



Distribution and health risk assessment of some organochlorine pesticides in water, sediments, and fish from Hawul river basin

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Abstract

The distribution of organochlorine pesticides Methoxychlor, DDT and its metabolites in water, sediments and fish were carried out to assess the contamination status in some surface waters. The QuChERS method was employed for pesticides extraction and clean up. Gas chromatography in tandem with mass spectrometer was used in identification and quantification of these pesticides. The results showed that total OCPs burden in water, sediments, and fish range between 0.1mg/L – 3.6mg/L, 0.07mg/kg - 0.38 mg/Kg and 0.25mg/kg – 3.6 mg/kg respectively. The mean concentrations of methoxychlor ranges between 0.01 mg/L – 0.1 mg/L, ND – 0.07mg/kg, 0.04mg/kg – 0.1mg/kg for water, sediments, and fish samples respectively. The Hazard index due to OCPs consumption of fish is in the sequence Garkida (WB) > Kiri > Ndabna > Kopri > Garkida > Daba. The incremental lifetime cancer risk (ILCR) due to water ingestion ranges between 6.75×10^{-4} – 3.1167×10^{-2} and 4.048×10^{-3} – 1.87×10^{-1} for adults and children respectively. The trend of ILCR is in a sequence Kopri > Garkida WB > Daba > Kiri > Ndabna > Garkida. The incremental lifetime cancer risk due to fish ingestion ranges between 3.86×10^{-5} - 5.17×10^{-4} and 2.31×10^{-4} - 3.103×10^{-3} for an Adult and a child of 10kg weight respectively. This risk value implies that between 39 to 231 people in a million who are exposed to these pollutants may develop cancer in their life time.

Keywords: Organochlorine, Pesticide, Pollution, Health Risk, Carcinogenic

1. Introduction

Agrochemicals consists of fertilizers, which are used as sources of nutrients to crops, and pesticides, which are applied before, during, and after cultivation to protect the crops [1-3]. Pesticides increases agricultural productivity [4-7], economic prosperity (through value chain) [8], as well as control insect and pest borne diseases such as malaria, dengue, and black plague [9-10].

Pesticides have been a major part of modern agriculture, boosting productivity by reducing losses from the effects of weeds, diseases, and insect pests that can significantly reduce the expected yield of harvestable produce [11]. Pesticides have shown great advantages to the survival of humanity, but their over usage and improper applications are of serious concern due to the considerable negative effects on biodiversity, environmental quality, food quality and human health [12].

The toxicity, persistence, non-biodegradability, and high potential for bioaccumulation of pesticides such as organochlorines (OCs) has made many advanced countries to prohibit their usage but are still used in many developing and third-world countries due to their low cost and wide applicability in both agriculture and public health [13-14].

Various point and non-point sources, such as Atmospheric deposition, sewage sludge, surface runoff

from agricultural fields, accidental spraying, accidental spills and effluents released from industries and wastewater have been identified as the sources of these pesticides [15-17].

Majority of these pesticides found their way into the environment, and due to their persistence, they left residual amounts in air, soil, surface water, ground water of many locations with different quantities [18-19].

Hawul River basin is the origin of both Tum River and Hawul River which are the major tributaries to River Gongola, which confluences with River Benue at Numan Local Government Area. It has been a source of water and Fish for domestic usage in many villages and towns whose inhabitants are largely farmers; therefore, there is need for continued monitoring of these chemical pollutants and their possible health hazard risk. The pesticides of interest to this very work were p, p'-DDT, its metabolites p, p'-DDD, p, p'-DDE, and Methoxychlor.

2. Materials and Methods

2.1 Study Area

The Study area lies between longitudes 11.00°N and 10.00°N and Latitude 12.00°E to 13.00° E as shown in the map below. The sample collection locations were Kopri (10° 28'2''N, 12°50'49''E) Ndabna (10° 23'2''N, 12°49'27''E) in Hong L.G.A, Garkida WB (10° 24'52''N, 12°33'58''E) Garkida (10° 24'52''N, 12°33'58''E) in

Gombi L.G.A, Kiri (9° 35'41'' N, 12°00'05'' E) and using stainless steel blade and then air dried to constant Daba (9° 40'0''N, 12°10'59''E) in Shelleng L.G.A. The weight.

sampling locations are steep part of the basin which receive their waters from the flood plains of the Hawul basin and keeps them throughout the year. The important human activities around the sampling areas are irrigation farming, fishing, laundry, swimming during the day and some pockets of illegal artisanal mining.

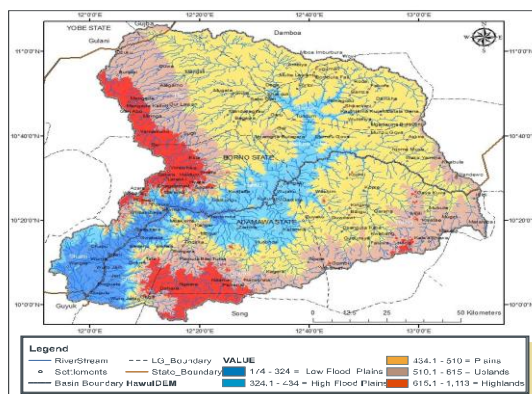


Figure 2.1: Map of Hawul basin showing Hawul River and its tributaries sourced from Mayomi *et al.*, [20].

2.2 Sample collection

The study area was divided into six sampling sites along the Adamawa part of Hawul River Basin, in which samples of water, sediments, and fish were collected. Each sample was taken in triplicate from which a representative sample was drawn from.

2.2.1 Water sampling

A total volume of 1 L water sample was collected as reported by Olawale *et al.*, [21] from each site in polyethylene bottles (twice rinsed with deionized water) and acidified with 3% HNO₃ then preserved in an ice box and transported to the laboratory for further analysis. Each sample was taken in triplicate from which a representative sample was drawn from.

2.2.2 Sediments sampling

An estimated 50g of sediment was taken from a depth of 2-5 cm under the riverbed at different points (North, east, west and south). The sediment samples were dried in an oven for about 48h at 120°C and then homogenized by grinding in a blender and sieved. It was stored in labelled bottles until chemical analysis.

2.2.3 Fish Sampling

Live sample of African Catfish (*Clarias gariepinus*) was caught from the sampling points with the help of local fishermen [21]. The fish samples were briefly rinsed with distilled water to remove any adhering substances and then immediately preserved on ice in an ice box then deep frozen in the laboratory before analysis. After identification at fisheries department of Modibbo Adama University, the fish samples were dissected into separate organs (flesh, liver, and gills)

2.3 Determination of OCPs concentrations

The QuEChERS method for pesticide analysis was adopted as reported by Akoto *et al* [22] and Modibbo *et al* [23] with slight modification in terms of sample size for all samples.

2.3.1 Extraction of pesticide residues in water

One hundred (100) mL of water sample was placed in a separating funnel and 50 mL of dichloromethane (DCM) was introduced and agitated vigorously for 5 mins to ensure thorough mixing. The mixture was then allowed to settle for 30 mins for effective separation of the aqueous and organic phases. The organic phase was then filtered off into a 250 mL volumetric flask through a funnel packed with anhydrous sodium sulphate (Na₂SO₄). This procedure was repeated twice with 50 mL aliquot of DCM/n-hexane (4:1). The extracts were then combined and concentrated to about 5mL using rotary evaporator at 45 °C.

2.3.2 Extraction of pesticide residues in sediments

About 10g of dry sediment was transferred into an extraction thimble of a Soxhlet extractor 150 mL aliquot of n-hexane/acetone (4:1) v/v was used to extract the pesticide residue in sediment for six hours. The extract was then concentrated to about 1 mL using rotary evaporator at 40 °C. This procedure was also repeated twice, and the extracts combined and dissolved in 10 mL n-hexane and preserved for clean-up and GC analysis [25].

2.3.3 Extraction of pesticide residues in fish

Ten-gram (10g) of grinded and homogenized fish was placed in 100mL conical flask and 20g of anhydrous sodium sulphate and mixed thoroughly. 50mL aliquot of n-hexane/acetone (2:1) v/v was then added and sonicated for 20mins. The supernatant was filtered off into a 250mL conical flask. The extraction was repeated twice, and the supernatants were combined and concentrated to about 5mL using rotary evaporator.

2.3.4 Sample clean-up

About 2.5g octadecyl (C18) was packed into a glass column plugged with glass wool and 1.0 g of anhydrous sodium sulphate [25]. The prepared column was then wet and rinsed with 10mL n-hexane. The extract was then introduced into the column and eluted with 20 mL aliquot of n-hexane/acetone mixture. The eluents were collected into a round bottom flask and concentrated to dryness. The residue was then dissolved in 2mL ethylacetate and kept in a GC vial for analysis.

2.4 Health risk estimation due to OCPs

The non-carcinogenic and carcinogenic health risk estimates for each of the organochlorine pesticides residues in water and fish were computed using basic standard indices: The Estimated Average Daily Intake

(EADI), Acceptable Daily Intake (mg/kg/d), Hazard Quotients, the Hazard Index (HI) and cancer risk as reported by Chen *et al.* [2], Akoto *et al.* [22] and Adeleye *et al.*, [26].

$$EADI = \frac{MRPC \times FCR}{MBW} \quad (1)$$

Where, MRPC= Mean Residual Pesticide Concentration (mg/kg)

FCR= Food Consumption Rate (kg/day)

MBW= Mean Body Weight (kg)

$$HQ = \frac{EADI}{ADI} \quad (2)$$

Where, HQ= Hazard Quotients

EADI= Estimated Average Daily Intake

ADI= Acceptable Daily Intake (mg/kg/d)

$$Hazard\ Index\ (HI) = \frac{\sum EADI}{ADI} \quad (3)$$

When the health risk index is > 1, the food involved is considered a risk to the consumers; when the index < 1, the food involved is considered acceptable.

Cancer risk = EDI x Cancer slope Factor (CSF)

Table 2.1: Constants adopted for estimation of Health risk index for OCPs based on USEPA as reported in the literatures [2, 23, 26]

Compound	CSF (ingestion)(1/(mg/kg/d))	MRL (mg/kg)	ADI (mg/kg/BW)	Reference
Methoxychlor	NC	0.01	0.10	[27]
P, p'-DDE	0.34	0.05	0.01	[27]
P, p'-DDD	0.24	0.05	0.01	[27]
P p'-DDT	0.34	0.05	0.01	[27]

NC = non-carcinogenic, the fish consumption of 13.3 kg/capita/year according to Bradley *et al* [28] was adopted.

3. Results and discussion

Table 3.1: Concentration of OCPs in water samples (mg/L)

	Kopri	Ndabna	Garkida WB	Garkida	Daba	Kiri
Methoxychlor	0.10	0.01	0.01	0.04	0.01	0.01
p,p'- DDE	0.07	0.03	0.02	0.02	0.04	0.03
p,p'-DDD	3.40	0.08	0.03	0.02	0.02	0.03
p,p'-DDT	0.03	0.03	0.13	0.02	0.08	0.07
Total OCPs	3.60	0.15	0.19	0.10	0.15	0.14

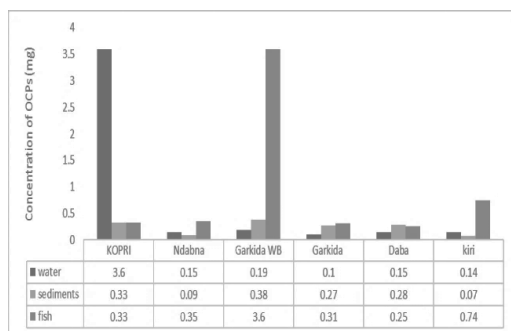


Figure 3.1: Total OCPs burden in water sediments and fish

The concentrations of OCPs in water samples are presented in Table 3.1, and the total OCPs in all the environmental compartments are presented in figure 3.1. The concentration of methoxychlor in all sampling locations were within the acceptable limits recommended by EPA as reported by ATSDR [29] except at Kopri which had a value of 0.1 mg/L which is far above the 0.04 ppm recommended.

P,p' DDT and its metabolites p,p' DDD and p,p' DDE concentration are presented in figure 1 and table 1. The concentrations of DDT and its metabolites in all the

sampling sites were greater than the MRL value of 0.02 mg/L [30] indicating contamination of the water by DDTs. Kopri had the highest (97.3%) \sum DDTs contribution to OCPs burden while Garkida had the lowest (60%) contribution of \sum DDTs to the overall OCPs residues.

The ratio of DDT to the sum of its metabolites is used as the basis for source apportionment in the environment i.e., how long it was in the environment. A ratio >1 is normally expected for aged mixtures in the environment and values <1 indicate relatively recent application of DDT [31]. In this study Kopri, Ndabna and Garkida had a ratio of <1 indicating recent application of the DDTs in the areas, while Garkida (WB), Daba and Kiri had a ratio of >1 indicating historic usage of DDTs in these areas.

Furthermore, the ratio of DDD/DDE is used in understanding the pathways of the degradation of their parent compound DDT [32]. A ratio of <1 indicates aerobic degradation, while a ratio of >1 indicates anaerobic degradation. For this present study, all the sampling sites had a ratio of >1 except Daba with a ratio of <1. This means that, in all the sampling site the parent DDT undergoes anaerobic degradation except for Daba.

Table 3.2: Concentration of OCPs in Sediment samples (mg/kg)

	Kopri	Ndabna	Garkida WB	Garkida	Daba	Kiri
Methoxychlor	ND	0.03	0.07	0.06	0.03	0.02
p,p'- DDE	0.22	0.03	0.09	0.03	0.05	0.01
p,p'-DDD	0.02	0.02	0.20	0.09	0.10	0.02
p,p'-DDT	0.09	0.01	0.02	0.09	0.10	0.02
Total OCPs	0.33	0.09	0.38	0.27	0.28	0.07

ND= not detected

Methoxychlor was also detected in all the sampling sites with the exception of Kopri. Methoxychlor had a range of ND – 0.07mg/kg in the sediment samples of the study area. Methoxychlor being an analogue of DDT was employed as replacement for DDT due to the toxicity and persistent of DDT in environmental compartments. It's mostly used in the control of wide range of insects [33].

The detection of methoxychlor in water and sediments in regions where regulations and phase out were implemented confirmed its persistent and capability of long-range transport [34]. It is highly hydrophobic compound with K_{ow} of 5.08. The concentration of methoxychlor in sediments are greater than that of water samples with exception of Kopri in this study can be attributed to its ability to bind to sediments and settle.

P,p' DDT and its metabolites p,p' DDD and p,p'DDE were also detected in 100% of the sediment samples with maximum concentration of 0.2 mg/Kg and a minimum of 0.01mg/kg. the concentration is within the acceptable MRL value of 0.2mg/kg, 0.3mg/kg and

0.4mg/kg for DDT, DDD and DDE respectively report by Akan *et al.*, [35]. The contribution of \sum DDTs to total OCP of interest burden in sediment ranges between 100% at Kopri and 66.77 % at Ndabna.

The ratio of DDT to the sum of its metabolites is an indication of the possible source of these persistent organic pollutants in the environment. Similarly, since DDD is an anaerobic degradation product of DDT and DDE is an aerobic product of DDT degradation, the ratio of DDD to DDE can also give a very important information about degradation pathways of this pollutants. A ratio of <1 indicates aerobic degradation, while a ratio of >1 indicates anaerobic degradation.

In this study, the ration of DDT to its metabolites is < 1 for all sampling sites in the study areas indicating historical application of DDT. In the same vein, the ration of DDD to DDE is < 1 for Kopri and Ndabna while > 1 in the remaining sampling sites. This simply implies that at Kopri and Ndabana the degradation of DDT in sediments follows the aerobic pathways while in other sites it follows the anaerobic pathways.

Table 3.3: Concentration of OCPs in fish samples (mg/kg)

	Kopri	Ndabna	Garkida WB	Garkida	Daba	Kiri
Methoxychlor	0.04	0.05	0.10	0.10	0.04	0.05
p,p'- DDE	0.01	0.02	0.07	0.07	0.03	0.14
p,p'-DDD	0.12	0.18	3.40	0.04	0.08	0.50
p,p'-DDT	0.16	0.10	0.03	0.10	0.10	0.05
Total OCPs	0.33	0.35	3.60	0.31	0.25	0.74

African Catfish (*Clarias gariepinus*) was the fish of commercial interest in the sampling sites and their characteristic of being omnivores and poor swimmers makes them spend most of their time at bottom of water bodies, hence they are referred to as benthic dwellers. Methoxychlor is detected in 100% of the sampling sites at concentration above the recommended MRL value of 0.01mg/kg according to [36].

P,p' DDT and its metabolites p,p'DDD and P,p' DDT were detected in 100% of the fish samples with varying concentrations. The concentration of DDT which is the parent compound ranges between 0.16mg/Kg – 0.03mg/kg. The total contribution to OCP burden by DDTs ranges between at Garkida and at Kopri.

The ratio of DDT/DDD+DDE from all sampling sites was less than 1 except at Kopri which was 1.2. This indicates nonrecent usage of DDT in the vicinities of the other sampling location while a recent usage in Kopri. The degradation of DDT follows the anaerobic pathways since the ration of DDD to DDE were far greater than 1, the only exception being Garkida with a DDD/DDE value of 0.5. DDT and its metabolites are known to be very toxic to aquatic animals, for instance it's reported to induce behavioural, Histopathological and haematological changes at sub lethal concentration [37].

3.1 Non-carcinogenic health risk hazards in water

Table 3.4: Hazard Quotient (EDI/ADI) for adults due to water ingestion

	KOPRI	Ndabna	GarkidaWB	Garkida	Daba	Kiri
Methoxychlor	0.0367	0.0037	0.0036	0.0147	0.0037	0.0036
p,p'- DDE	0.2566	0.1100	0.0733	0.0733	0.1467	0.1100
p,p'-DDD	12.4667	0.2933	0.1100	0.0733	0.0733	0.1100
p,p'-DDT	0.1100	0.1100	0.4767	0.0733	0.2933	0.2567
HI=∑HQ	12.8700	0.5170	0.6636	0.2346	0.517	0.4803

Table 3.5: Hazard quotient for children (30kg) due to water ingestion

	KOPRI	Ndabna	GarkidaWB	Garkida	Daba	Kiri
Methoxychlor	0.0733	0.0073	0.0073	0.0293	0.0073	0.0073
p,p'- DDE	0.5133	0.2200	0.1466	0.1467	0.2933	0.2200
p,p'-DDD	24.9333	0.5866	0.2200	0.1467	0.1467	0.2200
p,p'-DDT	0.2200	0.2200	0.9533	0.1466	0.5867	0.5133
HI=∑HQ	25.7400	1.0340	1.3272	0.4693	1.0340	0.9606

The non-carcinogenic health risk hazards were assessed by computing the estimated daily intake (EDI) due to ingestion of water and fish which in turn were used to calculate the Hazard quotient (HQ) and Hazard index (HI). The computed HQ for the respective OCPs in water can be seen in tables 3.4 and 3.5. From table 3.4 and 3.5 it can also be seen that the Hazard Quotients for the OCPs are < 1 for adults and > 1 for children at Kopri indicating high probabilities of non-carcinogenic health hazards occurring due to consumption of the waters from the sampling sites in the study area in children.

It can also be observed that the Hazard quotients decreases in with increase in body weight. This means people of lower body weight (especially children) will be more susceptible to health Hazard posed by these OCPs in water than those with higher body weight. The HI which are the cumulative effect of the individual OCPs are in the sequence Kopri > Garkida (WB) > Ndabna = Daba > kiri Garkida. This simply implies that people in Kopri may experience more health hazard due to water ingestion than other sampling sites.

3.2 Non-carcinogenic health risk hazards due to fish consumption

Table 3.6: Hazard Quotients (EDI/ADI) due to fish ingestion in adults

	Kopri	Ndabna	GarkidaWB	Garkida	Daba	Kiri
Methoxychlor	0.000243	0.000304	0.000608	0.000608	0.000243	0.000304
p,p'- DDE	0.000608	0.001217	0.004258	0.004258	0.001825	0.008517
p,p'-DDD	0.007300	0.010950	0.206833	0.002433	0.004867	0.030417
p,p'-DDT	0.009733	0.006083	0.001825	0.006083	0.006083	0.003042
HI=∑HQ	0.017885	0.018554	0.213525	0.013383	0.013018	0.042279

Table 3.7: Hazard Quotients (EDI/ADI) due to fish ingestion in Children (30) Kg

	Kopri	Ndabna	GarkidaWB	Garkida	Daba	kiri
Methoxychlor	0.000487	0.000608	0.001217	0.001217	0.000487	0.000608
p,p'- DDE	0.001217	0.002433	0.008517	0.008517	0.003650	0.017033
p,p'-DDD	0.014600	0.021900	0.413667	0.004867	0.009733	0.060833
p,p'-DDT	0.019467	0.012167	0.003650	0.012167	0.012167	0.006083
HI=∑HQ	0.035770	0.037108	0.427050	0.026767	0.026037	0.084558

The HQ of OCPs due to fish consumption from all sampling sites are mostly < 1. This simply implies very low probability of non-carcinogenic adverse effect with regards to OCPs due to consumption of fish.

since as the body weight increases the HQ decreases. The HI which is the cumulative effect of the individual OCPs in consumption of fish is in the sequence Garkida (WB) > Kiri > Ndabna > Kopri > Garkida > Daba.

Furthermore, HQ to due fish consumption follow the same trend with water in terms of body weight effect

3.3 Carcinogenic health risk due to ingestion of OCPs in water

Table 3.8: Cancer risk for water ingestion in adults

	Kopri	Ndabna	GarkidaWB	Garkida	Daba	kiri
p,p'- DDE	0.000873	0.000374	0.000249	0.000249	0.000499	0.000374
p,p'-DDD	0.029920	0.000704	0.000264	0.000176	0.000176	0.000264
p,p'-DDT	0.000374	0.000374	0.001621	0.000249	0.000997	0.000873
ΣCancer Risk	0.031167	0.001452	0.002134	0.000675	0.001672	0.001511

Table 3.9: Cancer risk for water ingestion in children (30Kg)

	Kopri	Ndabna	GarkidaWB	Garkida	Daba	kiri
p,p'- DDE	0.001745	0.000748	0.000499	0.000499	0.000997	0.000748
p,p'-DDD	0.059840	0.001408	0.000528	0.000352	0.000352	0.000528
p,p'-DDT	0.000748	0.000748	0.003241	0.000499	0.001995	0.001745
ΣCancer Risk	0.062333	0.002904	0.004268	0.001349	0.003344	0.003021

The Carcinogenic health risk is considered for all OCPs with establish cancer slope factor except methoxychlor which is non-carcinogenic according [33]. From table 3.10, 3.11 and 3.12, the computed Cancer risk for all OCPs with established cancer slope were all greater than the range 1.0×10^{-4} to 1.0×10^{-6} recommended by US EPA [38].

The incremental lifetime cancer risk ranges between 6.75×10^{-4} to 3.1167×10^{-2} and 4.048×10^{-3} to 1.87×10^{-1}

for adults and children respectively. The trend of ILCR is in a sequence Kopri > Garkida WB > Daba > Kiri > Ndabna > Garkida. The risk is inversely proportional to body weight i.e., as the body weight increase the risk reduces. This can be ascribed to the fact that, increase in body weight is liken to growth dilution.

3.4 Carcinogenic health risk due to ingestion of OCPs in fish

Table 3.10: Cancer risk for fish ingestion in adult

	Kopri	Ndabna	GarkidaWB	Garkida	Daba	Kiri
p,p'- DDE	2.06833E-06	4.14E-06	1.45E-05	1.45E-05	6.21E-06	2.90E-05
p,p'-DDD	1.752000E-5	2.63E-05	49.60E-05	5.84E-06	1.17E-05	7.30E-05
p,p'-DDT	3.30933E-05	2.07E-05	6.21E-06	2.07E-05	2.07E-05	1.03E-05
ILCR	5.26817E-05	5.11E-05	51.7E-05	4.10E-05	3.86E-05	11.2E-05

Table 3.11: Cancer risk due to fish ingestion in children (30kg)

	Kopri	Ndabna	GarkidaWB	Garkida	Daba	Kiri
p,p'- DDE	4.14E-06	8.27E-06	2.9E-05	2.9E-05	1.24E-05	5.79E-05
p,p'-DDD	3.50E-05	5.26E-05	99.3E-05	1.17E-05	2.34E-05	14.6E-05
p,p'-DDT	6.62E-05	4.14E-05	1.24E-05	4.14E-05	4.14E-05	2.07E-05
ILCR	10.50E-05	10.2E-05	103.4E-05	8.20E-05	7.71E-05	22.5E-05

The computed carcinogenic health risk due to fish consumption are presented in table 3.13, 3.14 and 3.15. From tables above the cancer risk value due to OCPs are all above the US EPA guidelines recommendation. The Cumulative cancer risk which is the incremental lifetime cancer risk ranges between 3.86×10^{-5} to 5.17×10^{-4} and 2.31×10^{-4} to 3.103×10^{-3} for an Adult and a child of 10 Kg weight respectively. This risk value implies that between 39 to 231 people in a million who are expose to these pollutants may develop cancer in their life time.

The hazard quotients in both water and fish indicates possibilities of non-carcinogenic health risk especially in children because the HQ and HI decreases with increase in body weight. The carcinogenic risk computed indicates high risk of cancer from both water and fish consumption in both Adults and children with

ILCR value far above the recommended 1.0×10^{-4} to 1.0×10^{-6} by USEPA.

4. Conclusion and recommendation

This work indicates the presence of methoxychlor, DDT and its metabolite in water, sediments and fish samples from the study area which are above the recommended threshold of WHO/FAO. The detection of the pollutants means their continuous usage despite their Ban by regulatory authorities in Nigeria.

A strict enforcement on the banned pesticides sale and usage should be implemented and continues monitoring of these contaminants in all the environmental compartment should also be emphasized.

5. Conflict of interest

The Authors declare no conflict of interest.

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