**RISK ASSESSMENT OF HUMAN EXPOSURE TO ORGANOCHLORINE PESTICIDES IN COMMERCIAL FISH FROM QUA IBOE RIVER, ORUK ANAM, AKWA IBOM STATE, NIGERIA.**

**ABSTRACT**

Organochlorine pesticides (OCPs) is a class of persistent organic pollutants in an environment that attracts global concern due to their persistency in the environment, chemical stability, long range of transport and tendency to bioaccumulate in plants, animals and humans. In this research, OCPs were determined in water and fish samples from Qua Iboe River, Oruk Anam, Nigeria to assess human health risk via fish consumption. The quantification of the detectable OCPs was done using a Hewlett Packard 6890 series Gas Chromatography (GC) – Electron Capture Detector (ECD). The GC column employed was a 30 m HP-5 capillary column coated with 0.25µm film thickness of 100% dimethyl polysiloxane. Separately, OCPs such as DDT and their metabolites examples DDTs: p,p’-DDD, and p,p’DDE including dieldrin, aldrin, endrin, endrin aldehydes, endrin ketone, methoxychlor, endosulfan-sulphate, endosulfan I, endosulfan II, alpha-chlordane, gamma-chlordane, beta-benzene hexachloride (BHC) and delta-BHC were measured. The detected OCPs concentrations in water samples were calculated from the peak area. Risk assessment of human exposure via consumption of the tested fish was done using hazard quotient (HQ). The generated OCPs data were subjected to statistical analysis using statistical package for social science for sperman correlation test. The results revealed that levels of Alpha-BHC recorded in water samples across sampling locations in both seasons ranged between 0.01±0.01 and 0.73±0.03; Heptachlor ranged between 0.24±0.32 and 0.99±0.07; p,p’DDT between 0.05±0.01 and 0.34±0.47. The data of the fish samples indicated that DDT and its metabolites (DDE and DDD) were the major OCPs measured. Concentrations p,p’DDT recorded ranged between 0.81±0.07 and 1.60±1.07; p,p’-DDD (0.40 – 0.51); p,p’-DDE (0.78 – 0.99); aldrin ranged between 0.21±0.01 and 1.04±0.01, endrin ranged from 0.60±0.07 and 0.87 ±0.07 across all the sampling locations in both seasons. Results in tables 1 to 4 revealed that OCPs not reported were not detected. Human exposure to OCPs in fish via consumption indicated that the levels OCPs detected in water and fish samples were within permissible limits except p,p’DDE whose levels (0.78 – 0.99) were approaching unity in some fish samples from some locations. It is worthy of note that Hazard quotient (HQ) < 1 indicates low risk while HQ > 1 indicates high risk of exposure. Statistically, levels of OCPs detected in the commercial fish in both seasons were less than unity, implying that the commercial fish from the studied river are suitability for human consumption. Thus for sustainability of the commercial fish for human consumption by present and future generations, strict compliance to good agricultural practices in the area and routine monitoring of these recalcitrant pollutants in studied river through researches are strongly recommended.

**Keywords:** Analysis, Ecosystem, Fish, Water, Statistical, Pesticides, GC-ECD.

**1. INTRODUCTION**

In an environment, status of pollutants is an aspect in environmental management that is gaining greater concern everyday due to significant release of these pollutants into the environment through anthropogenic sources. These substances are capable of distabilising natural cycles of atmosphere, lithosphere and hydrosphere resulting in their pollution. In aquatic ecosystem, pollution results significantly from diverse anthropogenic activities around the environment. These activities include industrial waste discharges, contamination from agricultural practices through run off, indiscriminate wastes disposal etc. These can result in introduction of varying kinds of pollutants such as organic, inorganic, radioactive etc. into the environment. Other kinds of water pollutants can emanate from domestic wastes, insecticides and herbicides, livestock operations, volatile organic compounds (VOCs) (Norman et al., 2012; Hale et al., 2010). Increasing usage of these chemicals in modern agriculture to boost food production for the demand of increasing population is a significant source of organochlorine pesticides pollution in water. Organochlorine pesticides (OCPs) are hazardous organic chemical compounds that are resistant to biodegration and thus remain in the environment for a long period of time with potential adverse effects on human health and environment. “Notably observed is that when it rains, OCPs are washed into the aquatic ecoystems and due to their low solubility in water, they become strongly bonded to particulate matter in aquatic sediment and in turn become available to biota such as fish and humans that eat the fish” (Akpan et al., 2024). “It is worthy of note that although OCPs are usually present in water at low levels, aquatic organisms have been shown to accumulate them in their tissues and also transfer to secondary feeders” (Essumag et al., 2009). ‘‘In aquatic ecosystem, water, sediment and fish are the ultimate reservoir of these organic chemicals, and they often accumulate them in such a way that can cause health problems such as kidney and liver damage, central nervous system damage, thyroid and bladder damage as well as kidney and liver cancer in animals which depends directly or indirectly on the fish and the water bodies’’ (Uwah et al., 2021). “These organic chemicals are lipophilic with low volatility and low water solubility and have been in use in both developed and developing countries for several decades. The organochlorine pesticides (OCPs), for example, are introduced into the environement deliberately and have played significant role in increasing worldwide food production as well as protecting human health and natural resources, example dichlorodiphynltrichloroethane (DDT), aldrin etc. These substances are sometimes applied directly to water bodies to control aquatic pests, snails, weeds and mosquito larvae. Misuse of these chemicals for killing fish in streams and rivers are also practiced. It is worthy of note however the types, quantities and usage pattern of OCPs in environment vary across the regions” (Adeyemi et al., 2008; Zhang et al., 2003). “Other sources of OCPs input into ecosystem include dumping of wastes/containers from public health, agricultural and industrial usage. Domestic and industrial effluents, especially effluents discharged from pesticide manufacturing or formulating industries including industries making use chlorinated hydrocarbons such as textile factories, food industry and thermal power plants. In addition accidental spillage from agricultural and industrial sites, road and rail vehicles and ships is also a major source of input. Other sources of input of OCPs include drainage and run-off from treated farmlands, garbage and industrial solid wastes dump as well as dumping of sewage sludge, municipal and industrial solid wastes”(El Barbary et al., 2008; Eqani et al., 2013). The OCPs being non-polar, toxic, semi-volatile and fairly persistent compounds on entry into aquatic ecosystems may remain within the water body unchanged for a long period of time and undergo, degradation to simpler compounds that may be more toxic/ or become more persistent than the parent compound such as DDE, dioxin etc.

“Organochlorine pesticides (OCPs) such as DDT, dieldrin and industrial chemicals have been reported to be ecologically harmful and toxic to human as well. To aquatic organisms, acute toxiticity of OCPs has become evident in the past as a result of significant fish kills caused by accidental release of DDT, toxaphone, dieldrin, aldrin and heptachlor into aquatic environment” (Hale et al., 2010). ‘‘In recent times, water bodies are more contaminated by these recalcitrant chemicals resulting in bioaccumulation in fish and other biota to biologically active levels. These chemicals have been suspected to cause cancer agents in fish and other aquatic organisms. Fish eating birds are at risk of population decrease and even extinction as a result of reproductive failures resulting from eating aquatic organsims contaminated with these chemicals. They may cause shell thining or impair the process of eggs shell formation in many species of birds by interfering with the deposition of calcium’’ (Yameshita et al., 2000; Darko et al., 2008 Norman et al., 2012). Eqani et al., (2013) conducted a research for the determination of pesticide residues in fish samples collected from several locations of River Ganga, India using GC method. They reported that the fish samples were contaminated with all the tested pesticide residues such as total-HCH, total-DDT, total-endosulfan, dimenthonate and malathion and were above the minimum reporting level (MRL) levels. They also noted that the pesticides contamination in fish may be due to various kinds of agricultural activities around the area and indiscriminate discharge of polluted and untreated sewage-sludge to the river. In addition, they reported that pesticide contents in some places were alarming, and recommended total compliance to good agricultural practices, treatment of sewage water and sludge prior to disposal to surface water bodies.

Qua Iboe River is a major source of commercial fish within and outside Akwa Ibom State of Nigeria. Over the years, Oruk Anam has witnessed tremendous anthropogenic activities such as roads construction, industrialisation, commercial fishing and various kinds of agricultural activities. Although the use of OCPs has been banned in developed and developing countries around the world, it is still being use unofficially in many parts of the Nigeria including Oruk Anam for agriculture to boost food production and protection of public health since they are relatively cheap. When it rains, the end products of these activities are usually washed into the river through runoff, a condition with higer tendencies to pollute the ecosystem and fish with various kinds of OCPs through bioaccumulation. Fish is a good indicator of OCPs pollution in aquatic ecosystem due to their inability to metabolise them in the food they eat as well as in their tissues and organs. The commercial fish in the study area has been exploited in commercial scale for human consumption over the years and there is no information on OCPs concentrations in the fish from the study area to assess human health risk via their consumption hence this research. The quantification of these persistent organic chemicals in the commercial fish from the river under study will give firsthand information on risk exposure of humans to OCPs via consumption of the fish. Data generated will serve as baseline information to other researchers and for sustainability of the ecosystem and seafoods by government.

**2.0 MATERIALS AND METHODS**

**2.1 Study Area**

Figure 1, is a map of the study area and the coordinates of the sampling locations were recorded using gobal positioning system (GPS). The coordinates were located within the latitude 04o28’31 and 07o10’12.4’’0’’ North of the equator and between 06o65’41.2’’ and 06o52’50.5’’ East of Greenwich Meridian.



**Figure 1: Map of study area**

**Samples Collection**

In any analysis, sampling is considered very crucial because it gives the assurance of the validity of the result. It is worthy of note that the choice of a good sampling technique is a pre-requisite for accurate data generation. In this study, water and fish samples were collected using appropraite apparatus and methods from five sampling locations namely: Inen Nsai, Umani, Ikot Okoro, Nung Ikot and Ibesit from the studied river for twelve months covering both wet and dry seasons.

**Samples analysis**

Prior to analysis, filleted muscle tissues of each fish were freeze - dried, ground into powder and extracted using soxhlet extractor for a period of 18 hours. Quantitative analysis of pesticides was achieved using a fractionating column and packed with 6g activated silica gel and maintained at 450oC (Udosen 2019). The GC capacity of 30 m HP-5 capillary column coated with 0.25 µm film thickness of 100% dimethyl polysiloxane was used for the analysis. A mixture of hexane and dichloromethane in a ratio of 80:20ml respectively was eluted which resulted in the collection several organochlorine pesticides. Each organochlorine pesticide such as DDT and its metabolites (DDTs: p,p’-DDD, and p,p’-DDE), dieldrin, aldrin, endrin, endrin aldehydes, endrin ketone, methoxychlor, endosulfan-sulphate, endosulfan I, endosulfan II, alpha-chlordane, gamma-chlordane, beta-BHC and delta-BHC were measured. Concentrations of organochlorine pesticides were calculated from the peak area of the sample and compared with standard. The pesticides data analysis was done using Sperman correlation test by Ststistical Package for Social Science (SPSS).

**Risk Assessment**

Evaluation of the potential risk to human health of tested fish, estimated daily intake (EDI), target hazard quotients (THQs), and carcinogenic risk ratio (R) were used in the risk assessment. The determination of THQ and R was reffered to method described by (Darko *et* *al.,* 2008; Eqani et al., 2013; Norman et al., 2012). The calculation of EDI, THQ and R were done according to following equations.

 EDI = FIR x C  [

Where:

C = pollutant concentration in fish (µg/g), WF = daily average consumption of fish in the area assuming (75 g/day/person), and WAB = average body weight (70 kg for adults).

THQ = ED x EF x FIR x C x10-3

 RFD x WAB x TA

R = ED x EF x FIR x SF x C x 10-3

 WAB x TA

Where: ED = exposure duration (70 years); EF = exposure frequency (350 days/year); FIR = food ingestion rate (g/person/day); RFD = oral reference dose (mg/kg/day)-1BW); TA = average exposure time (365 days /year x lifetime, assuming 70 years) and SF = oral cancer slope factor (mg/kg/day)-1. Risk-based concentration table was used in the study to search for Oral Reference Dose (RFD) and Slope Factor (SF) values (Ubon et al., 2023; USEPA, 2009).

**Quality Control**

The implementation of laboratory quality assurance and quality laboratory methods, including the use of standard operating procedures and analysis of replicates guaranteed the quality of the analytical data. All chemicals and reagents used were of analytical grade. Quantification of detected organochlorine pesticides in the digested samples was obtained using Gas Chromatography - Electron Capture Detector (Hewlett Packard 6890 series) equipped with auto injector and sampler (Hewlett Packard 7683 series)

**Statistical Analysis**

Data generated were subjected to statistical analysis using statistical package for social sciences (SPSS).

**RESULTS AND DISCUSSION**

* 1. **Results**

The results of analysis of organochlorine pesticides in water and fish samples fromfive sampling locations of the study area were presented in this section. Tables 1 and 2 showed mean levels of organochlorine pesticides (OCPs) in water for wet and dry seasons respectively.

Human health risks assessment of OCPs through consumption of fish from the river are shown in Tables 5 and 6.

**Table 1: Levels of OCPs in water samples from sampling locations in wet season**

|  |  |
| --- | --- |
|  | Sampling locations  |
|  OCPs(ng/l) | IB | NI | IO | UM | IN |
| Alpha-BHC | 0.40± 0.01 | 0.48± 0.03 | 0.01± 0.01 | 0.01 ± 0.01 | 0.01± 0.01 |
| Heptachlor | 0.24± 0.32 | 0.04± 0.02 | 0.01 ± 0.01 | 0.01 ± 0.01 | 0.01± 0.00 |
| Heptachlor-Epoxide | 0.01± 0.01 | 0.01± 0.00 | 0.02± 0.01 | 0.01 ± 0.01 | 0.01± 0.01 |
| Gamma-chlordane | 0.01 ± 0.01 | 0.01± 0.02 | 0.01 ± 0.00 | 0.02 ± 0.00 | 0.01± 0.00 |
| P,P’-DDE | 0.01 ± 0.01 | 0.01 ± 0.01 | 0.01± 0.01 | 0.01± 0.01 | 0.01± 0.01 |
| P,P’-DDT | 0.05 ± 0.01 | 0.25± 0.01 | 0.01± 0.01 | 0.01± 0.00 | 0.01± 0.00 |
| Endrin-aldehyde | 0.01± 0.00 | 0.10± 0.01 | 0.06± 0.02 | 0.02± 0.01 | 0.01± 0.01 |

 OCPs not reported were not detected. IN = Inen Nsai, UM = Umani, IO = Ikot Okoro, NI =

 Nung Ikot, IB = Ibesit.

**Table 2: Levels of OCPs in water samples from sampling locations in dry season**

|  |  |
| --- | --- |
|  |  Sampling locations  |
|  OCPs (ng/l) | IB | NI | IO | UM | IN |
| Alpha-BHC | 0.73 ± 0.03 | 0.71 ± 0.04 | 0.23 ± 0.32 | 0.21 ± 0.28 | 0.17± 0.23 |
| Beta-BHC | 0.04± 0.06 | 0.04± 0.05 | 0.03 ± 0.04 | 0.03± 0.04 | 0.14± 0.27 |
| Heptachlor | 0.99± 0.07 | 1.00± 0.06 | 0.39± 0.52 | 0.37 ± 0.50 | 0.32± 0.46 |
|  Delta-BHC | 2.95 ± 4.04 | 2.79± 3.86 | 2.34± 3.19 | 2.41± 2.80 | 2.05± 2.61 |
| Aldrin | 0.58 ± 0.80 | 0.52 ± 0.71 | 0.54± 0.66 | 0.59± 0.62 | 0.33± 0.51 |
| Heptachlor-Epoxide | 1.38± 1.89 | 1.28± 1.77 | 1.20± 1.65 | 1.22 ± 1.45 | 1.02± 1.45 |
| Gamma-chlordane | 0.29± 0.40 | 0.28 ± 0.38 | 0.27± 0.37 | 0.26 ± 0.36 | 0.21 ± 0.28 |
| P,P’-DDE | 1.23 ± 1.07 | 1.46 ± 0.76 | 0.23± 0.32 | 0.19 ± 0.26 | 0.06 ± 0.14 |
| Dieldrin | 0.75± 1.02 | 0.71 ± 0.97 | 0.66± 0.90 | 0.65± 0.89 | 0.55± 0.75 |
| P,P’-DDD | 0.12± 0.16 | 0.00± 0.00 | 0.00± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| P,P’-DDT | 0.34± 0.47 | 0.13 ± 0.17 | 0.09 ± 0.13 | 0.08± 0.12 | 0.04 ± 0.08 |
| Endrin-aldehyde | 0.07± 0.10 | 0.51± 0.47 | 0.00 ± 0.00 | 0.00 ± 0 .01 | 0.00 ± 0.01 |

OCPs not reported were not detected. IN = Inen Nsai, UM = Umani, IO = Ikot Okoro, NI = Nung Ikot, IB = Ibesit.

**Levels of OCPs obtained in water samples in Wet Season**

Results in Table 1 revealed that the levels of alpha-BHC across all sampling locations ranged between 0.01$\pm $0.01 and 0.48±0.03 ng/L. Heptachlor ranged between 0.01$\pm $0.01 ng/L and 0.24 $\pm $0.32 ng/L. The level of p,p’ DDT ranged between 0.01$\pm $0.01 and 0.25 $\pm $0.01 ng/L while endrine aldehyde ranged between 0.01$\pm $0.01 and 0.06 $\pm $0.02 ng/L. The results also show that there was no significant differences in Alpha-BHC, heptachlor, aldrin, heptachlor-expoxide and Alpha-cholride between different sampling locations ($p>$ 0.05) while alpha-BHC and heptachlor in Ibesit and Nung Ikot locations were significantly higher than levels obtained in other locations (p$<$0.05). The results revealed that lowest levels of all the OCPs detected were recorded in Inen Nsai (control station) while higher levels were obtained in Nung Ikot location downstream, reflecting significant historical use of those chemicals in those locations as well as increased anthropogenic activities such as roads construction, urbanization, agricultural activities, palm oil mill operation including domestic and urban run-off from Ikot Okoro highway and adjoining roads into the river body within those locations when it rains. Level of p,p’ DDT was significantly higher in Ibesit and Nung Ikot sampling locations than other locations (p$<$0.05) while between Umani and Inen Nsai (control station) there was no significant difference. Levels of all the OCPs detected in water samples during wet season were within permissible limit as given by World Health Organisation (WHO) guidelines. OCPs not reported were not detected. The results obtained in this study were similar to those reported by Chen *et al.* (2006).

**Levels of OCPs in Water samples in Dry Season**

 Results in Table 2 showed the mean levels of OCPs in water across sampling locations in dry season. The results revealed that the levels of Alpha-BHC in all the samples ranged between 0.17$\pm $0.23 and 0.73$\pm $0.03 ng/L; Beta-BHC ranged between 0.03$\pm $0.04 and 0.14$\pm $0.27 ng/L, Heptachlor ranged between 0.32$\pm $0.46 and 1.00 $\pm $0.06 ng/L and delta-BHC ranged between 2.05$\pm $2.61 and 2.95$\pm $4.04 ng/L; Gamma chlordane ranged between 0.21$\pm $0.28 and 0.29$\pm $0.40 ng/L while deldrine and p,p’ DDD ranged between 0.55$\pm $0.75 and 0.75$\pm $1.02 ng/L and between 0.00$\pm $0.00 and 0.12$\pm $0.16 ng/L respectively. The result revealed that there was no significant difference (p$>$0.5) in levels of some OCPs detected across the sampling locations, except Alpha-BHC, Heptachlor, p,p’ DDE, and p,p’ DDT were significantly higher in Ibesit and Nung Ikot locations compared with Inen Nsai location being control station (p$<$0.05). The results revealed that lowest levels of OCPs detected were recorded in Inen Nsai (control station) and gradually increased to Umani then to Ibesit location (downstream). These higher levels of OCPs in water samples recorded downstream reflect a corresponding increase in OCPs pollution-induced activities carried out downstream. Other causes may include unofficial use of DDT and its metabolites for public health purposes by riverine communities due to its low cost and inadequate regulation and control on the use of these chemicals. These results were similar to those reported by Eqani *et al.* (2013).

 Varriations in levels of OCPs detected in water samples in both seasons may be attributed to varriations in metheological conditions in the two seasons.

**Table 3: Levels of OCPs in fish samples from sampling locations in wet season**

|  |  |
| --- | --- |
|  |  Sampling locations  |
|  OCPs(ng/kg) | Ibesit | Nung Ikot  | Ikot Okoro | Umani | Inen Nsai |
| Beta-BHC | 0.44± 0.02 | 0.39 ± 0.01 | 0.38± 0.01 |  0.32±0.08 | 0.36± 0.01 |
| Delta-BHC | 0.42± 0.01 | 0.32± 0.01 | 0.22± 0.01 |  0.22± 0.01 | 0.21± 0.01 |
| Aldrin | 1.03± 0.01 | 0.22± 0.02 | 0.21± 0.01 | 0.16±0.05 | 0.19± 0.00 |
| Gamma-chlordane | 0.40± 0.01 | 0.35± 0.00 | 0.32± 0.01 | 0.31±0.01 | 0.30± 0.01 |
| Endosulfan1 | 0.30 ± 0.01 | 0.19± 0.01 | 0.20± 0.00 | 0.19±0.00 | 0.18± 0.01 |
| P,P’-DDE | 1.85 ± 0.07 | 1.87± 0.01 | 1.76± 0.07 | 1.71±0.01 | 1.67± 0.06 |
| Endrin | 0.60± 0.07 | 0.63± 0.03 | 0.55± 0.07 | 0.50±0.00 | 0.46± 0.08 |
| P,P’-DDD | 0.10± 0.00 | 0.10± 0.00 | 0.10± 0.00 | 0.09±0.01 | 0.08± 0.01 |
| P,P’-DDT | 0.81± 0.07 | 0.78± 0.00 | 0.73± 0.03 | 0.65±0.00 | 0.66± 0.07 |
| Endrin-aldehyde | 0.48± 0.01 | 0.51± 0.01 | 0.47± 0.01 | 0.43±0.01 | 0.36± 0.01 |
| Endosulfan-sulphate | 0.20± 0.00 | 0.31± 0.00 | 0.21± 0.00 | 0.19±0.01 | 0.18± 0.00 |
| Methoxychlor | 0.41± 0.01 | 0.31± 0.01 | 0.32± 0.01 | 0.30±0.00 | 0.21± 0.01 |
| Endrin-ketone | 0.10± 0.01 | 0.09± 0.01 | 0.08± 0.00 | 0.08±0.01 | 0.07± 0.00 |

 OCPs not reported were not detected

**Table 4: Levels of OCPs in fish samples from sampling locations in dry season**

|  |  |
| --- | --- |
|  |  Sampling locations |
|  OCPs (ng/kg) | Ibesit |  Nung Ikot | Ikot Okoro | Umani | Inen Nsai |
| Beta-BHC | 0.49± 0.06 | 0.47± 0.05 | 0.41± 0.07 | 0.39± 0.08 | 0. 0.30± 0.10 |
| Delta-BHC | 0.52± 0.07 | 0.49± 0.09 | 0.43± 0.13 | 0.38± 0.12 |  0.30± 0.08 |
| Aldrin | 1.04± 0.01 | 0.53± 0.58 | 0.61± 0.48 | 0.58± 0.46 | 0.25± 0.29 |
| Gamma-chlordane | 0.39± 0.05 | 0.37 ± 0.00 | 0.33± 0.04 | 0.29± 0.02 | 0.23± 0.02 |
| Alpha-Chlordane | 0.04± 0.09 | 0.04± 0.08 | 0.03± 0.07 | 0.03± 0.06 |  0.03± 0.06 |
| Endosulfan1 | 0.79± 0.92 | 0.77± 0.93 | 0.72± 0.95 | 0.70± 0.93 |  0.67± 0.89 |
| P,P’-DDE | 1.60± 1.07 | 1.82± 1.34 | 1.73± 1.26 | 1.68± 1.25 |  1.65± 1.25 |
| Dieldrin | 0.21± 0.42 | 0.20± 0.41 | 0.18± 0.35 | 0.17± 0.35 |  0.16± 0.33 |
| Endrin | 0.87± 0.07 | 0.76± 0.12 | 0.72± 0.15 | 0.66± 0.16 |  0.54± 0.10 |
| P,P’-DDD | 0.27± 0.46 | 0.26± 0.46 | 0.23± 0.45 | 0.21± 0.41 |  0.18± 0.36 |
| Endsulfan ll | 0.50± 1.00 | 0.49± 0.98 | 0.48± 0.96 |  0.40± 0.81 |  0.38± 0.76 |
| P,P’-DDT | 0.97± 0.04 | 0.92± 0.07 | 0.84± 0.10 |  0.76± 0.07 |  0.71± 0.08 |
| Endrin-aldehyde | 0.66± 0.02 | 0.61± 0.05 | 0.59± 0.06 |  0.49± 0.13 |  0.44± 0.13 |
| Endosulfan-sulphate | 0.71± 0.27 | 0.68± 0.24 | 0.62± 0.29 |  0.53± 0.27 |  0.48± 0.26 |
| Methoxychlor | 0.41± 0.08 | 0.41± 0.08 | 0.31± 0.08 |  0.28± 0.09 |  0.23± 0.10 |
| Endrin-ketone | 0.12± 0.02 | 0.11± 0.02 | 0.09± 0.06 |  0.08± 0.05 |  0.23± 0.31 |

 OCPs not reported were not detected**.**

**Levels of OCPs recorded in fish samples in Wet Season.**

The results in Table 3, revealed that levels of Beta-BHC ranged between 0.32$\pm $0.08 and 0.44$\pm $0.02 ng/kg, Delta-BHC ranged between 0.21$\pm $0.01 and 0.42 $\pm $0.01 ng/kg, aldrin ranged between 0.16$\pm $0.05 and 0.22$\pm $0.02 ng/kg, endrine ranged between 0.46$\pm $ 0.08 and 0.63$\pm $0.03 ng/kg while methoxychlor ranged between 0.21$\pm $0.01 and 0.41 $\pm $0.01 ng/g, and endrin-ketone ranged between 0.07$\pm $0.00 and 0.10$\pm $0.10 ng/kg. Levels of Delta-BHC, aldrin, gamma chlordane, edosulfan 1, edosulfan sulphate, methoxychlor between Ibesit and Nung Ikot were significantly higher than levels recorded in other locations. The result further revealed that for Beta-BHC, endrine and endrin-aldehyde, there was no significant difference in levels across all the sampling locations. Regional variations in levels of the detected OCPs across the sampling locations in fish samples could be attributed to variations in levels of historical use, their sources depending on human activities across sampling locations. Higher levels of some of the OCPs recorded in Ibesit, Nung Ikot and Ikot Okoro could be due to impact of increased pollution induced-anthropogenic activities within those locations. The results also revealed that lowest levels of all the OCPs detected were recorded from fish samples obtained from Inen Nsai location (control station). This could be a reflection of variation in human activities as earlier stated. As expected, pollutants flow downstream of the river course in line with the direction of flow of the river. The results further revealed that a section of the river with tremendous anthropogenic activities is more vulnerable to higher level of pollution. The higher levels of pollution by these contaminants in surface water has significant relationship with level of pollution in sediment lying beneath and to also to fish that live in the water and also feeds on particulate matter adsorbed unto the sediment. The results obtained in this study were similar to those reported by Kurt and Ozkoc (2004) and were within the maximum permissible range by WHO guideline. OCPs not reported were not detected.

**Levels of OCPs in fish Samples in Dry Season**

The results of OCPs levels in fish during dry seaon as presented in Table 4 revealed that Beta-BHC ranged between 0.30$\pm $0.10 and 0.49$\pm $0.06 ng/kg, Delta-BHC ranged between 0.30$\pm $0.08 and 0.52 $\pm $0.07 ng/kg, endosulfan I ranged between 0.67$\pm $0.89 and 0.79$\pm $0.92 ng/kg, p,p’, DDE ranged between 1.60$\pm $1.07 and 1.82$\pm $1.34 ng/kg while deldrin ranged between 0.16$\pm $0.33 and 0.21$\pm 0.42 ng/kg$, p,p’DDD ranged between 0.18 $\pm $0.36 and 0.27$\pm $0.46 ng/kg and Endrin-ketone ranged between 0.08$\pm $0.05 and 0.12$\pm $0.02 ng/kg and were not significantly different across the different sampling locations. Other OCPs such as Aldrin, ranged between 0.25$\pm $0.29 and 1.04 $\pm $0.01 ng/kg, gamma chlorodane between 0.23$\pm $0.02 and 0.39$\pm $0.05ng/kg, and methyoxchlor ranged from 0.23$\pm $0.10 to 0.41$\pm $0.08 ng/kg. Levels of endrin aldehyde, p,p’ DDT , methoxychlor, gamma-chlordane and aldrin between Ibesit, Nung Ikot and Ikot Okoro locations were not significantly different but were significantly higher than levels recorded in Umani and Inen Nsai (control station) (p<0.05). Since organic pollutants find their ways into aquatic ecosystem through a number of anthropogenic activities including the natural biogeochemical circles, the significant increase in levels of some of these OCPs downstream could be attributed to run-off from urban and agricultural fields, massive roads construction, including other anthropogenic activities culminating in the overall higher level of these pollutants at those locations of the river.

**Table 5: Human health risk in Terms of Hazard Quotient (HQ) of OCPs via of fish**

 **Consumption in wet season**

OCPs Ibesit Nung Ikot Ikot Okoro Umani Inen Nsai

Beta-BHC 0.24 0.22 0.21 0.18 0.20

Delta-BHC 0.23 0.18 0.12 0.12 0.11

Aldrin 0.58 0.12 0.11 0.90 0.10

Gramma 0.22 0.19 0.18 0.17 0.17

-chlordome

Endosulfan 1 0.17 0.10 0.11 0.10 0.10

P,P’-DDE 0.91 0.94 0.91 0.97 0.94

Endrine 0.50 0.50 0.31 0.28 0.26

P,P’-DDD 0.46 0.50 0.50 0.50 0.40

P,P’-DDT 0.46 0.44 0.41 0.36 0.37

Endrine- 0.27 0.28 0.26 0.24 0.20

Aldchehyde

Endosulfan- 0.11 0.17 0.11 0.10 0.10

sulphate

Methoxychlor 0.23 0.17 0.18 0.17 0.11

Endrin-ketone 0.40 0.50 0.40 0.40 0.30

**Table 6: Human health risk in Terms of Hazard Quotient (HQ) of OCPs via of fish**

 **Consumption in dry season**

 Ibesit Nung Ikot Ikot Okoro Umani Inen Nsai

Beta-BHC 0.27 0.26 0.23 0.22 0.28

Delta-BHC 0.29 0.27 0.24 0.21 0.17

Aldrin 0.59 0.30 0.34 0.32 0.14

Ƴ-chlordane 0.22 0.21 0.18 0.16 0.13

α-chlordane 0.22 0.22 0.10 0.10 0.10

Endosulfan 1 0.44 0.43 0.40 0.32 0.38

P,P’-DDE 0.90 0.80 0.97 0.78 0.93

Dieldrin 0.11 0.11 0.10 0.90 0.90

Endrin 0.49 0.43 0.40 0.37 0.30

P,P’-DDD 0.15 0.14 0.13 0.11 0.10

Endosulfan II 0.28 0.27 0.27 0.22 0.21

P,P’DDT 0.55 0.52 0.47 0.43 0.40

End.aldehyde 0.37 0.34 0.33 0.27 0.24

Endosulfan- 0.40 0.38 0.35 0.30 0.27

sulphate

Methoxychlor 0.23 0.23 0.17 0.15 0.13

Endrin-ketone 0.60 0.60 0.50 0.15 0.13

OCPs not reported were not detected.

**Human Health Risks of OCPs via Fish Consumption**

Evaluation of cancer risk to human health associated with the consumption of fish containing OCPs contaminants was undertaken and the results are summarised in Tables 5 and 6 for wet and dry seasons respectively. The health risk of cancer was based on concentration of p,p’ DEE (0.74 – 0.94ng/g) across all sampling locations in both seasons. The results indicated that the concentrations of p,p’ DDE across all the sampling locations in both seasons were less than unity, although were all approaching unity. The concentrations of other OCPs detected in all the sampling locations were all less than unity. The results generally indicated that of all OCPs concentrations measured in fish samples in both seasons, p,p’ DDE was of particular concern as the concentrations recorded across all the sampling locations were approaching unity. That could be attributed to historical use of higher amount of the chemical in the study area. It may also be due to unregulated use of the chemical in agriculture and protection of public health by riverine communities due to their relatively cheap rate. Whereas those detected within background levels could be due to their regulated, limited historical and current use for agriculture and public health purposes. In this study the limits of detection were used in estimating the exposure concentrations for fish tissue samples containing concentrations of specific contaminant before detecting limits that the exposure concentrations may have been overestimated.

**CONCLUSION**

Results of the determination of OCPS in water and fish samples from the studied river revealed that the concentrations of the detected OCPs in the samples were within safe limits given by regulatory bodies. The result also indicated that of all OCPs detected in fish samples in both seasons, p,p’DDE was of particular concern as the concentrations recorded in all the fish samples across the sampling locations were approaching unity. These higher levels of p,p’DDE in the fish samples may be attributed to long historical unofficial use of the chemicals for agriculture and protection of public health by riverine coummunities due to the fact that they are readily available and relative cheap. Statistically, since the hazard quotients of all OCPs detected in fish samples were less than unity, it implies that consumers of the commercial fish from the studied river are of low risk exposure to OCPs contamination. Strict compliance to good agricultural practices (GAP) and regulated use of agrochemicals by farmers including routine monitoring of OCPS in the river through researches are strongly advocated to prevent escalation beyond tolorebility range specified by regulatory bodies. Data generated in this research will serve as baseline information to other researchers and environmental protection agency in the area.

**REFERENCES**

Adeyemi, D., Ukpo, G., Anyakora, C. and Unyimadu, J. (2008). Organochlorine pesticides residues in fish samples from Lagos lagoon. *American Journal of Environmental Sciences*, 4: 649 – 649.

Akpan NA, Udombeh RB, Ukpong MB, Iboroakam EU. (2024). Effects of Human Activities

 On Trace Metals in Qua Iboe River, Ikot Ekpene Stretch, Akwa Ibom State, Nigeria.

*International Journal of Science Research Archive.* 11(01): 2120-2128.

Darko, G., Akoto, O. and Oppong, C. (2008). Persistent organochlorine pesticide residues in fish, sediments and water from Lake Bosomtwi, Ghana. *Chemosphere*, 72: 21 – 24.

El-Barbary, A., Yehia, M. and El-Bouraie, M. (2008). Evaluation of organochlorine pesticides (OCPs) in surface water and bed sediment samples from the Nile River at Rosetta branch, Eyght. *Journal of Applied Science Resources,* 4: 1985 – 1993.

Essumang, D.K., Togoh, G.K and Chokky, L. (2009). Pesticides residues in the water and fish (Lagoom Tilapia) sample from lagoon in China. Bullitine of Chemical Soc. Ethiop

Eqani, D., Malik, R., Cincinelli, A., Zhang, G., Mohammad, A., Qadir, A., Rashid, A., Bokhari, H., Jones, K. and Katsoyiannis, A. (2013). Uptake of organochlorine pesticides (OCPs) and polychlorinated bihpenyls (PCBs) by river water fish: the case of River Chenab. *Science Total Environment*, 45: 83 – 91.

Hale, S., Martin, T., Goss, K., Arp, H. and Werner, D. (2010). Partitioning of organochlorine pesticides from water to polyethelene passive samplers. *Environmental Pollution*, 34: 87 – 95.

Ido UH, Akpan NA, Udombeh RB, Udoidiong OM. (2023). Bioaccumulation of Trace Metals in Fish From Issiet River, Uruan, Nigeria. *Science Journal of Analytical Chemistry*. 11(4):40 – 48.

Kunisue, T., Omeya, M., Kayama, F., Jin, Y. and Tanabe, S. (2004). Persistent organochlorines in human breast milk collected from primiparac in Dalian and Shenyang, China. *Environmental pollution*, 131: 381 – 392.

 Kurt, P. and Ozkoc, H. (2004). A survey to determine levels of organochlorine pesticides (OCPs) and PCBs in mussels and seawater from the Mid-Black Sea Coast of Turkey. *Marine Pollution Bullrtin,* 48: 1076 – 1083.

Norman, J. E., Kuivila, K.M and Norwell, L.H (2012). Prioritizing pesticides compounds for analytical methods development: U.S. geological Survey Scientific Investigations Report 5041, p201.

Ubon UU, Ikpe EE, Ekwere IO, Uwanta EJ. Physicochemical and Polycyclic Aromatic

Hydrocarbons (PAHs) Analysis in Soil and sediment from Vicinty of Ikot Akpaden, Akwa Ibom State, Nigeria. *Asian Journal of Biology*. 2023; 19(1): 16-24.

Udosen ED. Enviro-chemical Pollutants:(2019). The Unwelcome yet Unavoidable Human companions, the 68th Inaugural Lecture, University of Uyo, University of press Ltd. 102p

Uwah EI, Rapheal U, Okon RU, Essien DU, Udoidiong OM. Atomic absorption spectrophotometric determination of elements in water, fish and sediment of Atabong River, Nigeria. *Science of Journal of Analytical Chemistry.* 2021; 9(4): 73-75.

USEPA. (United States Environmental Protection Agency). (2009). Types of pesticides. Retrieved from http://www.epa.gov/pesticides/about/types.htm

Yamashita, N., Urushigawa, Y., Masunaga, S., Walash, M. and Miyazaki, A. (2000). Organochlorine pesticides in watefr, sediment and fish from Nile River and Manzala lake in Egypt. *International Journal of Analytical chemistry*, 77: 389 – 303..

Zhang, Z. L., Hong, H. S., Zhou, J. L., Huang, J. and Yu, G. (2003). Fate and assessment of persistent organic pollutants in water and sediment from Minjiang River Estuary, Southeast China. *Chemosphere*, 52: 1423 – 1430.