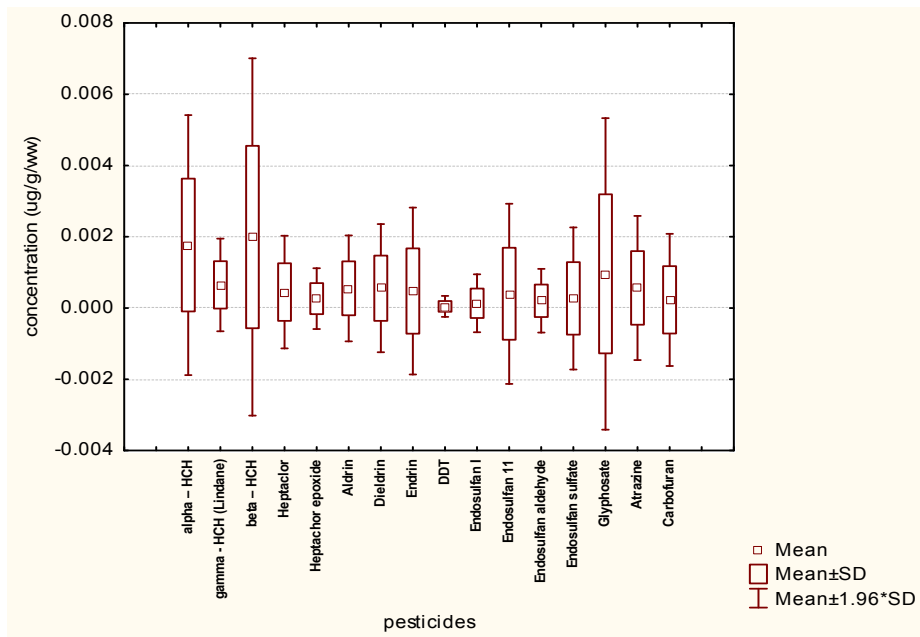
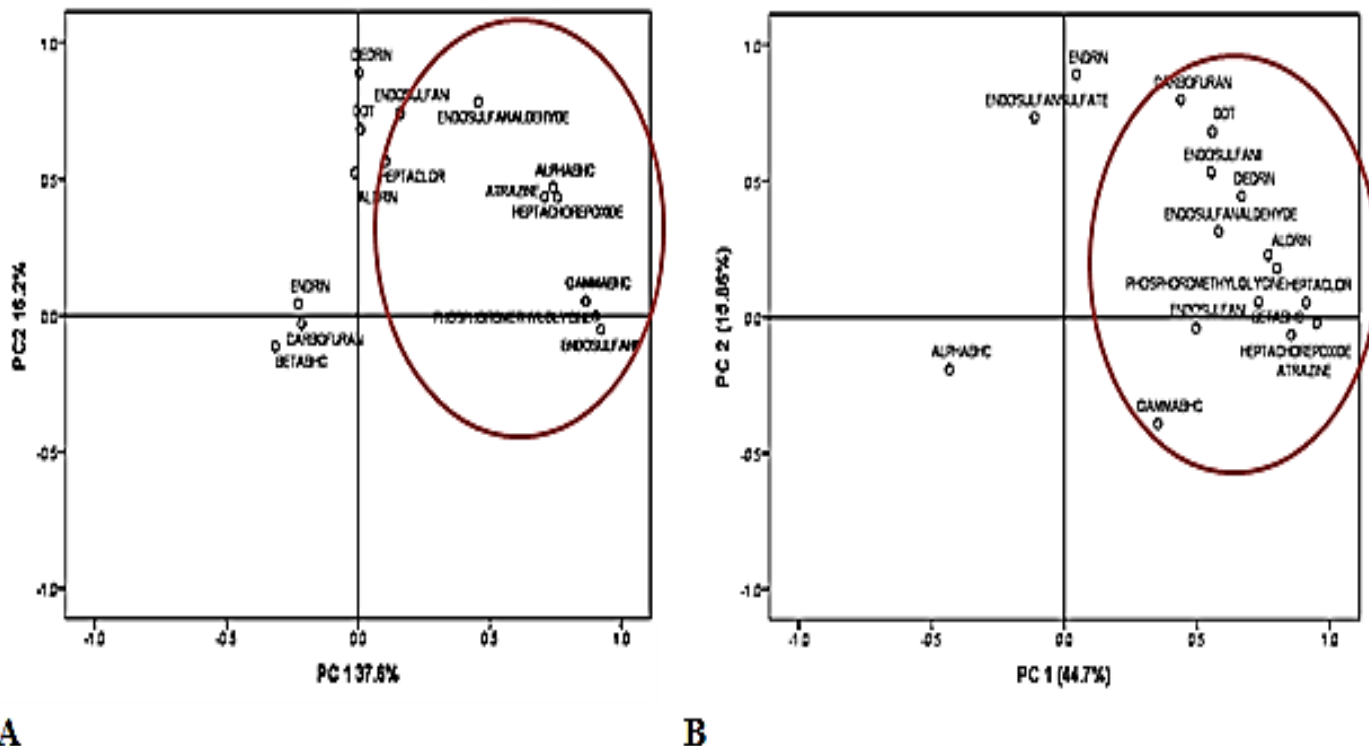


Figure 6. Profile of pesticide residues in *Clarias gariepinus* samples from Ogbesse River.

environment. The levels and occurrence of residues in fish samples seem to be governed by feeding mode, age and mobility of the biota; consequently, higher concentrations of pesticide residues observed in *C. gariepinus* may be attributed to the feeding mode of the

fish (Mwevura et al., 2002). This is corroborated by Biego et al. (2010) and Mwevura et al. (2002) who related the habitation and feeding habit of *C. gariepinus* to an increased concentration of pesticide residues compared with other pelagic fish species. Murano et al. (1997) and



**Figure 7.** Principal component plot of pesticide residues in (a) water and (b) sediment samples from Ogbesse River, Edo State.

Kidwell et al. (1990) equally adds that pesticide accumulation in fish was due to their lipid content; this implies that due to the high lipid content in *C. gariepinus*, more pesticide residues tend to be trapped in their lipid stores.

## PRINCIPAL COMPONENT ANALYSIS

### Water samples

Principal component analysis (PCA) of pesticide residues in water samples represented in Figure 7a showed that two components (PC1 and PC2) accounted for 49% of the total variance. PC1 was distinguished by positive loading for the variables; Aldrin, Endrin, Dieldrin, DDT, Endosulfan II and Endosulfan sulfate. PC2 was positively loaded for Alpha HCH, Gamma HCH, Endosulfan Aldehyde, Atrazine and Glyphosate. This implies that the distribution and degradation patterns of these pesticide residues in water samples obtained from Ogbesse River is highly correlated, while the occurrence of HCH, Endosulfan alongside its isomers on the same group of PC1 and PC2 could suggest the same source of origin of these pesticides.

This is similar to the findings of Hu et al. (2009) and Frimpong et al. (2013) in their studies of pesticides in China and Ghana respectively using multivariate

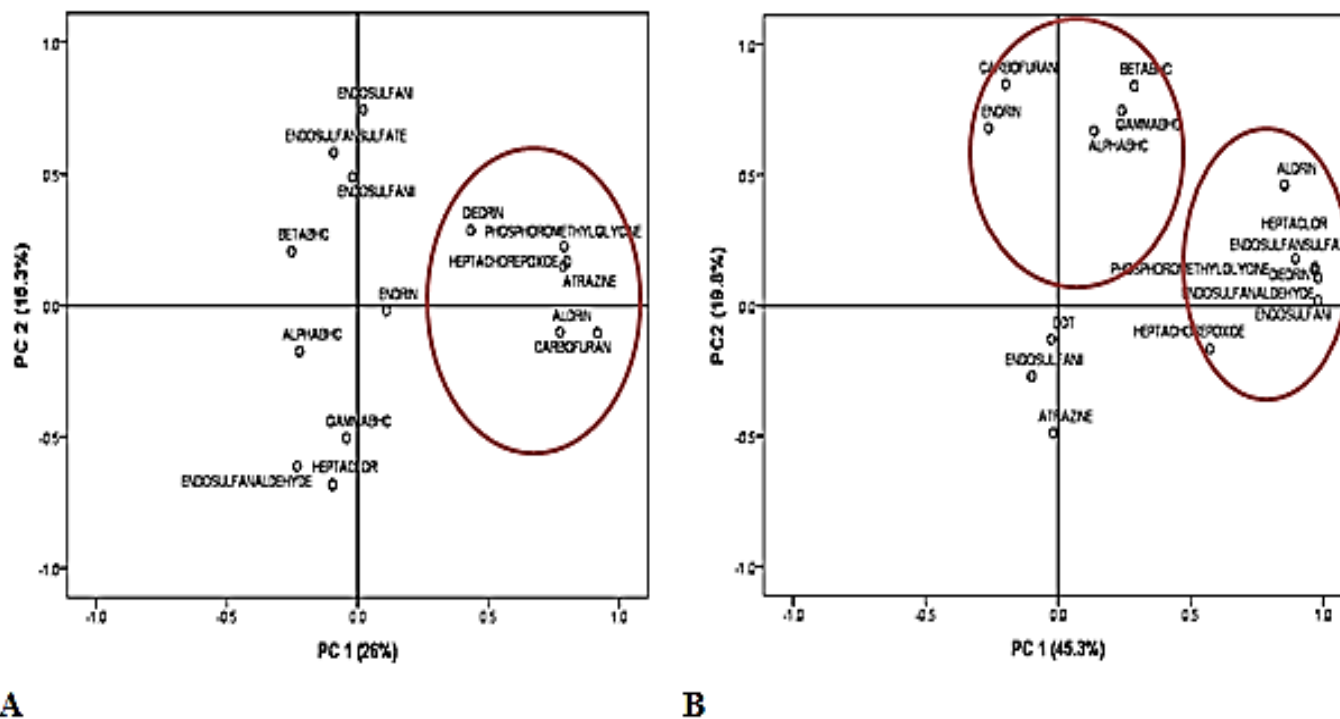
analysis. It also agrees with Kilulya and Mhinzi (2012) who evaluated the patterns and spatial trends of pesticide residues in Vikuge farm, coast region, Tanzania using principal components analysis.

### Sediment samples

Analysis of pesticide residues in sediment samples using PCA (Figure 7b) shows two principal components accounting 67.93% of the total variance. PC1 (46.9%) is explained by positive correlated loadings for gamma HCH, Heptachlor, Heptachlor epoxide, Aldrin, DDT, Endosulfan I, Endosulfan II, Endosulfan aldehyde, Glyphosate and Atrazine. PC 2 (21.03%) was distinguished by positive loadings for Dieldrin, DDT, Endrin Endosulfan I, Carbofuran and Endosulfan sulfate. Positive loadings of pesticide residues in a component imply that each pesticide undergo similar degradation and distribution patterns in sediment samples (Kilulya and Mhinzi, 2012).

### Biota samples

Principal component analysis of pesticides residues in *T. zilli* and *C. gariepinus* is presented in Figure 8a and b respectively. Two principal components accounted for



**Figure 8.** Principal component plot of pesticide residues in (A) *Tilapia zilli* and (B) *Clarias gariepinus* samples from Ogbesse River, Edo State.

39% of the total variance of data for *T. zilli* obtained from Ogbesse River. It was observed that Heptachlor, Aldrin, Dieldrin, DDT, Endosulfan II, Endosulfan Aldehyde and Endosulfan Sulfate were positively loaded in PC1, while Endosulfan I and Endosulfan II were positively loaded in PC2. Principal component analysis of pesticide residues in *C. gariepinus* showed that two components (PC1 and PC2) accounted for 50.4% of the total variance. Endrin, DDT, Endosulfan sulfate, Carbofuran and Glyphosate were positively loaded in PC1 while PC2 was positively loaded for beta HCH, Aldrin, Endosulfan Aldehyde and Atrazine.

### Risk assessment of pesticide residues

Risk assessment using the Risk Quotient deterministic method, where MEC (Measured Environmental concentration) was divided by the PNEC (Probable No Effect Concentration), is presented in Table 2. Risk Quotient for pesticide residues in water samples for both fish species showed that Endosulfan I, Endosulfan II, Endosulfan Aldehyde, Endrin, and Dieldrin are likely to cause adverse effects to each fish species ( $RQ \geq 1$ ). Fatemeh et al. (2012) and Sanchez-bayo et al. (2002), report that  $RQ \geq 1$  indicates a high risk, while  $0.1 \leq RQ \leq 1$  indicates medium risk, and  $0.01 \leq RQ \leq 0.1$  indicates low risk. Concentrations of pesticide residues in sediment

were below Freshwater Sediment Screening Benchmark (FSSB). However, Dieldrin and Endrin in sediment samples were above the Effect Low Range (ERL), indicating potential risk to benthic organisms due to exposure to contaminated sediments (Table 2). This is similar to studies carried out in India where DDT concentrations were reported to be above the ERL, and also similar to a study on ecological effects of pesticides in Nigeria Delta region of Nigeria, where DDT values were above the ERL (Olatubosun et al., 2012).

### Human health risk assessment of pesticide residues in biota

*C. gariepinus* and *T. zilli* are commercial aquatic products for Ogbesse community in Edo State. Hence, assessing the potential human health risk from the consumption of these fishes is an extremely important step towards public health safety. Table 3 shows the Estimated Average Daily Intake (EADI) and the Hazard Quotient for each pesticide. Three population groups with varying body weights were used for this study. EADI for Aldrin, Dieldrin, Endrin and Heptachlor epoxide in *C. gariepinus* were higher than the ADI for all weight groups, while EADI for gamma HCH exceeded the ADI for 10 kg category. Table 3 also showed that Hazard Quotient (HQ) values were above one suggesting that health risks



**Table 2.** Ecological risk assessment of pesticides in water detected in Ogbesse River.

Pesticides	(MEC)	(PNEC)	RQ	ERL
Heptachlor epoxide	0.43	0.25	1.72	
Dieldrin	0.14	0.0062	22.85	0.5
Endrin	0.06	0.0032	18.23	0.02
4, 4 DDT	0.12	0.087	1.40	
Endosulfan 1	0.22	0.0033	66.50	
Endosulfan 11	0.08	0.0685	1.22	
Endosulfan aldehyde	0.23	0.015	15.56	
Glyphosate	0.27	0.13	2.09	

**Table 3.** Human health risk associated with the consumption of *Clarias gariepinus*.

Pesticides	Residual concentration (ug/kg/ww)	FAO consumption rate (kg/ capita/year)	ADI	10 kg		30 kg		70 kg	
				EADI	HQ-Baby	EADI	HQ-Child	EADI	HQ-Adult
Heptachlor epoxide	0.25	9	0.013	0.23 <sup>■</sup>	17.31*	0.08 <sup>■</sup>	6.41*	0.03 <sup>■</sup>	2.47*
Aldrin	0.63	9	0.03	0.57 <sup>■</sup>	18.90*	0.21 <sup>■</sup>	7.00*	0.08 <sup>■</sup>	2.70*
Dieldrin	0.53	9	0.05	0.48 <sup>■</sup>	9.54*	0.18 <sup>■</sup>	3.53*	0.07 <sup>■</sup>	1.36*
Endrin	0.45	9	0.03	0.41 <sup>■</sup>	13.50*	0.15 <sup>■</sup>	5.00*	0.06 <sup>■</sup>	1.93*

associated with intake of Aldrin, Dieldrin, Endrin and Heptachlor epoxide through the consumption of *C. gariepinus* was high. On the other hand, human health risk estimates presented in Table 4 showed that EADI for Heptachlor epoxide, Endrin, Aldrin and Dieldrin in *T. zilli* were higher than the ADI for 10 kg weight groups, EADI for Heptachlor epoxide and Endrin, exceeded the ADI for 30 kg category, while EADI for Heptachlor epoxide exceeded the ADI for 70 kg category.

All pesticides with EADI above the ADI equally had their HQ greater than 1, suggesting potential health risk through the consumption of *T. zilli*. For *C. gariepinus* and *T. zilli* the hazard index estimations showed that mixtures of organochlorine pesticides were above one (1) for all the population groups, while hazard estimates for Glyphosate, Triazine and Carbamate pesticides were below one. It has been reported that if the hazard index >1, the mixture has exceeded the maximum acceptable level (Tsakiris et al., 2011) and there might thus be risk. Therefore, results from this study suggest a great potential for chronic toxicity through the consumption of pesticide contaminated *C. gariepinus* and *T. zilli* obtained from Ogbesse River because hazard index >1.

The results of Human Health Risk estimations obtained from this study, conforms with studies by Darko and Akoto (2008), who reported that the life time consumption of eggplant and tomatoes from Kumasi market could pose some health risks because HQ>1, and also agrees with Sohair et al. (2013) who reported potential health risk from consumption of fruits from Egypt because Health hazard >1.

In similar studies, Fianko et al. (2011) and Andoh et al. (2013) reported potential risk to humans through the

consumption of fish, maize and cowpea from Ghana because estimated hazard quotient was above 1.

## Conclusion

This study presents evidence of pesticide contamination of water, sediment and fish species, arising from various agricultural practices in Ogbesse River. Overall, sediment samples had the highest concentrations of pesticides residues, with the concentration of pesticide residues in the following order; Sediment > *C. gariepinus* > *T. zilli* > water. Ecological and human health risk assessment provided evidence of potential risk to aquatic organisms and humans. Therefore, there is the need for continuous monitoring of Ogbesse River and its vital fish resource for pesticides in order to ensure the safety of consumers. Proper orientation exercises for farmers are needed to ensure the proper handling of pesticides and its application instruments. Finally, public health educational programs should be introduced to prevent or reduce exposure of the population to pesticides from different sources.

## Conflict of Interest

The authors have not declared any conflict of interests.

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**Table 4.** Human health risk associated with the consumption of *Tilapia zilli*.

Pesticides	Residual concentration (ug/kg/ww)	FAO consumption rate (kg/ capita/year)	ADI	10 kg		30 kg		70 kg	
				EADI	HQ-Baby	EADI	HQ-Child	EADI	HQ-Adult
Heptachor epoxide	0.17	9	0.013	0.15☐	11.54*	0.05☐	3.85*	0.02☐	1.65*
Aldrin	0.12	9	0.03	0.11☐	3.67*	0.04☐	1.22*	0.02	0.52
Dieldrin	0.08	9	0.05	0.08☐	1.50*	0.03	0.50	0.01	0.21
Endrin	0.07	9	0.03	0.06☐	2.00*	0.02	0.67	0.01	0.29

ADI: Acceptable daily intake; EADI: Estimated average daily intake; HQ: Hazard quotient; \* = above 1 (potential health hazard) ☐ = above ADI.

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## REFERENCES

- Adeboyejo OA, Clarke EO, Olanrinmoye MO (2011). Organochlorine pesticides residues in water, sediments, fin and shell-fish samples from Lagos lagoon complex, Nigeria. *Researcher* 3:38-45.
- Adeyemi D, Anyakora C, Ukpo G, Adedayo A, Darko G (2011). Evaluation of the levels of organochlorine pesticide residues in water samples of Lagos Lagoon using solid phase extraction method. *J. Environ. Chem. Ecotoxicol.* 3:160-166.
- Andoh H, Osei A, Godfred D (2013). Health risk assessment of pesticide residues in maize and cowpea from Ejura, Ghana. Paper presented at 5th International Toxicology Symposium in Africa. Jointly Hosted by College of Science, Kwame Nkrumah University of Science and Technology, Ghana and Hokkaido University, Japan sponsored by Japan Society for Promotion of Science.
- Biego GHM, Yao KD, Ezoua P, Kouadio LP (2010). Assessment of Organochlorine Pesticides Residues in Fish Sold in Abidjan Markets and Fishing Sites. *Afr. J. Food Agric. Nutri. Dev.* 10:3.
- Chen W, Mingming J, Jianwei B, Julia EB, Shihua Q, Qi S, Yibing K, Jinjie M, Meng L, Chen Y (2009). Organochlorine pesticides in the surface water and sediments from the Peacock River Drainage Basin in Xinjiang, China: a study of an arid zone in Central Asia. *Environ. Monit. Assess.* 177:1-21.
- Chopra AK, Sharma MK, Chamoli S (2010). Bioaccumulation of organochlorine pesticides in aquatic system – an overview. *Environ. Monit. Assess.* 173:905-916.
- Darko G, Akoto O (2008). Dietary intake of organophosphorus pesticide residues through vegetables from Kumasi, Ghana. *Food Chemical Toxicol.* 46:3703-3706.
- Darko G, Babayo AU (2013). Studies of persistent organic and inorganic pollutants in water and fish samples around irrigation sites and its environs in north eastern part of Nigeria. Paper presented at 5<sup>th</sup> International Toxicology Symposium in Africa. Jointly Hosted by College of Science, Kwame Nkrumah University of Science and Technology, Ghana and Hokkaido University, Japan sponsored by Japan Society for Promotion of Science.
- Devi NL, Chakraborty PQ, Zhang SG (2013). Selected Organochlorine Pesticides (OCPs) in Surface Soils from Three Major States from the North Eastern part of India. *Bull. Environ. Sci. Res.* 2:1.
- Ezemonye LIN, Ikpesu TO, Tongo I (2008a). Distribution of Lindane in Water, Sediment, and Fish from the Warri River of the Niger Delta, Nigeria. *J. Arh. Hig. Toksikol.* 59:261-270.
- Ezemonye LIN, Ikpesu TO, Tongo I (2008b). Distribution of Diazinon in Water, Sediment and Fish from Warri River, Niger Delta, Nigeria. *Jordan J. Biol. Sci.* 1(2):77-83.
- Ezemonye LIN, Ikpesu TO, Tongo I (2009). Distribution of Propoxur in water, sediment and fish from Warri River, Nigeria Delta, Nigeria. *Turk. J. Biochem.* 34(3):121-127.
- FAO (1997). Pesticide residues in food – 1997. Report of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and Environment and the WHO Core Assessment Group on Pesticide Residues, Lyon, France, 1997. FAO plant production and protection paper 145, FAO, Rome.
- FAO (2011). Fishery and Aquaculture Statistics. 2009. Statistics and Information Service of the Fisheries and Aquaculture Department/Service. 2009. Rome/Roma, FAO. 2011. P. 78.
- Fateme K, Moattar F, Farshchi P, Savari A, Parham H (2012). ERA: Suitable Method for Estimation of Ecological Effects of Pesticide Contamination on Aquatic Species. *J. Persian Gulf (Marine Science).* 3:67-73.
- Fianko RJ, Augustine D, Samuel TL, Paul OY, Eric TG, Theodosia A, Augustine F (2011). Health Risk Associated with Pesticide Contamination of Fish from the Densu River Basin in Ghana. *J. Environ. Protection* 2:115-123.
- Frimpong S, Philip Y, Fletcher JJ, Dickson A, Osei-Fosu P, Acheampong K, Gustav G, Israel D, Courage E, Samuel D, John P (2013). Organochlorine pesticides levels in fermented dried cocoa beans produced in Ghana. *Elixir Agriculture* 44(2012):7280-7284
- Hamilton DJ, Ambrus A, Dieterle RM, Felsot AS, Harris CA, Holland PT, Katayama A, Kurihara N, Linders J, Unsworth J, Wong SS (2003). Regulatory limits for pesticide residues in Water (IUPAC Technical Report). *Pure Appl. Chem.* 75(8):1123-1155.
- Hu L, Zhang G, Zheng B, Qin Y, Lin T, Guo Z (2009). Occurrence and distribution of organochlorine pesticides (OCPs) in surface sediments of the Bohai Sea, China. *Chemosphere* 77:663-672.
- Ize-Iyamu OK, Asia IO, Egwakhide PA (2007). Concentrations of residues from organochlorine pesticide in water and fish from some rivers in Edo State Nigeria. *Int. J. Phys. Sci.* 2(9):237-241.
- Kidwell JM, Phillips LJ, Birchard GF (1990). Comparative analysis of contaminants levels in bottom feeding and predatory fish using the national contaminants bio-monitoring program data. *Bull. Contam. Toxicol.* 55(6):919-923.
- Kilulya KF, Mhinzi GS (2012). Evaluation of patterns and spatial trends of pesticide residues from Vikuge Farm, Coast Region, Tanzania By Principal Components Analysis. *Tanz. J. Sci.* 38(3).
- Konstantinou IK, Hela DG, Albanis TA (2006). The status of pesticide pollution in surface waters (rivers and lakes) of Greece. Part I. Review on occurrence and levels. *Environ. Pollut.* 141(3): 555-570
- Masia A, Ibanez M, Blasco C, Sancho JV, Pico Y, Hernandez F (2013). Combined use of liquid chromatography triple quadrupole mass spectrometry and liquid chromatography quadrupole time-of-flight mass spectrometry in systematic screening of pesticides and other contaminants in water samples. *Anal. Chem. Acta* 761:117-127.
- Murano FM, Guida G, Melluso GS (1997). Accumulation of Pesticide Residues in Fishes and Sediments in the River Sele (South Italy) *J. Preventive Med. Hygiene.* 38:3-4.
- Munn MD, Gilliom RJ, Moran PW, Nowell LH (2006). Pesticide toxicity index for freshwater aquatic organisms, 2nd Edition: U.S. Geological Survey Scientific Investigations Report. 5148:81.
- Murty AS (1986). Toxicity of pesticides to fish Volume II LRC Press Boca Roton F. L.
- Mwevura H, Othman CO, George LM (2002). Organochlorine Pesticide Residues in Edible Biota from the Coastal Area of Dares Salaam City. Pesticide Residues in Coastal Dar Western Indian Ocean. *J. Marine Sci.* 1(1):91-96.
- Okeniyia SO, Eqwikhide PA, Akporhonore EE, Obazed EI (2009). Distribution of organochlorine and polychlorinated pesticides residues

- in water bodies of some rivers in northern Nigeria, *EJEAFChe*, 8(11):1269-1274.
- Okoya AA, Ogunfowokan AO, Asubiojo OI, Torto N (2013). Organochlorine Pesticide Residues in Sediments and Waters from Cocoa Producing Areas of Ondo State, Southwestern Nigeria. International Scholarly Research Network (ISRN) Soil Science.
- Olatunbosun SS, Sojiru O, Sonibare E, Eddy O, Zeng Y (2011). Occurrence of Organochlorine Pesticides (OCPs) in Surface Sediments of the Niger Delta, Nigeria. *J. Appl. Sci. Res.* 7(8):1299-1305.
- Osibanjo O, Adeyeye A (1997). organochlorine pesticide residues in foodstuffs of animal origin in Nigeria. *Bull. Environ. Contam. Toxicol.* 58:206-21
- Randall RC, Young DR, Lee IJH, Echols SF (1998). Lipid methodology and pollutant normalization relationships for neutral nonpolar organic pollutants. *Environ. Toxicol. Chem.* 17(5):788-791.
- Sangchan W, Huginschmidt C, Ingwersen J, Thavornnyutikarn P, Pansombat K, Streck T (2012). Short-term dynamics of pesticide concentrations and loads in a river of an agricultural watershed in the outer tropics. *Agric., Ecosystems Environ.* 158(1):1-14.
- Sohair A, Gad A, Mohsen M, Ayoub MAA, Wasfi MT (2013). Dietary Intake of Pesticide Residues in some Egyptian Fruits. *J. Appl. Sci. Res.* 9(1):965-973.
- Steinwandter H (1992). Development of Microextraction Methods in Residue Analysis. Cairns, T and Sherma, J., (eds.) Emerging strategies for pesticide analysis, 3-50. CRC. Boca Raton, FL.
- Tsakiris IN, Maria T, Manos K, Mitlianga P, Aristides MT (2011). A Risk Assessment Study of Greek Population Dietary Chronic Exposure to Pesticide Residues in Fruits, Vegetables and Olive Oil, Pesticides - Formulations, Effects, Fate: Prof. Margarita Stoytcheva (Ed.), ISBN: 978-953-307-532-7,
- United States Environmental Protection Agency (USEPA) (2004). Guidelines for Water Reuse. EPA/625/R-04/108.US EPA. CampDresser & McKee Inc.
- Upadhi F, Wokoma OAF (2012). Examination of some pesticide residues in surface water, sediment and fish tissue of Elechi Creek, Niger Delta. *Nigeria Res. J. Environ. Earth Sci.* 4(11):939-944.
- WHO (World Health Organization) (1997), Guidelines for predicting dietary intake of pesticide residues (revised) global environmental programme (GEMS/Food) in collaboration with Codex Committee on pesticide residues. Programme of Food Safety and Food Aid. pp.1-44.
- Williams BA (2013). Levels and distribution of chlorinated pesticide residues in water and sediments of Tarkwa Bay, Lagos Lagoon. *J. Res. Environ. Sci. Toxicol.* 2(1):1-8.
- Zhou R, Zhu L, Yang K, Chang Y (2006). Distribution of organochlorine pesticide in surface water and sediment from Qiantang River, East China. *J. Hazard. Mat. A* 137:68-78.