

Assessing pesticides residue in water and fish and its health implications in the Ivo river basin of South-eastern Nigeria

Abstract

This study assessed the concentration of pesticides residue in an agriculturally endemic basin in southeastern Nigeria, where pesticide is freely used without any form of regulations. Analysis of water and fish from the streams and tributaries in the basin reveal a very high level of pollution from organochloride pesticides and atrazine which occur above international drinking water standards and at health hazard levels where ecosystem and human health can be compromised. Some of these chemicals have been outrightly banned or their use restricted by international conventions, yet they are freely used in the study area. There is therefore a need for Nigeria to adhere to the provisions of the Stockholm Convention and the earlier Rotterdam Convention which list more chemicals for various forms of restriction to protect man and the environment.

Keywords: aquatic biota; hazard quotient (hq); health risk index; ishiagu; persistent organic pollutants; water quality

Volume 11 Issue 2 - 2022

Asiegbu Onyebuchi Victoria,¹ Ezekwe Ifeanyichukwu Clinton,¹ Raimi Morufu Olalekan²

¹Department of Geography and Environmental Management, University of Port Harcourt, Nigeria

²Department of Community Medicine, Faculty of Clinical Sciences, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria

Correspondence: Raimi Morufu Olalekan, Department of Community Medicine, Faculty of Clinical Sciences, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria, Tel +2347038053786, Email morufuolalekan.raimi@gmail.com

Received: August 05, 2022 | **Published:** August 17, 2022

Introduction

Although the Ivo River area is surrounded by rich arable agricultural lands that are cultivated regularly by the local farmers to supply food for them and their immediate families. This region is an intractably water scarce region, as such suffers from clean water scarcity.¹ Ezekwe² had observed an extensive use of pesticides and fertilizers and recommended further scientific investigation of impacts in the ecosystem. Farmers in communities within the Ivo River Ecosystem use of pesticides to lighten their labour burden by extensive use of herbicides and to improve their harvests. These pesticides remain in soil after the seasonal farming; some find their ways into water bodies then bottom sediments. When aquatic organisms: fish, plankton, and benthic organisms bioaccumulate these contaminants, they become a threat to other organisms through the food chain.³⁻⁵ Also, the contaminated streams become sources of danger to organisms including man that depend on them for survival.⁶⁻¹³

Pesticide residues poisoning has been documented as a killer by so many: cases include the mysterious deaths of over 18 people in Ode Irele, in Ondo State, Nigeria that was attributed to pesticides poisoning by the WHO (Sahara Reporters, 2015) and the poisoning of children reported as a major health problem in Zhejiang, China.¹⁴ The United Nations has also noted that an average of about 200,000 people die from the toxic exposure of pesticides per year across the world, calling for tougher global regulation of substances meant to control pests or weeds for plant cultivation. Rifai, 2017;¹⁵⁻²² Notwithstanding this level of alarm raised about pesticide poisoning, the native inhabitants and subsistent farmers in the Ivo River basin still embrace their use. This peculiar behaviour of rural farmers has also been reported elsewhere by scholars. For instance, Chaudhry & Malik (2017) and

Letchinger (2017), who opined that agricultural pollution occurs more in rural areas where population is less and mostly contains fertilizers, pesticides and eroded soil and these pollutants reach to water bodies through runoff after rain and flood.

Pesticide residues refer to pesticides components that may remain on or in soil after they are applied to food crops.¹⁵⁻²³ They are said to be “any substance or mixture of substances in food for man or animals resulting from the use of a pesticide and includes any specified derivative, such as degradation and conversion products, metabolites, reaction products, and impurities that are considered to be of toxicological significance”.²⁴ They also mean residues, including active substances, metabolites and/or breakdown or reaction products of active substances currently or formerly used in plant production products, including those which may arise because of use in plant protection, in veterinary medicine and as a biocide.²⁵

Pesticides are used to control pest impacts on crops, increase crop yield, increase crop quality and reliability as well as reducing production cost. Amongst the major group of pesticides mostly used worldwide are the organochlorines.^{26,15-22} The organochlorines (OC) are synthetic hydrocarbons generally termed “chlorinated hydrocarbons”. They contain Chlorine, hydrogen, carbons, and sometimes oxygen. Amongst this group are aldrin, chlordane, dieldrin, endrin, endosulfan, DDT (dichlorodiphenyltrichloroethane), heptachlor, lindane, and methoxychlor. These compounds are known for their high toxicity, slow degradation or high persistence, and bioaccumulation.²⁶

According to Akoto et al.,²⁷ the occurrence of pesticides residue, especially organochlorines (OCs) in the environment is a great worry due to their tendency for long-range transport. Also, their capacity

to bioaccumulate in food chain poses a threat to human health and the environment.^{28,29,18} Pesticides enter and pollute any component of the environment in several ways, including application, accidental spillage or through the unauthorized dumping of pesticide products or their containers.^{30,15–22} Contamination of water bodies for example is a major concern for fish and other aquatic organisms such as mussels, oysters, prawns, and lobsters which are major sources of protein.^{31,32} Accumulation of pesticides in these organisms has become a serious public health issue worldwide. Fish are used extensively for environmental monitoring because they concentrate pollutants directly from water and diet, thus enabling the assessment of transfer of pollutants through the food web.^{33,34,18}

Study area

The Ivo River ecosystem covers Ishiagu, Uturu, Lokpaukwu, Akaeze, Mpu, Okpanku and other towns where Ivo River tributaries extends. This covers an area of about 450 square kilometres and falls within latitudes 5° 51' N and 5° 59' N and longitudes 7° 24'E and 7° 40'E. The area is accessible through the Enugu-Port Harcourt Railway line which runs North-South through the centre of the study area; the Kaduna-Port Harcourt oil pipe line which runs north east- south west; the Enugu-Port Harcourt Express Road which passes through the extreme north western corner of the study area; the Lekwesi-Obiagu Road which runs east-west in the northern part of the study area and the Okigwe - Afikpo Road which runs East-Northeast – East in the southernmost part of the study area (Figure 1). This whole area includes the Ishiagu area of Ebonyi State, the Lokpaukwu and Lekwesi areas of Abia State and up to Okpanku Ikoli in Enugu State all in Southeastern Nigeria.²

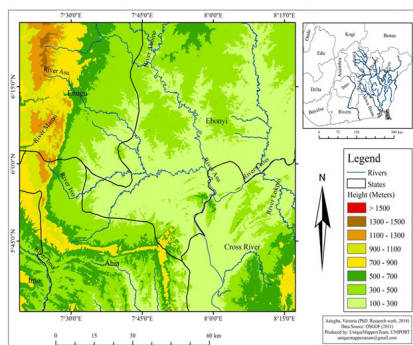


Figure 1 Digital Elevation Model of the Ivo River Basin.

Ezekwe² also noted that the physiography of the area is largely controlled by the underlying geologic formations. The area is an extensive low-lying terrain of about 200 to 400 feet (70-140 M) above mean sea level. Many streams like Nwaomaiyi, Obe and Aku (the head stream of the Ivo River) take their origin from the Umuelem Escarpment in the northeast. The streams are mainly seasonal and attain their full discharge during the rainy season between May and October. They flow generally south easterly and north easterly towards the Ivo River. Other streams like the Ikwo and Akwukwu originate from the mining areas and the central area of Ishiagu and flow south eastwards and eastwards into the Ivo River system (Figure 1). The study area is mainly, a level - gently undulating plains covered to a large extent by shales with minor local topographic features and some isolated hills of igneous bodies. The impervious nature of the underlying shales, clay soils and the presence of igneous intrusives have created numerous but ephemeral run-off. Response is so quick that much of the precipitation incident in the area is lost by direct run-off or overland flow. The Ishiagu area also experience satisfactory rainfall all year round. The rainy season lasts from April to October;

and is characterised by heavy downpours, thunderstorms, heavy surface flow and soil leaching, while the dry season prevails through the remaining months of the year. The rainy season has double maxima which peak in July and September. Mean annual climatic Figure 1, 2 include 1750 – 2000mm for rainfall; up to 1750 hours of sunshine and 70% for relative humidity.³⁵



Figure 2 Map of Nigeria showing study location (Wikipedia, 2021).

The area is made up of less than 300,000 rural dwellers,³⁶ who depend on their immediate environment for survival as native Africans. They practice subsistence farming which supply them enough food to feed themselves and their families with some surplus for trade. Notwithstanding, the exponentially growing human population further stresses the need for enhancing food production.³⁷ These farmers employ the use of pesticides to eliminate unwanted insects and weeds in their various farming practices, for maximum yield of their crops. These pesticides have been known to reach water-bearing aquifers below ground from applications on crops, seepage of contaminated surface water, accidental spills/leaks, and improper disposal.^{38,15–22} Runoff from rain fall and wind can carry pesticides from their point of use to contaminate surface waters. This endangers the life of thousands of inhabitants and species that depend on the water sources for survival/water supply.

These water sources provide the inhabitants with water for domestic use including drinking, also fish for nutrition thereby exposing them to high doses of the contaminants. Further Pollution of these natural resources is a serious problem because the local dwellers depend on them for survival. It could also affect organisms' free existence as they tend to exit from unfavourable conditions and migrate to less stressed environments, while some can possibly die out of this pressure. Further, it is suspected to affect the people's health as so many mysterious deaths have been attributed to witchcraft by the people of the study area, hence, this study.

Materials and methods

The Sampling Sites

Eight sampling sites including 4 points along the main channel of the Ivo River and 4 major tributaries shortly before their tipping point were purposively selected to meet the objectives of the study. Each tributary was sampled shortly before joining the Ivo River System and the main channel sampled shortly after to evaluate the number and concentration of pollutants coming from each of the sub-systems of the Ivo River System. The 4 sample sites along the main channel of the Ivo River Basin were:

- I. Aku stream at Obohia Mile 2
- II. Ikwo stream at Amagu
- III. Ivo stream at Okue
- IV. Ivo stream at Okpanku-ikoli.

While the remaining 4 sample sites from the major tributaries of the River System were:

- I. Aku stream at Uturu
- II. Ivo stream at FCA Ishiagu
- III. Ngada stream at Ntavu
- IV. Ehu stream at Mpu dam

Data collection and analysis

Surface water sampling and analysis

Water samples were collected from these sites during the wet season while fish samples were sampled by a combination of gill net and diving. Water sampling and handling followed methods established by the American Public Health Association for water and wastewater and analysis.³⁹ Surface water samples were collected for analysis of pesticide residues in pre-rinsed 250ml glass bottles with aluminium foil covers and metal caps to prevent any form of interference in the expected variables. These samples were stored in ice packed coolers during transportation and kept refrigerated at 4°C until they were analysed.

Extraction of pesticide residues from surface water

Fish samples were identified at the department of Fisheries in the nearby Federal College of Agriculture, Ishiagu. Fish caught during the study include Schilbe mystus in the Schilbedae the Okpanku Ikoli Site (8); clams and mussel (the endangered (*Margaritifera Auricularia*) from the Ikwo system and *Clarias Gariepinus* from the Aku stream and Ivo head stream systems.

Sample preparation and extraction

Water samples were filtered through 0.45 µm fiber glass filters (Whatman) to remove suspended materials while fish samples were thawed, cleaned with distilled water and scales sloughed off. Muscle tissues were dissected, minced into smaller pieces, and homogenized. Methods used for the extraction of pesticides residue in water and fish are as described in Mohammed et al.,⁴⁰

Extraction of water samples for organochlorine pesticides

Liquid-liquid extraction method was used for the determination of pesticide residue according to the procedure described by Pandit et al.,²⁸ A 50 mls volume of n-hexane was introduced into a 2-litre separating funnel containing 1 litre of filter water and were shaken manually for 5 minutes and allowed to settle. After complete separation, the organic phase was drained into a 250 mls conical flask, while the aqueous phase was re-extracted twice with 50 mls of n-hexane. The three extracted organic phases were combined and dried by passing through a glass funnel containing anhydrous sodium sulphate. The organic fraction was concentrated using rotary evaporator.

Extraction of organochlorine pesticides from fish samples

Extraction of fish samples were carried out according to method described by Michelle⁴¹. The fish samples (20g) were weighed into a 150 mls conical flask followed by the addition of 20 g and 5 g of anhydrous sodium sulphate and sodium hydrogen carbonate, respectively. 100 mls of 1:1 (v/v) ethyl acetate/dichloromethane mixture was transferred into the 20g fish samples and were thoroughly mixed by shaking the conical flask while cork. 20g of anhydrous sodium sulphate were added to the content of the conical flask followed by addition of 20g of sodium hydrogen carbonate. The conical flask was corked tightly and the mixture was shaken thoroughly

for 10 min. The content was allowed to stand for 3h. The organic layer was decanted into a 200 mls round bottom flask and was evaporated using the rotary evaporator at 40°C. The pesticide in the rotary flask were dissolved and was collected with 2 mls of ethyl acetate and transferred into a 2 mls vial and ready for the clean-up.

Silica gel clean-up of fish sample extracts for organochlorine pesticides

Extraction of samples were carried out according to method described by Michelle⁴¹. Ten grams (10g) portion of deactivated silica gel was weighed and transferred into a 10 mm glass chromatographic column followed by addition of 3g of anhydrous sodium sulphate. Ten (10mls) of the 1:1 (v/v) ethyl acetate/dichloromethane mixture were used to wet and rinse the column. The extract residue that is water and fish in 2 mls ethyl acetate was transferred into the column and the extracted vial rinsed (three times) with 2 mls ethyl acetate. The columns were eluted with 80 mls portion of ethyl acetate/dichloromethane at a rate of 5mls/min into a conical flask as fraction one. The column was eluted again with 50 mls portion of ethyl acetate/dichloromethane for the second elution and added to the first extract. All the fractions of each sample were concentrated to dryness using a rotary evaporator at 40 °C. Each residue was dissolved and collected in 2 mls ethyl acetate for gas chromatograph analysis.

De-fattening of the fish sample extracts for organochlorine pesticides

De-fattening of fish samples was carried out according to method described by Michelle⁴¹. Fifty (50) mls of 1:1 (v/v) hexane/acetonitrile solution were added to 2 mls pesticide extracted from the fish samples in a 100 mls separator funnel. The separator funnel was shaken gently for 3 min while releasing the gas pressure. The separator funnel was allowed to stand for 20 min to allow for phase separation of the organic solvents. The acetonitrile fractions containing the pesticides were collected into a 50 mls beaker while the fat containing hexane solvent phase was discarded. The acetonitrile solvent extract obtained was further clean-up using 25 mls of the pure hexane. The acetonitrile fraction was concentrated with rotary evaporator at 40°C and the content of the flask dissolved and collected with 2 mls of ethyl acetate into a 2 mls vial. The vial containing the pesticides extracts was stored in the refrigerator at 4°C for GCMS analysis.

Hazard risk estimation

Hazard risk estimation for consuming pesticides contaminated fish from the Ivo River ecosystem will be calculated using standard methods. For instance, the target hazard quotient (THQ) will be calculated using the methods described in Sarka et al.,⁴²

Target hazard quotient (THQ)

The THQ is used to determine non-carcinogenic risk level due to pollutant exposure. To assess the health risk from pesticide contaminated fish, the THQ was calculated as per USEPA Region III Risk Based Concentration⁴³ by using the following equation:

$$THQ = \frac{EF \times ED \times FIR \times C}{RfD \times BW \times AT} / 100$$

Where EF is the exposure frequency (350 days/year), ED is the exposure duration (30 years) for non-cancer risk as used by USEPA⁴⁴ FIR, is 9kg (FAO, 2011 per capita consumption of fish in Nigeria); RfD is the reference dose⁴⁵ of individual pesticide (0.035 mg/kg for atrazine, 0.0005 mg/kg for DDT and 0.0003 mg/kg for lindane); BW is an average adult body weight (68 kg) of Nigerians, Akinpelu et al., 2015, NIMED Health, 2021) and AT is the average exposure time

or life expectation (55 years for Nigerians; Macrotrends, 2021) and C, the concentration of pesticides in a fish sample, derived from fish laboratory analysis. It should be noted that results were divided by a factor of 1,000 to convert concentrations of pesticides from gm/g to mg/kg and concentrations were converted from dry weight to wet weight of fish by dividing by a factor of 7 for fish and 5 for mussels. AT=ED when pesticide is also a known carcinogen. Health risk assessment of consumers from the intake of pesticides contaminated fish was characterized by using health risk index (HI). The estimated HIs were obtained from the summation of THQs. When the HI is less than 1, the food concerned is considered acceptable. If it is greater than 1, the food concerned is considered a risk to the consumer Akoto et al.,²⁷

Results and discussions

Pesticides in water and fish from the Ivo river basin

The results of the analyses for pesticide residues concentration in water and fish are presented in (Table 1, 2). Eight pesticide residues were detected in the analysis of stream tributaries in the study area, out of which five namely: DDT, lindane, endrin, aldrin and chlordane were persistent organic pollutants banned out rightly by the Stockholm Convention because of their negative impacts on human and environment. The other three namely: atrazine, carbofuran, and paraquat are also restricted in different capacities by WHO and other environmental protection agencies.

Table 1 Pesticides Residues in water in Ivo River Ecosystem for Rainy Season

Parameters/Sites	1	2	3	4	5	6	7	8
Aldrin µg/L	10.21	20.22	15.38	8.55	13.23	13.34	13.45	8
Atrazin µg/L	2	2	2	1.22	2	2	1.6	0.88
Carbofuran µg/L	1.32	2.1	4	1.74	2.82	2.34	0	1.88
Chlordane µg/L	1.34	1.34	0.9	1.42	2.3	0	0.82	1.2
DDT µg/L	30.34	24	32.23	23.67	24.56	34.33	13.52	20.56
Endrin µg/L	10.21	12.33	12	8.23	12.2	8.23	12.2	6.22
Lindane µg/L	3	2	2.1	0	2.34	0	0	0
Paraquat µg/L	3.23	1.6	1.6	0	3.4	2.31	0	2
	61.65	65.59	70.21	44.83	62.85	62.55	41.59	40.66

Table 2 Pesticides Residue in fish in the Ivo River Ecosystem

Parameters/Sites	1	2	3	4	5	6	7	8
Aldrin mg/g	x	x	-	x	-	-	-	-
Atrazin mg/g	0.08	0.03	-	x	-	-	-	-
Carbofuran mg/g	x	x	-	-	-	-	-	-
Chlordane mg/g	x	x	-	x	-	-	-	-
DDTmg/g	0.65	0.42	-	0.1	-	-	-	-
Endrin mg/g	x	x	-	x	-	-	-	-
Lindane mg/g	0.098	0.896	-	x	-	-	-	-
Paraquat mg/g	x	x	-	-	-	-	-	-

N/B: X= Not Detected; - = No Fish Found

Aldrin ranged between 8ug/l and 20.22ug/l, Atrazine (0.88-2); Carbofuran (0.00-4.00); Chlordane (0.00-2.3); DDT (13.52-34.33); Endrin (6.22-12.33); Lindane (0.00-3.0); Paraquat (0.00-3.4). The table above shows that the tributary systems of Ikwo (site ii) and Okue (Site ii) that drain the central parts of the study area is the most polluted with pesticides. Further excel spreadsheet analysis revealed (Table 1a & 1b) that the concentration of Aldrin is highly correlated with Endrin while DDT occurrence seem highly determined by Carbofuran concentrations or use.

Table 2 shows that fish were caught in only three (Ivo, Ikwo and Mpu) out of the eight sampling sites during the study in the rainy season. Analysis revealed that Lindane or gammalin 20 had the highest concentration of 0.896 in the clam found in Ikwo tributary and an average concentration of 0,497 in the environment indicating a higher level of uptake. Lindane ranged between 0.098-0.896 (mg/g); DDT (0.10-0.65) and Atrazin 0.03-0.08. DDT was also the most common pesticide in the fishes.

Table 3 compares results from the analysis of water and fish samples with maximum permissible limits of pesticides concentration

of the WHO and some national governments. A closer look at the table shows that Nigeria (NESREA) does not have yet a standard for pesticide residue in the different environmental segments. However, these results show that concentrations of pesticides in water far exceeds the WHO, Australian and the United States limits by many orders of magnitude⁴⁶ indicating a highly polluted environment with a corresponding worrisome health risk implication.

Table 1a Aldrin/Endrin correlation

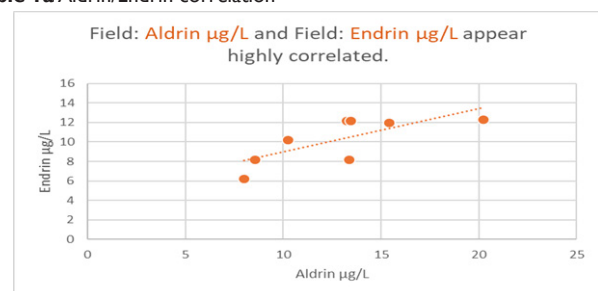


Table 1b DDT/Carbofuran correlation

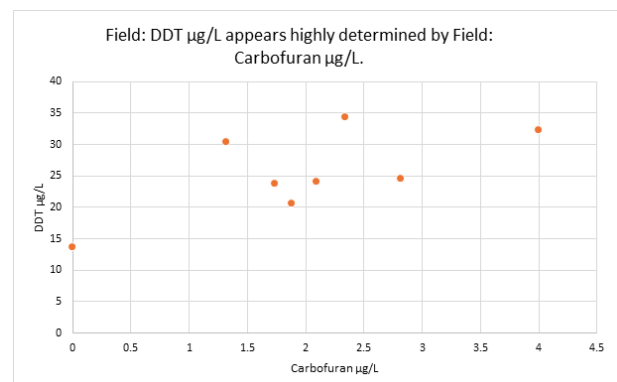


Table 3 Comparison of pesticides in water and fish with standards

Parameter	Unit	WHO	NESREA	Australia	United States	Desirable for fishpond	IVO River basin	
							Water	Fish
Aldrin	µg/L	0.03		< 0.01	3	0.003	16.9	-
Atrazine	µg/L	2					9.84	0.055
Carbofuran	µg/L	7					13.62	-
Chlordane	µg/L	0.2		< 0.01	2.4	0.0043	14.23	-
DDT	µg/L	2		< 0.0015	1.1	0.001	36.21	0.39
Endrin	µg/L	0.6		< 0.002	0.086	0.004 -0.0023	18.96	-
Lindane	µg/L	2					14.62	0.497
Paraquat	µg/L	3					8.19	-

(Adapted from IUPAC, 2003)

Table 4 Target Hazard Quotient of Pesticides Residue in fish in Ivo River Ecosystem

Arameters/Sites	1	2	3	4	5	6	7	8
Aldrin mg/g	x	x	-	x	-	-	-	-
Atrazin mg/g	0.008	0.0043	-	x	-	-	-	-
Carbofuran mg/g	x	x	-	-	-	-	-	-
Chlordane mg/g	x	x	-	x	-	-	-	-
DDT mg/g	10.03	7.9	-	1.32	-	-	-	-
Endrin mg/g	x	x	-	x	-	-	-	-
Lindane mg/g	2.16	45.2	-	x	-	-	-	-
Paraquat mg/g	x	x	-	-	-	-	-	-
ΣTHQ = HI	12.198	53.1		1.32				

N/B: X= Not Detected; - = No Fish Found

Human and aquatic health implications

According to the USEPA⁴⁷, for the maximum protection of human health from the potential carcinogenic effects due to exposure of Aldrin through ingestion of contaminated water and contaminated aquatic organisms, the ambient water concentration should be zero based on the non-threshold assumption for this chemical. However, zero level may not be attainable at the present time. Therefore, the levels which may result in incremental increase of cancer risk over the lifetime are estimated at 10⁻⁵, 10⁻⁶ and 10⁻⁷. The corresponding recommended criteria are 0.74 ng/l, 0.074 ng/l, and 0.0074 ng/l, respectively. If the above estimates are made for consumption of aquatic organisms only, excluding consumption of water, the levels are 0.79 ng/l, 0.079 ng/l, and 0.0079 ng/l, respectively. Lindane on the other hand, is highly toxic to aquatic organisms and was toxic to the kidney and liver after administration orally, dermally or by inhalation in short and long-term studies of toxicity and reproductive toxicity in rats. The renal toxicity of lindane was specific to male rats and was considered not to be relevant to human risk assessment, as it is a consequence of accumulation of α2u-globulin, a protein that is not found in humans (WWF, 1999); while atrazine has been associated with mammary tumors and an increased relative risk of ovarian neoplasia.⁴⁸

Ingestion of small to medium amounts of paraquat may lead to development low blood pressure, acute dehydration and may generate adverse health effects within several days to several weeks leading to; Heart, kidney, liver failure and lung scarring; while the ingestion of carbofuran can induce vomiting, lassitude, nausea and Hypersalivation. Neurological symptoms, including headache, dizziness, vision problems, incoordination, irritability, excitability,

weakness, muscle twitching and convulsions, have also been reported with human exposures by inhalation or ingestion to un quantified concentrations of chlordane.⁴⁹ Mammals exposed to moderate doses (500 mg/kg) of DDT (technical) have an increased risk of liver tumors and has been categorized the USEPA as a B2 carcinogen. This means that DDT has been shown to cause cancer in laboratory animals, but there is inadequate or no evidence that it may cause cancer in humans. Also, high levels of exposure of humans to endrin poisoning may lead to intoxication as excitability and convulsions, and death. It can also be deduced from the result above that the Ivo River ecosystem is sick and suffering from pesticide pollution induced perturbations. All tested parameters were above limits for natural resource preservation, desirable fishpond conservation, and aquaculture maintenance and preservation. These coupled with factors already identified by Asiegbu et al.,⁵⁰ may be making the ecosystem unusually stressful for aquatic life sustenance.

According to Asiegbu et al.,⁵⁰ the Ivo River System has an average temperature higher than the threshold for tolerable stream water for aquatic survival and this may affect the abundance of fish and other biota. They stated that the ecosystem is characterized by low dissolved oxygen and pH which may result in fish kill, and this could be the reason for low fish abundance at some sites in the study area Asiegbu et al.,⁵⁰ Pesticides may also undergo alkaline hydrolysis in which a pH greater than 7 causes some pesticides to endure a chemical degradation process.⁵¹ The implication is that pesticides (insecticides) which are acidic in nature are most effective in acidic environment. This explains why the Ivo River Basin with its established acidic environment cannot degrade the pesticides which reflected in the measured high concentrations.

Health risk assessment

Table 4 shows the results of health hazard analysis derived from target hazard quotient (THQ) calculated using the methods described in Sarkar et al.,⁴² and based on the USEPA Region III Risk Based Concentration⁴³ Health risk assessment reveals that atrazine concentrations do not occur at levels that may adversely affect human health in the two stations (Aku at Mile 2 Railway Station and Iwo stream at Amagu); however, the two stations have very high level of hazardous index especially with the consumption of clams and mussel (the endangered (*Margaritifera Auricularia*) from the Ikwo system and *Clarias Gariepinus* from the Aku stream and Ivo head stream systems.⁵²

Fish from the outlying and tipping point of the Ivo basin into the EzeAku system seem less polluted by pesticides, although, it still has a health hazard index of more than 1. The central portion of the Ivo River especially the Ikwo tributary which receives drainage from the

central Ishiagu area and the mining and farming districts of Ihetutu has the highest concentrations of pesticide residues both in water and biota.⁵³⁻⁶¹

Conclusion

This study assessed the concentration of pesticides residue in an agriculturally endemic basin in southeastern Nigeria, where pesticide is freely used without any form of regulations. Analysis of water and fish from the streams and tributaries in the basin reveal a very high level of pollution from organochloride pesticides which occur above international drinking water standards and at health hazard levels where ecosystem and human health can be compromised. Some of these chemicals have been out rightly banned or their use restricted by international conventions, yet they are freely used in the study area. The Stockholm Convention⁵² stated that these pesticides are Persistent Organic Pollutants because they are not easily degradable and they bio accumulate in the food chain, as such, Parties must take measures to eliminate the production and use of the chemicals listed under Annex A including aldrin, chlordane, endrin and lindane; while Parties must take measures to restrict the production and use of the chemicals listed under Annex B including DDT. There is therefore a need for Nigeria to adhere to the provisions of the Stockholm Convention and the earlier Rotterdam Convention which list more chemicals for various forms of restriction to protect man and the environment.

Acknowledgments

None.

Conflicts of interest

The authors declare that there is no conflict of interest.

References

1. Ezekwe IC, Aisubeogun AO, Chima GN, et al. TDS-Eh graph analysis: a new water quality index and rural water supply implications of a river affected by mining in south-eastern Nigeria. *Frontiers of Earth Science*. 2012;6(1):66–74.
2. Ezekwe IC. *Impact of mining on water Resources in the Ishiagu Area of Southeastern Nigeria*. An unpublished PhD thesis, Abia State University, Uturu, Nigeria. 2009.
3. Suleiman Romoke Monsurat, Raimi Morufu Olalekan, Sawyerr Henry Olawale. A Deep Dive into the Review of National Environmental Standards and Regulations Enforcement Agency (NESREA) Act. *International Research Journal of Applied Sciences*. 2019;1(4):108–125.
4. Lateefat HM, Faith A, Yusuf AB et al. Food for the Stomach Nourishing our Future: Assessment of Potassium Bromate in Local and Packaged Bread Sold in Ilorin Metropolis. *Public H Open Acc*. 2022;6(1).
5. Adiamo YB, Sawyerr OH, Olaniyi OA, et al. Assessment of Microbiological Quality of Ready to Eat Food Served in Ships Along Warri, Koko and Port Harcourt Water Ways, Nigeria. *Online Journal of Microbiological Research*. 2022;1(1):1–7.
6. Food and Agriculture Organization of the United Nations (FAO). *The state of the world's land and water resources for food and agriculture; Managing systems at risk*. Earthscan, Abingdon. 2011.
7. Morufu Raimi, Clinton Ezekwe. *Assessment of Trace Elements in Surface and Ground Water Quality*. LAP Lambert Academic Publishing, Mauritius. 2017.
8. Raimi MO, Clinton IE, Olawale HS. *Problematic Groundwater Contaminants: Impact of Surface and Ground Water Quality on the Environment in Ebocha-Obrikom Oil and Gas Producing Area of Rivers State, Nigeria*. Oral Presentation Presented at the United Research Forum. 2021.
9. Raimi MO, Sawyerr HO, Ezekwe IC, et al. *Toxicants in Water: Hydrochemical Appraisal of Toxic Metals Concentration and Seasonal Variation in Drinking Water Quality in Oil and Gas Field Area of Rivers State, Nigeria*. IntechOpen; 2022a.
10. Raimi O, Ezekwe C, Bowale A, et al. Hydrogeochemical and Multivariate Statistical Techniques to Trace the Sources of Ground Water Contaminants and Affecting Factors of Groundwater Pollution in an Oil and Gas Producing Wetland in Rivers State, Nigeria. *Open Journal of Yangtze Oil and Gas*. 2022b;7(3):166–202.
11. Olalekan MR, Olawale HS, Clinton IE, et al. Quality Water, Not Everywhere: Assessing the Hydrogeochemistry of Water Quality across Ebocha-Obrikom Oil and Gas Flaring Area in the Core Niger Delta Region of Nigeria. *Pollution*. 2022;8(3):751–778.
12. Raimi M, Sawyerr H. Preliminary Study of Groundwater Quality Using Hierarchical Classification Approaches for Contaminated Sites in Indigenous Communities Associated with Crude Oil Exploration Facilities in Rivers State, Nigeria. *Open Journal of Yangtze Oil and Gas*. 2022;7(2):124–148.
13. Raimi OM, Sawyerr OH, Ezekwe CI, et al. Many oil wells, one evil: comprehensive assessment of toxic metals concentration, seasonal variation and human health risk in drinking water quality in areas surrounding crude oil exploration facilities in rivers state, Nigeria. *International Journal of Hydrology*. 2022c;6(1):23–42.
14. Yimaer A, Chen G, Zhang M, et al. Childhood pesticide poisoning in Zhejiang, China: a retrospective analysis from 2006 to 2015. *BMC Public Health*. 2017;17(1):602.
15. Hussain Muhammad Isah, Morufu Olalekan Raimi, Henry Olawale Sawyerr. Probabilistic Assessment of Self-Reported Symptoms on Farmers Health: A Case Study in Kano State for Kura Local Government Area of Nigeria. *Environmental Analysis & Ecology Studies*. 2021a;9(1):975–985.
16. Hussain Muhammad Isah, Morufu Olalekan Raimi, Henry Olawale Sawyerr. Patterns of Chemical Pesticide Use and Determinants of Self-Reported Symptoms on Farmers Health: A Case Study in Kano State for Kura Local Government Area of Nigeria. *Research on World Agricultural Economy*. 2021b;2(1):37–48.
17. Morufu Olalekan Raimi, Tonye Vivien Odubo, Ogah Alima, et al. Articulating the effect of Pesticides Use and Sustainable Development Goals (SDGs): The Science of Improving Lives through Decision Impacts. *Research on World Agricultural Economy*. 2021a; 2(1).
18. Olalekan Morufu Raimi, Tonye Vivien Odubo, Adedoyin Oluwatoyin Omidiji. Creating the Healthiest Nation: Climate Change and Environmental Health Impacts in Nigeria: A Narrative Review. *Scholink Sustainability in Environment*. 2021;6(1).
19. Isah HM, Sawyerr HO, Raimi MO. Assessment of Commonly Used Pesticides and Frequency of Self-Reported Symptoms on Farmers Health in Kura, Kano State, Nigeria. *Journal of Education and Learning Management (JELM)*. 2020a;1(1):31–54.
20. Isah Hussain Muhammad, Morufu Raimi Olalekan, Sawyerr Henry Olawale, et al. Qualitative Adverse Health Experience Associated with Pesticides Usage among Farmers from Kura, Kano State, Nigeria. *Merit Research Journal of Medicine and Medical Sciences*. 2020b;8(8):432–447.
21. Olalekan RM, Muhammad IH, Okoronkwo UL, et al. Assessment of safety practices and farmer's behaviors adopted when handling pesticides in rural Kano state, Nigeria. *Arts & Humanities Open Access Journal*. 2020;4(5):191–201.
22. Raimi MO, Sawyerr HO, Isah HM. Health risk exposure to cypermethrin: A case study of kano state, Nigeria. *Journal of Agriculture*. 2020;1(1).
23. Mc Naught AD, Wilkinson A. *Compendium of chemical terminology: IUPAC recommendations (2nd ed)*. Oxford: Blackwell. 1997.

24. WHO. *Pesticide residues in food*. In: World Health Organization; 2017.
25. Gottvaldova E Mgr. *Multianual control plan for pesticide residues 2017 - 2019*. 2016;
26. Jayaraj R, Megha P, Sreedev P. Review Article. Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. *Interdisciplinary Toxicology*. 2016;9(3-4):90–100.
27. Akoto Osei, Augustine Asore A, KD Adotey. Pesticide residues in water, sediment and fish from Tono Reservoir and their health risk implications. *SpringerPlus*. 2016;5(1):1849.
28. Pandit GG, Sahu SK, Sharma S. et al. Distribution and Fate of Persistent Organochlorine Pesticides in Coastal Marine Environment of Mumbai. *Environmental Toxicology and Chemistry*. 2006;32(2):240–243.
29. Guo Y, Meng X, Tang H, et al. Tissue distribution of organochlorine pesticides in fish collected from the Pearl River Delta, China: implications for fishery input source and bioaccumulation. *Environ Pollut*. 2008;155(1):150–156.
30. Cox JR. *Pesticide residue analysis facilities: experiences from the Natural Resource Institute's Support Program*. In: Hanak E, ET AL., editors. Food safety management in developing countries, Proceedings of the International Workshop, CIRAD-FAO, December 11–13, 2000. Montpellier, France. 2002.
31. Essumang DK, Chokky L. Pesticide residues in the water and fish (Lagoon tilapia) samples from Lagoons in Lagoons in Ghana. *Bull Chem Soc Ethiopia*. 2009;23(1):19–27.
32. Afolabi Abiodun Segun, Raimi Morufu Olalekan. When Water Turns Deadly: Investigating Source Identification and Quality of Drinking Water in Piwoyi Community of Federal Capital Territory, Abuja Nigeria. *Online Journal of Chemistry*. 2021;1(1):38–58.
33. Lanfranchi AL, Menone ML, Miglioranza KSB, et al. Stripped weakfish (*Cynoscion guatucupa*): a biomonitor of organochlorine pesticides in estuarine and near-coastal zones. *Mar Pollut Bull*. 2006;52(1):74–80.
34. Okoyen E, Raimi MO, Omidiji AO, et al. Governing the Environmental Impact of Dredging: Consequences for Marine Biodiversity in the Niger Delta Region of Nigeria. *Insights Mining Science and technology*. 2020;2(3):555–586.
35. *Imo State Ministry of Works and Transport (IMWT)*. Atlas of Imo State Nigeria. C& G Company, Italy. 1984.
36. National Population Commission (NPC). *Nigeria National Census: Population Distribution by Sex, State, LGAs and Senatorial District: 2006 Census Priority Tables (Vol. 3)*. 2006.
37. Carvalho FP. Pesticides, environment, and food safety. *Food and Energy Security*. 2017;6(2):48–60.
38. Chukwu-Okeah GO, Ezekwe IC, Ezenwa I. Pesticide residue pollution in the groundwater system of ishiagu and potential health impacts. *International Journal of Ground Sediment & Water*. 2021;13:789–806.
39. American Public Health Association Standard. *Standard Methods for the Examination of Water & Wastewater, Volume 21*. APHA, AWWA, WEF. Washington DC. 2005.
40. Mohammed Zakari, Akan Joseph C, Ahmad Shamsu. Organochlorine Pesticide Residues in Water, Sediment and Various. Species of Fish from Komadugu River Basin, Yobe State, Nigeria. *Journal of Environmental Science, Toxicology and Food Technology*. 2017;11(6):19–30.
41. Michelle LH, Megan MM. Method of Analysis Determination of Pesticides in Sediment using Gas Chromatography/ Mass Spectrometry. *US Geological Survey Techniques and Method*. Reston Virginia. 2012;8–10.
42. Sarkar T, MM Alam, N Parvin, et al. Assessment of heavy metals contamination and human health risk in shrimp collected from different farms and rivers at Khulna-Satkhira region, Bangladesh. *Toxicology reports*. 2016;3:346–350.
43. USEPA. *EPA Region III Risk-Based Concentration Table*. RL Smith. February 9, 1995.
44. USEPA (US Environmental Protection Agency). *Guidance manual for assessing human health risks from chemically contaminated, fish and shellfish*. EPA-503/8-89-002, US EPA Office of Marine and Estuarine Protection, Washington, DC. 1989.
45. Watts RJ, AL Teel. *Groundwater and Air Contamination: Risk, Toxicity, Exposure Assessment, Policy, and Regulation*. Treatise on Geochemistry (Second Edition). Elsevier. 2014.
46. IUPAC. Regulatory limits for pesticide residues in water (IUPAC Technical Report): *Pure and Applied Chemistry*. 2003;75(8):1123–1155.
47. USEPA. *Ambient Water Quality Criteria for Aldrin/Eldrin*. Office of Water. Washington, D.C. 1980.
48. WHO. *Atrazine in Drinking-water: Background document for development of WHO Guidelines for Drinking-water Quality*. Geneva; 2003.
49. WHO. *Chlordane in Drinking-water: Background document for development of WHO Guidelines for Drinking-water Quality*. Geneva. 2004.
50. Asiegbu VO, Ajiboye GO, Ezekwe IC. “Preliminary Investigation of the Distribution and Relative Abundance of Plankton and Fish Species in Ivo River Basin Southeastern Nigeria.” *Acta Scientific Microbiology*. 2019;2(4):1–15.
51. Cloyd RA. *Effects of pH on Pesticides*; 2016.
52. Stockholm Convention. *All POPs listed in the Stockholm Convention*. 2019.
53. Fatoki OS, Awofolu OR. Levels of Organochlorine Pesticide Residues in Marine-, Surface-, Ground- and Drinking Waters from the Eastern Cape Province of South Africa. *Journal of Environmental Science and Health, Part B*. 2004;39(1):101–114.
54. Han BC, Jeng WL, Chen RY, et al. Estimation of target hazard quotients and potential health risks for metals by consumption of seafood in Taiwan. *Arch Environ Contam Toxicol*. 1998;35(4):711–720.
55. <https://nimedhealth.com.ng/2020/10/25/average-body-weight-of-a-nigerian-weight-of-a-man-and-a-woman-in-kg-in-nigeria/><https://www.macrotrrends.net/countries/NGA/nigeria/life-expectancy>
56. <http://saharareporters.com/2015/04/19/world-health-organization-blames-pesticide-%E2%80%98mysterious-deaths%E2%80%99-nigerian-town>.
57. Morufu Olalekan Raimi. “Self-reported Symptoms on Farmers Health and Commonly Used Pesticides Related to Exposure in Kura, Kano State, Nigeria”. *Annals of Community Medicine & Public Health*. 2021;1(1):1002.
58. Olalekan Morufu Raimi, Abiola Ilesanmi, Ogah Alima, et al. Exploring How Human Activities Disturb the Balance of Biogeochemical Cycles: Evidence from the Carbon, Nitrogen and Hydrologic Cycles. *Research on World Agricultural Economy*. 2021;2(3):23–44.
59. Rufai R. *UN: 200,000 die each year from pesticide poisoning*. 2017.
60. WHO. *Guidelines for Drinking-Water Quality*. Geneva: World Health Organization; 2011. WHO Environmental Health Indicators: Framework and Methodologies. Environmental Health Indicators: Framework and Methodologies. Geneva: World Health Organization; 1995.
61. *World Wildlife Fund Canada (Wwf)*. Lindane – A Review Of Toxicity and Environmental Fate; 1999.