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ORIGINAL PAPER

Human Health Risk Associated with Dietary and Non-Dietary Intake of Organochlorine Pesticide Residues from Rice Fields in Edo State Nigeria

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Abstract The levels, distribution patterns, ecological risk and human health risk of fourteen organochlorine pesticides in surface water, sediment, and fish (*Tilapia zilli* and *Clarias gariepinus*) collected from a massive rice field in Illushi, were monitored. Samples obtained were extracted and analyzed using gas chromatography equipped with electron capture detector while risk assessment was carried out using standard models (risk quotient and Chronic daily intake). Pesticide concentration in water samples ranged from ND to 1.65 µg/l, while the concentration of pesticide residues in sediment, *C. gariepinus*, and *T. zilli* ranged from ND to 8.45 µg/kg dw, 0.03 to 1.57 µg/kg/ww, and 0.03 to 0.85 µg/kg/ww, respectively. There was a clear dominance of the organochlorine; Hexachlorocyclohexane (α-HCH, γ-HCH, β-HCH) in all matrices. Risk quotient estimates for heptachlor, heptachlor epoxide, aldrin, dieldrin, DDT, endosulfan I, endosulfan II, and endosulfan aldehyde showed risk to aquatic organisms under extreme conditions. Health risk estimations showed that there is a potential risk to humans exposed to contaminated water, sediment, and fishes through ingestion, inhalation, and dermal routes of exposures. Cumulative hazard quotient estimated for pesticide mixtures in each matrix further confirmed that there was potential risk to human health especially children. Furthermore, the risk of non-carcinogenic effects followed the following sequence; biota > sediment > water. This study presents evidence of the multiple contamination of water, sediment, and biota from the Illushi River Basin which would possibly lead to non-cancer effects in humans especially children when exposed. Therefore, water bodies draining agricultural farmlands should be monitored regularly to prevent the contamination of the aquatic environment by toxic and banned pesticides, while efforts should be intensified to regulate the sales, application, and disposal of pesticide products in Nigeria.

Keywords Pesticides · Non-dietary exposures · Risk quotient · Estimated daily intake · Hazard quotient

Introduction

There is concern that lowland and upland rice production systems are the major non-point sources of pesticide pollution of surface and groundwater, both of which are used for domestic purposes (Ecobichon 2001). Rice, as the main staple of the developing countries (including Nigeria), is the most important cereal crop in Nigeria and its consumption is increasing rapidly because of urbanization, relative ease of preparation, and convenience in storage (Ekeleme et al. 2008). Hence there are massive farms for the indigenous cultivation of rice. However, in recent times, there has been low yields in rice production due to

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the impact of adverse weather conditions (floods, drought, typhoons, etc.) and pest epidemics. Reports have shown that the yield potential of rice cultivated in West Africa including Nigeria is continually challenged by chronic pest infestation and outbreaks (Nwilene et al. 2011). In a bid to improve rice production by combating pest epidemics and outbreaks, rice farmers in Edo state and Nigeria at large resort to the use of various pesticides to protect their crops. By design, pesticides are toxic, bioaccumulative and due to their vertebrate and non-vertebrate toxicity can affect non target organism and human health (Ize-Iyamu et al. 2007; Lamers et al. 2011; Masia et al. 2013). These pesticides are used without proper training on application and warning of the harmful effect on the environment. More worrisome is the fact that reports have shown that many of the pesticides sold to rural farmers are banned and illegal stockpiles (Zhou et al. 2006; Nwilene et al. 2011; Masia et al. 2013). Pesticides applied during rice cultivation are transported in the environment through various pathways. However, water has been reported to be the primary pathway of pesticides residues into the environment (Schulz 2004). These residues of pesticides might ultimately pass unto humans through the routine consumption of drinking water, fish, contact with contaminated sediment, and inhalation of pesticide dust trapped in sediments (Zhou et al. 2006; Qu et al. 2014). In Nigeria, pesticide contamination levels in various environmental compartments (water, sediment and several aquatic species) has been reported (Ize-Iyamu et al. 2007; Ezemonye et al. 2008a, b, 2009; Okeniyia et al. 2009; Adeboyejo et al. 2011; Adeyemi et al. 2011; Upadhi and Wokoma 2012; Williams 2013). Unfortunately, these studies have concentrated on monitoring the levels of pesticide residues in these compartments without going a step further in determining the risk associated with the presence of these concentrations to both non-target organisms and humans. This has prompted recent studies by members of the pesticide research group at the laboratory for ecotoxicology and environmental forensics (LECTOX), University of Benin to include the use of risk assessment models/indices to project the potential effects of pesticide contamination on non-target organisms including humans (Ezemonye et al. 2015a, b; Ogbeide et al. 2015a, b; Tongo and Ezemonye 2015; Tongo et al. 2015). Estimation of potential risk of pesticide exposure to non-target organisms involves the use of the risk quotient (RQ) deterministic method. This is the ratio of the measured environmental concentration (exposure) and the toxicant reference value (Faggiano et al. 2010). For human health risk estimations, two exposure routes are considered: dietary and non-dietary exposures. Dietary exposures include: 1. the consumption of pesticide contaminated food stuffs here, health risk is predicted using the estimated daily intake (EDI) (Ezemonye et al. 2015a, b), and 2. The ingestion of contaminated water where health risks are estimated using estimated chronic daily intake (ECDI) (Papadakis et al. 2015). Non-dietary exposures include: 1. accidental ingestion of contaminated sediments, 2. inhalation of pesticide dust, and 3. dermal contact. For these exposure routes, health risk estimates are obtained using the chronic daily intake (CDI) (Huang et al. 2014). Non-Cancer effects that could arise from dietary and non-dietary exposures to pesticides can also be predicted by dividing EDI/CDI/ECDI with the corresponding reference dose (RfD) for each pesticide (Tongo and Ezemonye 2015) while cancer effects are predicted by multiplying EDI/CDI/ECDI with the cancer slope factor for each pesticide. To the best of authors' knowledge, this is the first study to evaluate the concentration of pesticide residues in the Illushi River. Therefore, the objectives of this study were to monitor 14 organochlorine pesticides in water, sediment, and biota collected from the Illushi River Basin, project the ecological risk associated with the presence of these pesticides in the environment and finally estimate the human health risk that may arise through dietary intake (the consumption of contaminated fish species and water) and non-dietary intake (direct contact with contaminated sediments) of these pesticides.

Materials and Methods

Site Description and Sampling

Edo State is typically an agrarian state, with various agro-ecological zones suitable for the production of several important food crops. The Illushi River is located in the Illushi River basin (N: 06°45′40″; E: 005°46′07.4″) (Fig. 1). The river basin is a flood plain, very close to the River Niger, a coastal region of Edo State, Nigeria. This terrain is known for large-scale rice farming. The river serves as a drainage for these massive rice farms located around it. Large amount of pesticides are used in preparing the land for farming and also used in routine maintenance of these rice farms. These farms are regularly inundated by overflows from the river leading to continuous contamination of the river. Samples used for analysis were collected for 18 months (January 2012 to June 2013). Water samples ($n = 216$) were collected from 0.3 m below the water surface with a pre-cleaned glass bottle using hydrobios sample based on the method described 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 was collected with a Teflon-coated spoon and wrapped in aluminum foil. Samples of *C. gariepinus* and *T. zilli* ($n = 30$) each were captured randomly using a fishing net, while 24 samples of

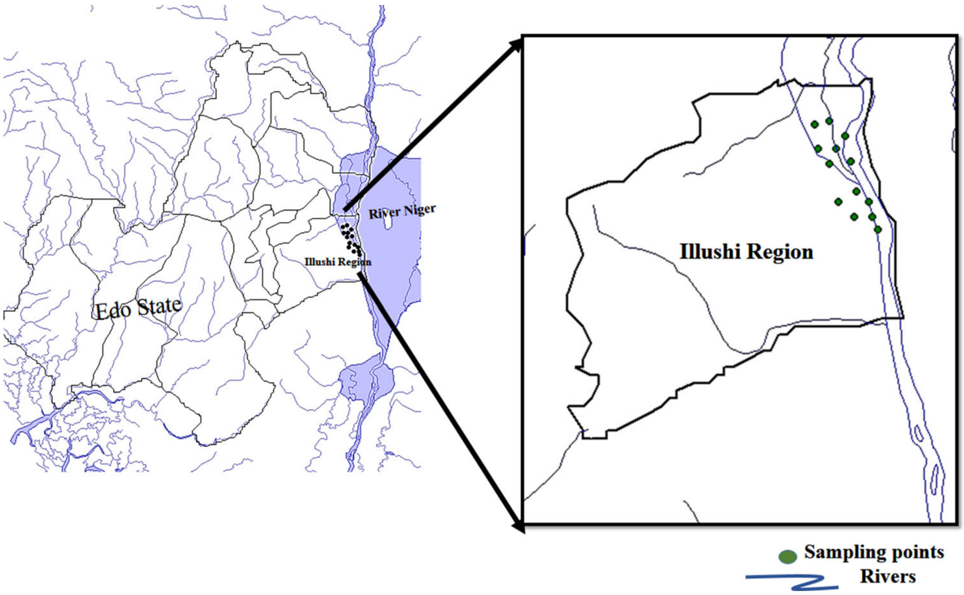


Fig. 1 Map showing the study area and sampling points

C. gariepinus and *T. zilli* were bought from fishermen around each river (Ize-Iyamu et al. 2007). Overall, a total of 54 samples of *C. gariepinus* and *T. zilli* (each) were obtained for this study.

C. gariepinus and *T. zilli* were selected because they are major aquatic resources of the Illushi River basin and they are also important elements in the diet of the population residing in this region. These species of fish are the most widely consumed freshwater fishes in Edo State, Nigeria, based on its large size at maturity, affordability, nutritional benefits, and rapid growth (Akinwumi 2003; Olaifa and Ayodele 2004). Ethical clearance has been obtained from the University of Benin Ethics Committee on handling of the fish species.

Extraction and Analysis

Sediment samples were extracted and cleaned up according to the method described by Hladik and McWayne (2012). Edible portions of *C. gariepinus* and *T. zilli* samples were extracted and cleaned up according to methods described by Steinwandter (1992), while water samples were extracted and cleaned up based on methods described by Osibanjo and Adeyeye (1997) and USEPA (2007). The cleaned up extracts were analyzed for pesticides (α-HCH, γ-HCH, β-HCH, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, DDT, endosulfan I, endosulfan II, endosulfan aldehyde, endosulfan sulfate). Results were obtained by Hewlett-Packard (hp) 5890 Series II gas chromatography (GC) equipped with 63 Ni electron capture detector (ECD) of activity 15 mCi with an auto sampler. The chromatographic separation was done using a VF-5 ms of 30 mm capillary column with 0.25 mm internal diameter and 0.25 µm film thicknesses and equipped with 1 m retention gap (0.53 mm, deactivated). The GC conditions were as follows: The oven temperature programme: Initial temperature was set at 60 °C for 2 min and ramped at 25 °C/min to 300 °C for 5 min and allowed to stay for 15 min giving a total run time of 58 min. The injector setting was a pulsed spit less mode with a temperature of 250 °C at a standard pressure. The injection volume was 1.5 µg/l. The detector temperature was 320 °C (held for 5 min). Helium was used as a carrier gas while Nitrogen gas (N_2) was used as the makeup gas, maintained at a constant flow rate of 29 ml/min. The efficiency of the analytical method (the extraction and clean-up methods) was determined by recoveries of an internal standard. The recoveries of observed pesticides were greater than 85 %. 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 0.01 µg/g/dw for pesticides in biota. Method detection limits (MDLs) ranged from 0.005 µg/l for pesticides in water and 0.01 µg/g/dw for pesticides in sediment and biota.

Risk Assessment of Pesticide Residues

Ecological Risk Assessment

Risk quotient (RQ) method was used to determine risk of pesticide exposure to non-target aquatic organisms. RQ is 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 LC_{50} with an assessment factor (AF) of 100. 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). The LC_{50} was obtained from Munn et al. (2006).

$$″\text{Risk quotient (RQ)} = ″″\text{MEC}″/″\text{PNEC}″ \quad (1)$$

(Papadakis et al. 2015).

Health Risk Estimations

To assess the health risk associated with exposures to pesticide residues through consumption of fish, drinking contaminated water (dietary intake), and contact with contaminated sediment samples (non-dietary intake); the guidelines for potential risk assessment drawn up by the US EPA were used.

Human Health Risk Assessment of Pesticide Residues in Biota (Dietary)

To estimate the carcinogenic and non-carcinogenic risk of detected pesticides to humans, using two population groups (young children and adults) the estimated acceptable daily intake (EADI) was used. EADI was obtained by multiplying the residual pesticide concentration (µg/kg) in each fish species by the consumption rate in Nigeria (l/day or kg/day) and dividing the product by the body weight (kg) (WHO 1997; Fianko et al. 2011). The hazard quotient (HQ) was then obtained from the ratio of EADI and reference dose. The reference dose (RFD) of each pesticides is the exposure that is likely to be without an appreciable risk of deleterious effects and was provided by the USEPA (1996). The food and agricultural organization (FAO 2011) quotes the per capita consumption of fishes in Nigeria as 9 kg. The following formula was used to estimate the dietary intake.

$$″\text{EADI} = ″″C(\text{biota}) \times \text{CR}″/″\text{BW}″ \quad (2)$$

(WHO 1997; Fianko et al. 2011).

EADI is the estimated average daily intake, C is the concentration of pesticide residues, CR represents consumption rate of each fish species while BW represents the body weight of age group. The food and agricultural organization (FAO 2011) quotes the per capita consumption of fishes in Nigeria as 9 kg. While body weight was set at 70 kg for adult population group.

Hazard quotient (HQ): Hazards quotients were obtained by dividing the EADI by their corresponding reference dose (RfD).

$$″\text{Hazard quotient (HQ)} = ″″\text{EADI}″/″\text{RfD}″ \quad (3)$$

(WHO 1997; Fianko et al. 2011).

Hazard index (HI): using the hazard quotient derived from Eq. 3, the hazard index (HI) was obtained. Hazard index is used to assess the risk involved in exposure to mixtures of the detected pesticides belonging to the same chemical group (organochlorines).

$$\text{Hazard index (HI)} = \sum_{i}^{n} \text{HQi} \quad (4)$$

(Tsakiris et al. 2011).

Human Health Risk Assessment of Pesticides in Water Samples

To estimate the risk of detected pesticides to humans (young children and adults) through drinking/ingestion of contaminated water, the hazard quotient (HQ) method was employed (Papadakis et al. 2015).

$$\text{Hazard quotient (HQ)} = \frac{\text{ECDI}}{\text{RfD}} \quad (5)$$

where ECDI is the estimated chronic daily intake. This was obtained by using the formula

$$\text{ECDI (ingestion)} = \frac{C_w \times I_R(\text{water}) \times E_F \times E_D}{B_W \times A_T} \quad (6)$$

where C_w is the concentration of water samples, $I_{R\ (\text{water})}$ is the ingestion rate of water, E_F is the exposure frequency, E_D is the exposure duration, B_W is the body weight, and A_T is the average life Span. The values for each of these parameter are provided in Table 1.

Human Health Risk Assessment of Pesticides in Sediment Samples (Non-Dietary)

This can be regarded as the human exposure to pesticide residues through other routes apart from diet. Non-dietary intake can be estimated using the chronic daily intake (CDI). Three routes of exposures were considered which include dermal contact, ingestion, and inhalation. Chronic daily intake is a model, designed by US Environmental Protection Agency (USEPA) (1992, 1997) to estimate the non-carcinogenic risks for adults and children from non-dietary exposure to contaminants. The CDI was estimated using the following formulae adapted from Huang et al. 2014 (Eqs. 7–9).

$$\text{CDI ingestion} = \frac{C(\text{sediment}) \times I_R(\text{sediment}) \times C_F \times E_F \times E_D}{\text{B}_W \times A_T} \quad (7)$$

$$\text{CDI inhalation} = \frac{C(\text{sediment}) \times (1/\text{PEF}) \times \text{IAR} \times E_F \times E_D}{B_W \times A_T} \quad (8)$$

$$\text{CDI dermal} = \frac{C(\text{sediment}) \times S_A \times C_F \times E_F \times E_D \times \text{ABS} \times A_F}{B_W \times A_T} \quad (9)$$

where C_S is the concentration of sediment samples, $I_{R\ (\text{sediment})}$ is the ingestion rate of sediment, C_F is the

Table 1 Values of the parameters used for the estimation of Risk

	Unit	Child	Adults	Reference
Ingestion rate (soil) (IR)	mg/day	200	100	USDOE (2011)
Ingestion rate (water)	L/day	0.87	1.41	Papadakis et al. 2015
Exposure frequency (EF)	Day/year	350	350	USDOE (2011)
Exposure duration (ED)	Year	6	30	Qu et al. (2014)
Body weight (BW)	kg	10	70	Ezemonye et al. (2015)
Average life span (AT)	Day	2190	8760	Huang et al. (2014)
Surface area (SA)	cm^2/day	2800	5700	USDOE (2011)
Dermal exposure ratio (FE)	Unit less	0.61	0.61	Qu et al. (2014)
Dermal surface factor (AF)	mg/cm	0.2	0.07	USDOE (2011)
Dermal absorption factor (ABS)	Unit less	0.13	0.13	USEPA (2002)
Inhalation rate (IAR) (air)	m^3/day	10.9	17.5	Qu et al. (2014)
Particle emission factor (PET)	m^3/kg	1.36E+09	1.36E+09	USDOE (2011)

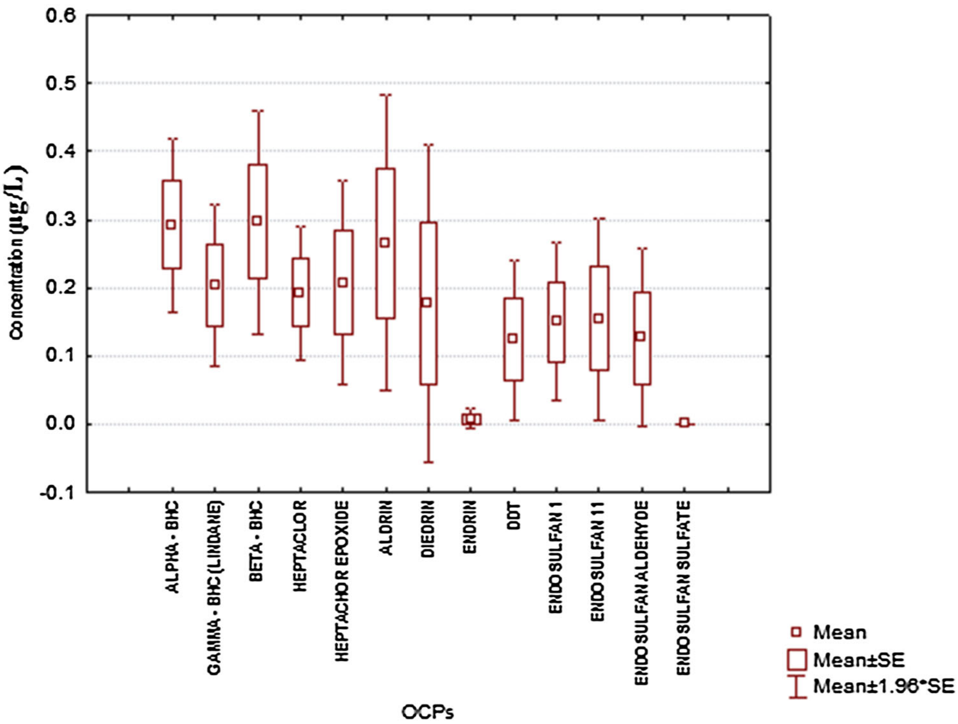


Fig. 2 Pesticide concentration (µg/l) profile in water samples from Illushi River

carcinogenic slope factor, (E_F) is the exposure frequency, E_D is the exposure duration, B_W is the body weight, F_E is the dermal exposure ratio, A_F is the dermal surface factor, ABS is the dermal absorption factor, A_T is the average life span, S_A is the surface area and PEF is the particle emission factor. The values for each of these parameter are provided in Table 1.

Results and Discussion

Spatial Distribution of Pesticides in Water

The concentration of pesticides in surface water from the Illushi River ranged from ND to 1.65 µg/l (Fig. 2). Fourteen (14) pesticides and their metabolic products were detected in this river (Table 2; Fig. 2) with α-HCH having the highest mean concentration (0.2772 µg/l) in water samples, while endrin had the lowest mean concentration (0.02 µg/l). Percentage distribution of pesticide residues in water samples shows that α-HCH, β-HCH, and γ-HCH were 11, 10, and 8 %, respectively, collectively making up 29 % of the total pesticide residues. Seasonal variations in pesticide distribution in water samples from the Illushi River showed that the highest concentrations of pesticides were measured during the peak of the rainy season where runoffs were highest. Runoffs have been reported to carry pesticides applied in farms into rivers (Ezemonye et al. 2008a; Papadakis et al. 2015). The presence of these

Table 2 Concentration of pesticide residues in water, sediment, and fish from the Illushi River

Illushi River	Water (µg/l)		Sediment (µg/g/dw)		*C. gariepinus* (µg/g/dw)		*T. zilli* (µg/g/ww)	
	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
Alpha—HCH	0.27 ± 0.21	0–0.75	1.52 ± 1.01	0–3.80	1.48 ± 2.71	0–8.90	0.38 ± 0.90	0–3.80
Gamma—HCH	0.19 ± 0.19	0–0.65	1.20 ± 2.11	0–8.45	0.68 ± 1.35	0–5.60	0.85 ± 2.04	0–8.80
Beta—HCH	0.26 ± 0.27	0–0.85	2.17 ± 1.90	0–6.10	1.58 ± 2.48	0–6.40	0.29 ± 0.35	0–1.00
Heptachlor	0.24 ± 0.19	0–0.60	1.31 ± 1.93	0–6.60	0.20 ± 0.37	0–1.50	0.60 ± 0.98	0–2.90
Heptachlor epoxide	0.19 ± 0.24	0–0.80	1.01 ± 1.31	0–4.20	0.21 ± 0.48	0–1.80	0.12 ± 0.27	0–1.00
Aldrin	0.23 ± 0.35	0–1.30	1.84 ± 2.11	0–6.20	0.82 ± 1.62	0–6.50	0.73 ± 1.64	0–5.20
Dieldrin	0.16 ± 0.37	0–1.55	1.05 ± 1.51	0–4.95	0.44 ± 1.57	0–6.70	0.08 ± 0.18	0–0.60
Endrin	0.03 ± 0.07	0–0.20	0.85 ± 1.42	0–4.85	0.31 ± 0.53	0–1.90	0.02 ± 0.07	0–0.30
DDT	0.09 ± 0.19	0–0.65	0.97 ± 1.36	0–3.95	0.03 ± 0.10	0–0.40	0.00 ± 0.00	0–0.00
Endosulfan I	0.16 ± 0.20	0–0.70	1.43 ± 2.86	0–12.30	0.25 ± 0.57	0–2.40	0.17 ± 0.34	0–1.40
Endosulfan II	0.13 ± 0.24	0–1.00	0.89 ± 1.41	0–4.80	0.11 ± 0.25	0–0.80	0.03 ± 0.10	0–0.30
Endosulfan aldehyde	0.09 ± 0.21	0–0.75	0.48 ± 1.18	0–4.90	0.38 ± 1.24	0–5.30	0.12 ± 0.29	0–0.90
Endosulfan sulfate	0.00 ± 0.00	0–0.00	0.71 ± 1.89	0–8.05	0.42 ± 1.72	0–7.30	0.03 ± 0.12	0–0.50

pesticides residues in water samples from the Illushi River is indicative for the contamination of the river through various routes of entry from farms located close by. With the full stretch of the river surrounded by rice farms, the proliferation of pesticide residues in rivers has become a common feature due to an increase in the use of pesticides during agricultural activities. Several studies have reported the presence of pesticide residues in surface water close to agricultural areas, within and outside this region. Some of these studies include Doong et al. (2002), Konstantinou et al. (2006), Zhou et al. (2006), Ize-Iyamu et al. (2007), Ezemonye et al. (2008a), Begum et al. (2009), Okeniyia et al. (2009), Muhayimana and Shihua (2009), Phillips et al. (2010), Adeboyejo et al. (2011), Adeyemi et al. (2011), Hu et al. (2011), Falahudin and Munawir (2012), Fatemeh et al. (2012), Upadhi and Wokoma (2012), Darko and Babayo (2013), Okoya et al. (2013), Stamatis et al. (2013), Yang et al. (2005), and Williams (2013). Furthermore, pesticide residues observed in this study were found to be higher than maximum residual limits (MRL) of pesticides in fresh water bodies set by European Union (EU) (0.01 µg/l) and the National Environmental Standard and Regulation Enforcement Agency (NISERA) (0.1 µg/l).

Spatial Distribution of Pesticides in Sediment

Sediment contamination with pesticide residues has become a common feature in areas with intense agricultural activities. Pesticides used during agriculture activities find their way to river systems which as a drain for adjacent farms. Concentrations of pesticides in investigated sediment samples are shown in Table 2 and Fig. 3, and concentrations ranged from ND to 8.45 µg/kg/dw. All fourteen (14) pesticides were detected in sediment samples with β-HCH having the highest mean concentration (2.17 µg/kg/dw), while Endosulfan aldehyde had the lowest mean concentration (0.5 µg/kg/dw). As observed in water samples, HCH and its isomers had the highest percentage distribution (25 %). Furthermore, temporal distribution of pesticide residues showed seasonal variations. High concentrations were observed during the dry season, when there was a remarkable decrease in runoff allowing for sedimentation. Sediments have been reported to be the sink of aquatic ecosystems with large proportion of pesticide residues binding to suspended particles and settling at the bottom of the river, leading to a compromise in the sediment quality (Aktar et al. 2009; Hellar-Kihampa et al. 2013). When compared with water samples, pesticide concentration in sediments was highest, which could be attributed to the hydrophobic nature of each pesticide detected (Ezemonye et al. 2008a, 2009; Williams 2013). The distribution patterns of HCH in sediment samples showed that the unstable α-HCH had the highest concentration, reflecting the recent use of technical HCH within these areas. This is further confirmed by the ratio of α-HCH and γ-HCH. In the investigated sediment samples obtained from the Illushi River, α-HCH/γ-HCH ratio was below 3 which indicates a fresh use of technical HCH. It has been reported that a ratio less than 3 indicates that the source of HCH in the environment is fresh input of technical HCH (Chen et al. 2009). This trend also corroborates the findings of Olatunbosun et al. (2011), Doong et al. (2002), and Chen et al. (2009) who reported high concentrations of α-HCH compared with other isomers in sediment samples.

Fig. 3 Pesticide concentration (µg/kg/dw) profile in sediment samples from Illushi River

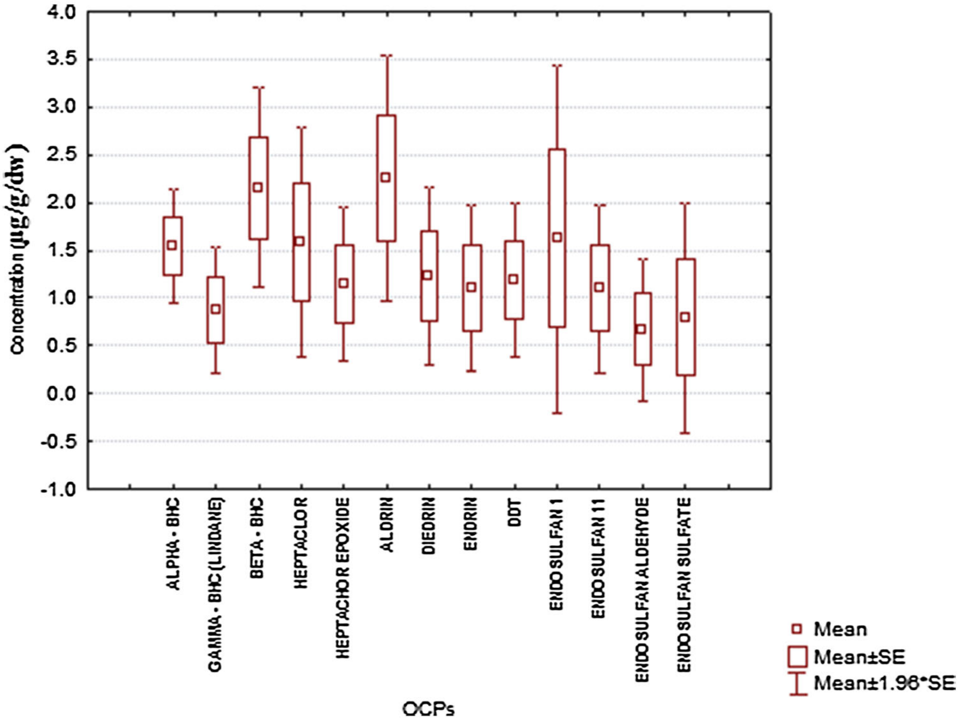
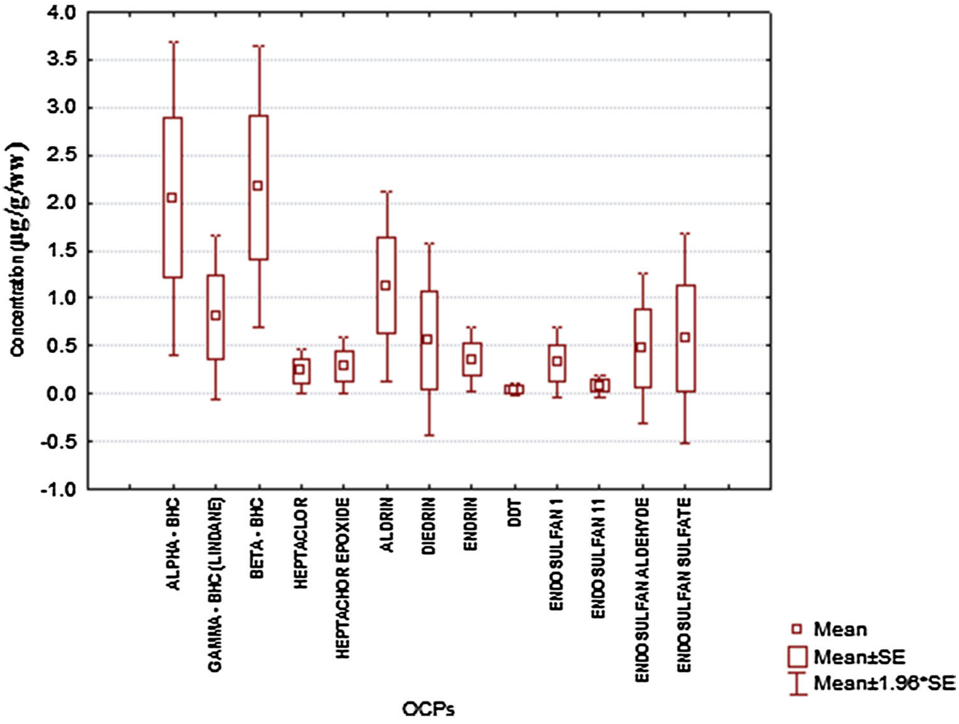


Fig. 4 Pesticide concentration (µg/kg/ww) profile in *Clarias gariepinus* samples from Illushi River



Spatial Distribution of Pesticide in Biota

All samples of *C. gariepinus* and *T. zilli* obtained from the Illushi River were observed to contain varying levels of pesticides residues (Table 2; Figs. 4, 5). The presence of pesticides in *C. gariepinus* and *T. zilli* could be attributed to the uptake of pesticide residues either through bioconcentration (from water through the gills or epithelial tissues) and through bioaccumulation (through water/food) leading to biomagnification (Murty 1986). In *C. gariepinus,*

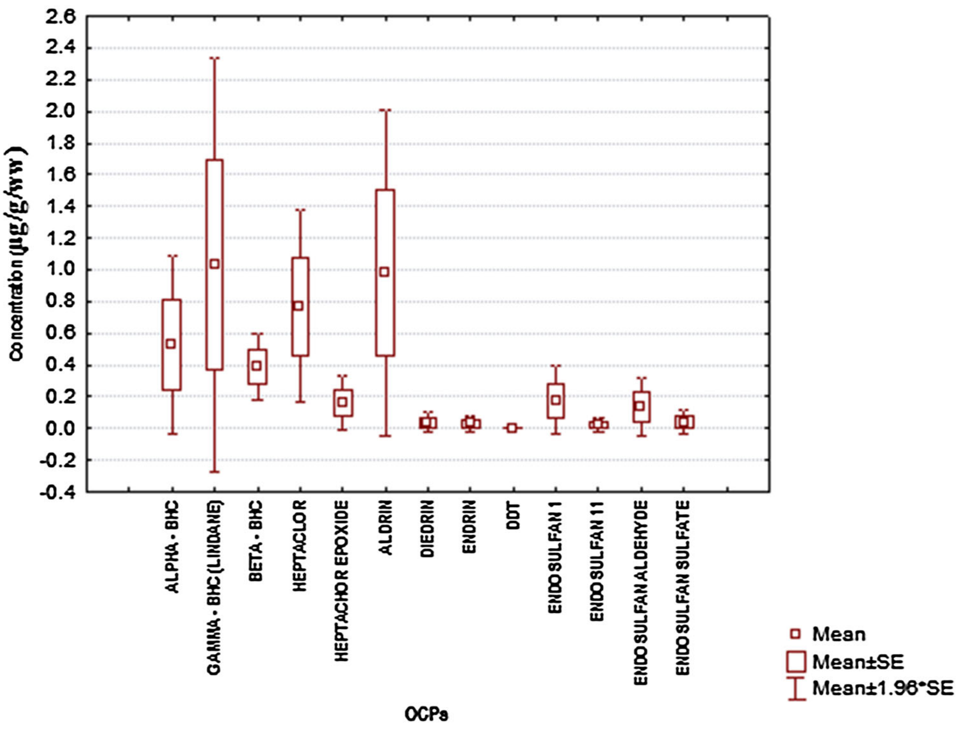


Fig. 5 Pesticide concentration (µg/kg/ww) profile in *Tilapia zilli* samples from Illushi River

β-HCH had the highest concentration (1.57 µg/kg/ww), while DDT had the lowest (0.03 µg/kg/ww) concentration (Fig. 4). 45 % of pesticide residues in *C. gariepinus* were HCH and its isomers, with β-HCH having the highest percentage distribution of 19 %. On the other hand, distribution of pesticide residues in *T. zilli* showed the dominance of ∑HCH, with γ-HCH (0.85 µg/kg/ww) having the highest pesticide concentration (Fig. 5). Higher concentration of pesticide residues was observed *C. gariepinus* when compared with *T. zilli.* This difference could be attributed to the feeding mode, age, and mobility of the fish species (Mwevura et al. 2002). Also *C. gariepinus* habituates levels closest to the sediments where it gets most of its food; hence, there is the likelihood of exposure to pesticides bound in sediment particles (Biego et al. 2010). Kidwell et al. (1990) and Murano et al. (1997) equally add that pesticide accumulation in fish is influenced by their lipid content, implying that the high lipid content in *C. gariepinus* allows more pesticide residues to be trapped in their lipid stores compared to *T. zilli.*

Ecological 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 3. The measured pesticide concentration comprised of the median and maximum detected water concentrations in other to reflect general and worst case scenario. It was observed that dieldrin, endosulfan I, endosulfan II, endosulfan aldehyde, heptachlor, heptachlor epoxide, aldrin, and DDT had risk quotient (RQ) values greater than 1. This is due to their high toxicity on fishes and aquatic invertebrates including algae. The implication of this is that concentrations of these pesticides in water from the Illushi River under medium and extreme conditions could pose high risk to non-target organisms in the river. It has been reported that when $RQ \geq 1$, there is high risk, while $0.1 \leq RQ \leq 1$ indicates medium risk, and $0.01 \leq RQ \leq 0.1$ indicates low risk (Sanchez-Bayo et al. 2002; Fatemeh et al. 2012). Risk assessment in this study agrees with similar studies by Hela et al. (2005), Vryzas et al. (2009) and Fatemeh et al. (2012).

Human Health Risk Assessment of Pesticides in Water Samples

The hazard quotient (HQ) or risk of non-cancer effect estimated for organochlorines pesticides residues in water samples is presented in Table 4. It was observed that HQ estimated for pesticide exposure for adults were lower than 1, indicating no potential health risk/non-cancer effects while HQ estimated for pesticide exposure for children were lower than one apart from heptachlor epoxide which was 1.21, indicating potential risk. These results implies that there is a high potential for non-

Table 3 Ecological risk assessment of pesticides in water detected in the Illushi River

Pesticides	MEC (median)	MEC (extreme)	(PNEC)	LC_{50}	AF	RQ (median)	RQ (extreme)
α-HCH	0.25	0.75	14.9	1490	100	0.02	0.05
γ-HCH	0.175	0.65	0.68	68	100	0.26	0.96
β-HCH	0.175	0.85	3.48	348	100	0.05	0.24
Heptachlor	0.15	0.6	0.25	25	100	0.60	**2.40**
Heptachlor epoxide	0.1	0.8	0.25	25	100	0.40	**3.20**
Aldrin	0.1	1.3	0.53	53	100	0.19	**2.45**
Dieldrin	0.025	1.55	0.0062	0.62	100	**4.03**	**250.00**
Endrin	0	0.2	0.0032	0.32	100	0.00	**62.50**
DDT	0	0.65	0.087	8.7	100	0.00	**7.47**
Endosulfan I	0.075	0.7	0.0033	0.33	100	**22.73**	**212.12**
Endosulfan II	0.05	1	0.0685	6.85	100	0.73	**14.60**
Endosulfan aldehyde	0	0.75	0.015	1.5	100	0.00	**50.00**
Endosulfan sulfate	0	0	0.015	1.5	100	0.00	0.00

Bold values represent the above acceptable threshold value (1)

MEC measured environmental concentration, *PNEC* probable no effect concentration, *RQ* risk quotient, *AF* assessment factor

Table 4 Chronic daily intake (CDI) and hazard quotient (HQ) for OCPs in water

	Child		Adults	
	CDI (ingestion)	HQ	CDI (Ingestion)	HQ
α-HCH	2.27E−05	0.0028	6.57E−06	0.0008
γ-HCH	1.62E−05	0.0541	4.69E−06	0.0156
β-HCH	2.2E−05	0.0028	6.37E−06	0.0008
Heptachlor	1.97E−05	0.0039	5.7E−06	0.0011
Heptachlor epoxide	1.58E−05	**1.2122**	4.56E−06	0.3508
Aldrin	1.9E−05	0.6334	5.5E−06	0.1833
Dieldrin	1.37E−05	0.2734	3.96E−06	0.0791
Endrin	2.32E−06	0.0772	6.71E−07	0.0224
DDT	7.88E−06	0.0158	2.28E−06	0.0046
Endosulfan I	1.32E−05	0.0022	3.82E−06	0.0006
Endosulfan II	1.07E−05	0.0018	3.09E−06	0.0005
Endosulfan aldehyde	7.88E−06	0.0013	2.28E−06	0.0004
Endosulfan sulfate	0	0.0000	0	0.0000
Hazard Index (HI)		**2.281**		0.66

Bold values represent the above acceptable threshold value (1)

cancer effects through the ingestion of pesticide contaminated water from the Illushi River by children. It has been reported that when the HQ is greater than 1, then adverse health effects are possible (Jiang et al. 2005). Cumulative risk assessment (hazard index) was calculated using a simplified additive approach by summing the individual HQ posed by each OCP; however, the synergistic, antagonistic or other interaction effects of pesticide mixtures were not considered. For adults, hazard index (0.66) was less than 1 indicating that the river water is relatively safe for portable consumption by adults. However, hazard index (2.28) estimated for pesticide exposures in children was above the threshold of 1. This implies that the river water is not safe for portable consumption by children. Results indicate that children were at higher risk compared to adults as a result of exposure to the contaminated river water. There has been no report of non-carcinogenic risk assessment of pesticide residues in Nigerian waters subjected to constant pesticide contamination; however, results from this study corroborate studies by Hu et al. (2011) and Papadakis et al. (2015).

Table 5 Estimated chronic daily intake (CDI) for OCPs in sediments

	Ingestion		Dermal		Inhalation	
	HQ child	HQ adults	HQ child	HQ adults	HQ child	HQ adults
α-HCH	3.63E−03	3.24E−04	1.33E−03	4.80E−04	1.45E−07	4.18E−08
γ-HCH	7.67E−02	6.83E−03	2.79E−02	1.02E−02	3.07E−06	8.80E−07
β-HCH	5.20E−03	4.64E−04	1.89E−03	6.89E−04	2.09E−07	5.98E−08
Heptachlor	5.00E−03	4.48E−04	1.82E−03	6.62E−04	2.00E−07	5.76E−08
Heptachlor epoxide	**1.48E+00**	1.32E−01	5.40E−01	1.96E−01	5.95E−05	1.71E−05
Aldrin	**1.15E+00**	1.03E−01	4.20E−01	1.52E−01	4.60E−05	1.32E−05
Dieldrin	4.02E−01	3.58E−02	1.46E−01	5.32E−02	1.61E−05	4.62E−06
Endrin	5.47E−01	4.87E−02	1.98E−01	7.20E−02	2.18E−05	6.27E−06
DDT	3.70E−02	3.32E−03	1.35E−02	4.90E−03	1.49E−06	4.26E−07
Endosulfan I	4.55E−03	4.07E−04	1.66E−03	6.03E−04	1.83E−07	5.23E−08
Endosulfan II	2.83E−03	2.53E−04	1.04E−03	3.77E−04	1.14E−07	3.27E−08
Endosulfan aldehyde	1.54E−03	1.37E−04	5.58E−04	2.03E−04	6.15E−08	1.77E−08
Endosulfan sulfate	2.28E−03	2.03E−04	8.30E−04	3.02E−04	9.15E−08	2.62E−08
Hazard index	**3.722**	0.332	**1.355**	0.492	0.00015	0.00004

Bold values represent the above acceptable threshold value (1)

Human Health Risk Assessment of Pesticides in Sediment Samples

Three routes of exposures were considered to determine the human health risk of exposure to contaminated sediments. The routes include ingestion of contaminated sediment, direct contact with skin, and inhalation of dust from sediments. Estimates were obtained using formulas 7–9 while results are presented in Table 5. For non-dietary exposures, potential human health risk is projected by comparing CDI estimates with the respective reference dose for each OCP. According to the USEPA's standards, when the estimated chronic daily intake (CDI) for a contaminant is more than the reference dose (RfD) of the contaminant via each exposure route, the contaminant level would exert an adverse human health effect (Huang et al. 2014). In this study, CDI estimates for all exposure routes were below the reference dose for each pesticides. This suggests that these contaminants under nondietary exposure to sediments are unlikely to pose any adverse health effects on individuals. Furthermore, CDI estimates were used to determine the hazard quotient (HQ) for each pesticide in other to project the risk of non-cancer effects. Results show all HQ calculated for each pesticide for all exposure routes where below 1 with exceptions to heptachlor epoxide (1.15) and Aldrin (1.48). Subsequently, cumulative risk assessment (hazard index) calculated for ingestion, dermal, and inhalation routes of exposures for adult were below the threshold (1). However, HI calculated for ingestion and dermal routes of exposure for children were above the threshold (1), implying that there is the high risk of non-cancer effects for children upon exposure to contaminated sediments. Model projections also showed that children were a higher risk population group, compared to adults while the risk of non-cancer effects is highest when the route of exposure is through the accidental ingestion of contaminated sediments.

Human Health Risk Assessment of Pesticide Residues in Biota

Clarias gariepinus and *T. zilli* are commercial aquatic products from the Illushi Region of Edo state (Ezemonye et al. 2015a, b). As shown in Tables 6 and 7, the estimated daily intake (EADI) and the hazard quotient (HQ) for each pesticide in each fish species were calculated using two population groups with varying body weights. Estimated average daily intake (EADI) for heptachlor epoxide, aldrin, dieldrin, and endrin in *C. gariepinus* were higher than their respective reference dose (RfD) for children and adults (Table 6). Consequently, hazard quotient (HQ) estimated for heptachlor epoxide (5.38), aldrin (9.11), dieldrin (2.93), and endrin (3.44) were above one (1) suggesting that there is the potential for non-cancer effects through the consumption of pesticide contaminated *C. gariepinus*. On the other hand, human health risk estimates for OCPs in *T. zilli,* presented in Table 7 showed that EADI for aldrin and heptachlor epoxide in *T. zilli* were higher than the acceptable daily intake for all weight groups suggesting that there is the potential for non-cancer effects through the consumption of pesticide contaminated *T. zilli.* This is further confirmed by hazard index (HI) calculations for *C. gariepinus* and *T. zilli* which showed that mixtures of OCPs were above one (1) for all the population groups implying that there could be risk (Tsakiris et al. 2011). Therefore, results from this study suggest a great potential for chronic

Table 6 Human health risk associated with the consumption of *Clarias gariepinus*

Pesticides	Concentration	CR	ADI	Child		Adult	
				EADI	HQ	EADI	HQ
α-HCH	1.48	9	8	0.49	0.06	0.19	0.02
γ-HCH	0.68	9	0.3	0.23	0.76	0.09	0.29
β-HCH	1.58	9	8	0.53	0.07	0.2	0.03
Heptachlor	0.2	9	5	0.07	0.01	0.03	0.01
Heptachlor epoxide	0.21	9	0.013	0.07[b]	5.38[a]	0.03[b]	2.08[a]
Aldrin	0.82	9	0.03	0.27[b]	9.11[a]	0.11[b]	3.51[a]
Dieldrin	0.44	9	0.05	0.15[b]	2.93[a]	0.06[b]	1.13[a]
Endrin	0.31	9	0.03	0.10[b]	3.44[a]	0.04[b]	1.33[a]
4, 4 DDT	0.03	9	0.5	0.01	0.02	0	0.01
Endosulfan 1	0.25	9	6	0.08	0.01	0.03	0.01
Endosulfan II	0.11	9	6	0.04	0.01	0.01	0
Endosulfan aldehyde	0.38	9	6	0.13	0.02	0.05	0.01
Endosulfan sulfate	0.42	9	6	0.14	0.02	0.05	0.01
Health Index					**21.84**		**8.44**

Bold values represent the above acceptable threshold value (1)

ADI acceptable daily intake, *EADI* estimated daily intake, *HQ* hazard quotient, *CR* consumption rate

[a] Above 1 (potential health hazard)

[b] Above ADI

Table 7 Human health risk associated with the consumption of *Tilapia zilli*

Pesticides	Concentration	CR	ADI	Child		Adult	
				EADI	HQ	EADI	HQ
α-HCH	0.38	9	8	0.12	0.01	0.05	0.01
γ-HCH	0.85	9	0.3	0.26	0.85	0.11	0.36
β-HCH	0.29	9	8	0.09	0.01	0.04	0
Heptachlor	0.6	9	5	0.18	0.04	0.08	0.02
Heptachlor epoxide	0.12	9	0.013	0.04[b]	2.69[a]	0.02[b]	1.15[a]
Aldrin	0.74	9	0.03	0.22[b]	7.39[a]	0.10[b]	3.17[a]
Dieldrin	0.08	9	0.05	0.03	0.5	0.01	0.21
Endrin	0.02	9	0.03	0.01	0.22	0	0.1
4, 4 DDT	0	9	0.5	0	0	0	0
Endosulfan 1	0.17	9	6	0.05	0.01	0.02	0
Endosulfan II	0.03	9	6	0.01	0	0	0
Endosulfan aldehyde	0.12	9	6	0.04	0.01	0.02	0
Endosulfan sulfate	0.03	9	6	0.01	0	0	0
Health Index					**11.73**		**5.02**

Bold values represent the above acceptable threshold value (1)

ADI acceptable daily intake, *EADI* estimated daily intake, *HQ* hazard quotient, *CR* consumption rate

[a] Above 1 (potential health hazard)

[b] Above ADI

toxicity through the consumption of pesticide contaminated *C. gariepinus* and *T. zilli* obtained from the Illushi. It was also observed that children were at greater risk of non-cancer effects when compared with the adult population group. This finding agrees with studies by Darko and Akoto (2008), Fianko et al. (2011), Andoh et al. (2013), and Sohair et al. (2013).

Conclusion

This study presents the first evidence of pesticide contamination of water, sediment, and fish species, arising from rice cultivation in the Illushi River Basin, Illushi town Edo State. Overall, sediment samples had the highest concentrations of pesticides residues, with the concentration of pesticide residues in the following order; Sediment > *Clarias gariepinus* > *Tilapia zilli* > water. Though the observed concentrations were minute, ecological risk assessment showed that there is a high potential of toxic effects to aquatic organisms upon exposure to organochlorine pesticides. Risk projections for humans from dietary and non-dietary intake also revealed that there is the potential for non-cancer effects. Projections showed that children were at higher health risk compared to adults. This calls for the need for the continuous monitoring of water bodies that drain agricultural fields because continuous exposure to pesticide contaminated resources obtained from the Illushi River (water, sediment, and fish) could affect the health of the population especially children. Thus, more efforts should be geared at reducing the indiscriminate and illegal use of pesticides (banned or approved). Orientation exercises for farmers to ensure proper application of pesticides, procurement of appropriate instrument of application, should be conducted regularly.

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