Organochlorine Pesticides in Callinectes Pallidus (Rochebrune, 1883) and Penaeus Monodon (Fabricius, 1798) from Lagos Lagoon and Badagry Creek, Lagos, Southwest Nigeria

Clarke, Edwin O
Associate Professor, Department of Fisheries, Lagos State University, Nigeria

Jimoh, Abayomi A
Associate Professor, Department of Fisheries, Lagos State University, Nigeria

Adeboyejo, Akintade O
Senior Lecturer, Department of Fisheries, Lagos State University, Nigeria

Abstract:
Organochlorine pesticides (OCPs) have been of great concern around the world owing to their chronic toxicity, persistence and bio-accumulation in aquatic organisms. The OCP concentrations were measured in water, sediment and shell fishes (Panaeus monodon and Callinectes pallidus) in Lagos State (Lagos lagoon and Badagry creek), between November 2018 and June 2019. The samples were analyzed for Alpha (HCH), Beta (HCH), Gamma (HCH), Delta (HCH), Heptachlor, Aldrin, Heptachlor epoxide, Gamma chlordane, Endosulfan1 Alpha chlordane, Dieldrin, DDE, DDD, DDT, Endrin, Endosulfan II, Endrin Aldehyde, Endosulfan sulfate, Endrin ketone and Methoxychlor. The detection and determination of the pesticide residues were carried out by Gas chromatography with electron capture detector. The mean concentration of OCPs in water samples ranged from 0.150 ± 0.012µg/l (Alpha HCH) to 147.60 ± 10.810 µg/l (Endosulfan II). The level of OCPs in sediments ranged from 0.150 ± 0.012 µg/kg (Alpha HCH) in Lagos lagoon to 243.500 ± 138.000 µg/kg (ppDDT) in Badagry creek. The highest mean concentration of OCPs in water and sediments were recorded in Lagos lagoon. The Concentration for shell fish ranged from 0.250 ± 0.009 µg/kg (Alpha HCH) in Lagos lagoon to 67.380 ± 22.860 µg/kg (Endosulfan II) in Badagry creek for Callinectes pallidus and from 1.310 ± 0.210 µg/kg (alpha HCH) to 143.500 ± 71.892 µg/kg (Eldrin Aldehyde) in Badagry creek for Penaeus monodon. Methoxychlor, Lindane and Aldrin were the commonly detected compounds in all the samples from both water bodies. The results showed that OCP levels in all shellfish samples analyzed were above the maximum acceptable limits of 0.01ppm (10 µg/kg) set by EU and Federal Ministry of Environment for aquatic life protection. The highest value was recorded in Penaeus monodon in Badagry creek. Indicating an urgent need for the monitoring of these pesticide residues in water, commercially important food species and the environment, as this will go a long way towards preventing various environmental and public health hazards.

Keywords: Organochlorine Pesticides (OCPs), Environment, Toxicity, Bio-accumulation and Health Hazards.

1. Introduction
Widespread use of organochlorine pesticides in agriculture and homes despite their known harmful effects is causing serious concern about human health and environment. Some of these have been banned worldwide due their persistence and their bio accumulative nature. One such group of organochlorine has been classified as persistent organic pollutants (POP). Organochlorine pesticides (OCP) are one of the most important persistent organochlorine pollutants (POPs) and have been of great concern around the world owing to their chronic toxicity, persistence and bio accumulation. OCPs such as DDT, Hexachlorocyclohexanes (HCH), Chlordanes (CHLs), Hexachlorobenzene (HCB), Aldrin, Dieldrin, Endrin, Endrin Aldehyde, Heptachlor, Heptachlor epoxide, Endosulfan I, Endosulfan II, Endosulfansulfate and Methoxychlor are only slightly soluble in water and highly resistant to degradation by biological, photochemical or chemical means, and their residues may persist in soil, aquatic sediment, and biomagnified in food web. In May 1995, UNEP recognized the POPs as an imminent danger to human health and made a short list of twelve POPs, commonly known as dirty dozen. In some cases, when they breakdown they form metabolites that are also toxic to aquatic life. Six more chemicals including isomers of HCH and polyaromatic hydrocarbons (PAHs) have been added to the dirty dozen. These chemicals are also harmful and bio-accumulative in nature. Isomers of HCH act as stimulants and central nervous depressants. Due to their to lipophilicy and persistence, isomers of HCH frequently accumulate in human adipose and breast tissue. Human studies have shown that exposure to HCHs is linked to cancer, Parkinson’s, Alzheimer’s, reproduction and fertility disruption (Chevrier et al, 2008).

Exposure to organochlorine pesticides can occur in several ways, such as via contaminated air, water or through the skin in countries where they are still used. However, the primary exposure route to people in developed nations (where organochlorines are no longer used) is through contaminated food. The most contaminated foods typically include oily fish.
and foods of animal origin such as fatty meats and dairy products. Various studies all over the world have shown the presence of a large variety of POPs in different forms such as water, air, fish, soil, solid wastes, human tissues etc. POPs health effects include cancer, neurological, behavioral, immunological, birth defects and reproductive discrepancies, in humans. Long term studies in animals have shown that HCB can harm the liver, endocrine (including thyroid), immune and nervous systems and can damage bones, kidneys, and blood (ASTDR, 2000b).

The impacts of DDTs on neurodevelopment have also been investigated. Other epidemiological studies have found that as the DDE levels in the blood of pregnant women increased, the chances of having a pre-term baby also increased, and this might also be linked with increased infant mortality (Torres-Arreola et al., 2003, Longnecker et al., 2001). This project focused on the quantitative detection of OCPs in water, sediment and commercially important shell fishes of the Badagry Creek and Lagos Lagoon axis in the Lagos Lagoon complex.

2. Study Area

Badagry creek in Lagos State is endowed with lagoon system, floodplains and mangrove swamps. It lies within longitude 2°42'E and 3°42'E and stretches between latitude 6°22'N and 6°42'N sharing boundary with the republic of Benin. Sources of water into the creek include Lagunede porto novo (in Republic of Benin), River Yewa and Owo, Ologe and Lagos lagoon (Nigeria). It is important for both artisanal and commercial fisheries and as well as transportation, recreation and domestic purposes. There are three Navigation Channels going into the Badagry Creek. These include the Apapa, Commodore and Elegbete channels. It is bordered by Ajegunle, Kirikiri, Apapa, Mile 2, Amuwo Odofin, Navy town, Ojo town, Ibeshe, Iduowu, Badagry town etc. There are two major Islands on the Creek, including Tin Can and Snake islands. The part of the Creek closer to the Lagos Lagoon is a very busy hub witnessing cargo ships plying the creek to and from Apapa Ports and Tin Can Island Port. Oil tankers also ply this route to and from various Oil tank farms in the area. They all indiscriminately release ballast waters into the creek. This stretch also receives effluents from key industries like Apapa Flour mills, Dangote cement and numerous commercial fishing companies.

Figure 1: Showing Badagry Creek and Lagos Lagoon. (Clarke et al, 2020)

The lagoon is located specifically on longitude 6°27'N and latitude 3°23'E sharing its name with Lagos in Nigeria. It empties into the Atlantic Ocean via Lagos Harbour, 0.5km to 1km wide and 10km long. To its north-east, the lagoon is connected by a channel passing south of the town of Epe to the Lekki lagoon. Pollution by domestic and industrial waste is a major problem as a large amount of wastewater is released into this lagoon daily from industries, residential areas and tourist centres including numerous hotels and beaches. Populated areas around the Lagoon include Ijora, Ajegunle, Aiyetoro, Iru, Apapa Eleko, Lawani Oguntayo, Oogoro, Obalende, Alayabiagba, Oroke, Ondotedo, Inupa, Agala, Coker, Tarkwa Bay etc. amongst which are distributed the Lagos Island, Victoria Island and Iddo Island.

3. Materials and Method

Persistent organochlorine pesticides (POPs) are present at parts per trillion level (µg/l) in water samples and at parts per billion level (µg/kg) in sediment and commercially important shellfish species. This requires highly specific, sensitive and reliable analytical methods for carrying out such trace and ultra-trace measurements. Gas chromatography with electron capture detector (GC-ECD) using mixed stationary phases on a packed glass column was utilized for this purpose.
4. Results

4.1. Water

The results of the mean concentration of persistent organochlorine pesticides in water samples from the two water bodies, revealed the occurrence of twenty (20) OCPs. In Badagry creek, the least concentration was recorded for Alpha HCH with a concentration of $0.420 \pm 0.032$ µg/l and the highest was recorded for Dieldrin with a concentration of $125.50 \pm 89.142$ µg/l. Beta HCH, Gamma Chlordane, ppDDE, Endrin, Endosulfan II and ppDDD were not detected.

In Lagos lagoon, Alpha HCH had the least concentration of $0.150 \pm 0.012$ µg/l and Endosulfan II had the highest concentration of $147.600 \pm 10.810$ µg/l. Alpha Chlordane, ppDDE, Endrin, ppDDD, Endrin Aldehyde were not detected. Figure 2 showed variation in the concentration of organochlorine pesticide residues in water samples from Badagry Creek and Lagos Lagoon. It was observed that Endosulfan II in Lagos lagoon had the highest concentration when compared with the concentration of OCP residues from Badagry Creek and Dieldrin also had the highest concentration in Badagry creek.

![Figure 2: Showing the Mean Variation of OCP Residues in Water Samples from Lagos Lagoon and Badagry Creek](image)

4.2. Sediment

Pesticide residues were found to be significantly higher in sediments than in water collected from the same station. In Badagry creek, Beta HCH, Gamma Chlordane, ppDDE, Endrin, ppDDD, Endosulfan sulphate and Endrin Ketone were not detected. Alpha HCH had the least concentration of $2.130 \pm 2.056$ µg/kg and ppDDT had the highest concentration of $243.500 \pm 138.100$ µg/kg. In Lagos lagoon, Alpha Chlordane, ppDDE, Endrin, ppDDD and Endrin Aldehyde were not detected. The least concentration was recorded for Alpha HCH with a concentration of $0.150 \pm 0.012$ µg/kg and Endosulfan II had the highest concentration of $147.600 \pm 96.120$ µg/kg. Figure 3 showed variation in the concentration of organochlorine pesticide residues in sediment from Badagry Creek and Lagos Lagoon. It was observed that Endrin Aldehyde had the highest concentration in Lagos lagoon while ppDDT had the highest concentration in Badagry creek.

![Figure 3: Showing the Mean Variation of OCP Residues in Sediment Samples from the Water Bodies in Lagos (Lagos Lagoon and Badagry Creek)](image)
4.3. Shell Fishes

4.3.1. Callinectes Pallidus

In Badagry creek, Alpha HCH had the least concentration of 0.350 ± 0.060 µg/kg while Endosulfan II had the highest concentration of 67.380 ± 22.860 µg/kg. Aldrin, Dieldrin, ppDDE, Endrin and Endosulfan sulphate were not detected. Alpha HCH had the least concentration of 0.250 ± 0.009 µg/kg and Endosulfan sulphate had the highest concentration of 55.000 ± 10.070 µg/kg in Lagos Lagoon. Alpha Chlordane, ppDDE, Endrin, ppDDD and ppDDT were not detected. Figure 4 showed variation in the concentration of organochlorine pesticide residues in Callinectes pallidus in Lagos lagoon and Badagry creek in Lagos state. It was observed that Endosulfan II in Badagry creek had the highest concentration when compared with the concentration of other OCP residues. Endosulfan sulphate had the highest concentration in Lagos lagoon. The OCPs concentration in Badagry creek were comparatively higher than that in Lagos lagoon.

The ppDDE and Endrin residues were not detected in shellfish samples from the two water bodies in Lagos. Eldrin aldehyde had the highest mean concentration in Penaeus monodon and Callinectes pallidus collected from Badagry creek in Lagos with concentrations of 99.900 ± 69.600 µg/kg and 41.120 ± 7.792 µg/kg respectively.

![Figure 4: Showing the Mean Variation of OCP Residues in Callinectes pallidus from Badagry Creek and Lagos Lagoon](image)

4.3.2. Penaeus Monodon

In Badagry creek, Alpha HCH had the least concentration of 1.300 ± 0.210 µg/kg while Endrin Aldehyde had the highest concentration of 143.500 ± 71.892 µg/kg. Endrin and ppDDE were not detected. In Lagos Lagoon, Alpha HCH had the least concentration of 1.320 ± 1.050 µg/kg and Endrin Aldehyde had the highest concentration of 56.300 ± 22.893 µg/kg. Alpha Chlordane, ppDDE, Endrin, ppDDD and ppDDT were not detected. Figure 5 shows the variation in concentration of organochlorine pesticide residues in Penaeus monodon of Lagos lagoon and Badagry creek. It was observed that Endrin Aldehyde had the highest concentration in both water bodies. The OCP concentration in Penaeus monodon of Badagry creek was higher than that in Lagos lagoon.

![Figure 5: Showing the Mean Variation of OCP Residues in Penaeus monodon from Badagry Creek and Lagos Lagoon](image)
Endosulfan I had the least mean concentration of 0.350 ± 0.123 µg/kg in Callinectes pallidus in Lagos lagoon while alpha HCH had the least mean concentration of 1.310 ± 0.014 µg/kg in Penaeus monodon in Badagry creek. Endrin Aldehyde had the highest concentration in shellfishes (Callinectes pallidus and Penaeus monodon) from Badagry creek in Lagos. The concentration in Penaeus monodon was higher than that in Callinectes pallidus.

5. Discussion

The results of the study showed that OCPs are present in water, sediment and shellfish in both Lagos lagoon and Badagry Creek. The main sources of pollution in the catchment areas are socio-economically related as it serves as a means of transportation by some of the local residents and smugglers using motorised canoes and it is also polluted by local residents who empty their wastes and effluents into the lagoons. Although the use of pesticides for agricultural activities is not a major occupation in the area, the OCP levels are most probably due to the discharge of domestic and industrial wastes into the water bodies from numerous towns and villages bordering these aquatic habitats. The levels of organochlorine pesticide residues exhibited in samples collected from the same point at different times were different. It is well known that most of the applied pesticides are subject to various means of transport. Thus, they don’t remain at their target site but often enter aquatic environment via soil percolation, air drift or surface run-off affecting abundance and diversity of non-target species producing complex effects on the ecosystems and altering trophic interactions.

Endosulfan II had the highest concentration in Lagos lagoon, with a concentration of 147.600 ± 10.810 µg/L. DDE and Endrin were not detected in all sample stations. The highest concentrations of OCPs recorded in Lagos lagoon may be attributed to its greater metropolitan status where OCP inputs are derived from an array of industrial and domestic sources. Pesticide residues were found to be significantly higher in shellfish than in water which is significantly lower than that in sediment.

The ppDDT had the highest concentrations in sediment samples of Lagos lagoon, with concentrations of 243.500 ± 138.100 µg/kg. The high concentration of DDT recorded in Lagos lagoon is attributed to its usage domestically in water bodies from numerous towns and villages bordering these aquatic habitats. DDE comes into the water either by run-offs, photolysis, anaerobic biodegradation, aerobic biodegradation and aerobic degradation. When DDT gets into water they are rapidly absorbed by organisms or volatilized which reduces its concentration in water. High DDT concentration in sediments is attributed to slow degradation of DDT cun recent inputs of DDT into the environment.

OCP residues in shellfishes were found to be high in samples analyzed. This conforms with the work of (Ize Iyamu, 2007) which states ‘that pesticides settle at the bottom of the water and tends to bind with the sediment and bio-accumulate in tissue of shellfish due to their benth-o-phagous adaptation’. Endrin Aldehyde had the highest concentration in Badagry Creek. DDE and Endrin were not detected in Peneaus monodon and Callinectes pallidus. The values in Peneaus monodon were higher than those from Callinectes pallidus. This may be an indication that Peneaus monodon have a greater residence time in the bentic habitat that promotes a higher level of bioaccumulation than Callinectes pallidus within the period of study. All shellfish samples analyzed had OCP concentrations beyond the acceptable limits which make them unsafe for human consumption. Peneaus monodon obtained from Lagos (Badagry creek) had the highest OCP value and this makes people that feed on it highly susceptible to neurological, behavioral, immunological, birth defects and reproductive dysfunctions.

The OCPs present in shellfish samples may be due to their lipophilic nature (fat soluble), they reside in fatty tissues entering by ingestion or dermal absorption and respiration. When these chemicals are taken in and they bio-accumulate, bio-magnify and remain until they are caught and consumed by bigger fishes and eventually eaten by humans (Clarke et al., 2013)

The concentrations of residues were comparatively lower in water than in sediment and this indicates that these compounds are hydrophobic and tend to accumulate in sediments and subsequently in fatty tissue of organisms. The results showed that OCP levels in all shellfish samples analyzed, were above the maximum acceptable limits of 0.01ppm (10 µg/kg) set by EU and Federal Ministry of Environment for aquatic life protection and the highest value was recorded in Peneaus monodon of Badagry creek.

6. Conclusion

Both water bodies sampled from Lagos get extremely polluted due to discharge of pesticide residues from point and non-point sources with the higher level of pollution experienced in Badagry creek. The concentration OCPs in Lagos lagoon being largely diluted by the great volume of marine water influx from the Atlantic Ocean. These toxic substances don’t degrade easily and remain persistent in the environment, and also have the ability to bio-accumulate in the food chain, and become potentially hazardous to man, in long run. A relatively high level of these compounds was observed in both study areas. Most of the organochlorine pesticides found in this study were officially banned, but they were still detected in these areas. Regular monitoring and strict law enforcement are needed to develop a strategy to manage the environmental hazards caused by these toxic substances and to improve environmental protection of the study areas.

7. References

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