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Assessment of organochlorinated pesticides (OCPS) residues in the muscles of frozen atlantic herrings (*clupea harengus*) in Ibadan southwest local government, Ibadan, Oyo state, Nigeria

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ABSTRACT

This study assessed organochlorinated pesticides (OCPs) residues in the muscle of frozen Atlantic herrings (*Clupea harengus*) and compared with the maximum residue limits set by European Union (EU), Food and Agricultural Organization (FAO) and World Health Organization (WHO). Frozen fish samples were purchased from Oke Ado market in Ibadan, Oyo State Nigeria and weighed per batch. Fish sample averaged 300grams were wrapped in aluminum foil paper and placed in cooler and taken to the Laboratory for analysis. OCPs were tested in *C. harengus* in February, March and April, 2023. The mean concentration and standard deviation of OCP congeners detected (concentration in ng/g) for February, March and April were 1368.74±47.49, 546.07±18.45, 788.40±35.36 respectively for a-HCH. p,p'-DDT had 0.14±0.06 with other values having b-HCH 0.36±0.15, d-HCH 0.52±0.23 in February, 0.00±0.00 in March and 0.20±0.08 in April. Aldrin and Endrin aldehyde concentration were 9.11±3.65 and 42.08±16.82 respectively for February only. Methoxychlor however recorded 1.12±0.47, 0.38±0.14 and 0.25±0.06 for February, March and April accordingly. The levels of OCPs detected exceeded Maximum Residue Limits (MRLs), indicating potential risks to human health. It is recommended that regulatory measures, public awareness and continuous monitoring should be undertaken to stem the effects of this pollution.

Keywords: organochlorinated pesticides, concentration, environment, Atlantic herrings, aquatic pollution.

INTRODUCTION

Water pollution refers to the contamination of water bodies such as lakes, rivers, oceans, and groundwater by harmful substances that negatively affect aquatic life and human health (Zakir et al., 2020). Water pollution is the leading worldwide cause of death and diseases and accounts for the deaths of more than 14,000 people daily (Balkis, 2012). Persistent Organic Pollutants (POPs) are a group of chemicals that are toxic; persist in the environment, and bioaccumulate in the food chain. POPs are typically formed as a result of human activity, including industrial processes, waste disposal, and agricultural practices (Kucklick et al., 2010).

Organochlorine pesticides (OCPs) are a class of Persistent Organic Pollutants (POPs). Exposure to OCPs can disrupt the thyroid hormone system, which can cause developmental disorders, affect the immune system, and contribute to cognitive impairments (Warner et al., 2018). OCPs are highly persistent, lipophilic and known for their low solubility in water (Yao, 2022, Ren et al., 2015; Byer et al., 2013). They are volatile which make them to evaporate into the air and travel long distance before being deposited back into the ground water (Degrendele et al., 2016). Many chlorinated moieties that are toxic and bio-accumulative have been banned (Eriksen, 2017). Consequently, there is growing scientific, regulatory, and social interest in measuring the levels of chlorinated chemicals in environmental media, and in determining the environmental effects of such contamination (Kucera et al., 2014). Overall, fish are important indicators of environmental pollution with persistent organic pollutants, including organochlorinated pesticides.

Atlantic Herring (*C. harengus*) is an economically important fish species that is widely consumed by humans, both domestically and internationally. It is a pelagic fish found in the North Atlantic Ocean and the Baltic Sea (Larsson, 2018). It is also known to accumulate high levels of persistent organic pollutants (POPs) in its tissues, including organochlorine pesticides (OCPs). The main objective of this study is to determine the levels of OCP residues (such as DDT, HCH, and endosulfan) in the muscles of frozen Atlantic herring (*C. harengus*) sold in Ibadan in relation to the established regulatory limits.

MATERIALS AND METHODS

Atlantic herring (*C. harengus*) is a small, silver-coloured fish found in the North Atlantic and occur in large schools and inhabit coastal and continental shelf waters from Labrador Southward to South Carolina, USA. They are important species both commercially and ecologically serving as a food source for larger fish, marine mammals, and seabirds. This study was carried out in Ibadan Oyo State Nigeria for three months: February, March and April 2023.

Fish Sample Collection

Samples were collected on every third day of each month from Oke Ado, a popular market in the Ibadan metropolis. The samples collected across the three months had an average weight of 300 grams and an average length of 26 cm. Nine (9) fish samples were collected from the market and weighed per batch. They were wrapped in aluminium foil paper, placed in sterile cooler with ice and taken to the laboratory for analysis.

Sample Preparation and Analysis

Fish samples were aseptically removed from the container and were placed on sterile tray. Fillets of the fish were removed from the fish without the skin using a sterile scalpel and were mashed with an electronic blender for a minute at high speed. An aliquot five grams (5g) of the homogenized fish samples was weighed into a beaker and 25ml of a mixture of acetone and hexane (1:1) was added. The beaker was sonicated for 10 min in an ultrasonic bath and the extract was transferred to another beaker. The extraction was repeated with 10 ml of the solvent mixture. The extracts were combined; concentrated to about 2.0 mL.

Clean up of the Extract

Clean-up of the extracts was done with a column chromatography using silica gel, and then eluted with 5 ml of hexane. The purified extracts were then re-constituted in 2 mL hexane.

Instrument Conditioning

Presence of organochlorinated pesticides in fish samples were accomplished using an Agilent Technologies 7890A equipped with 5975 MSD for GC analysis. The separation was done on an HP-5 Capillary column (30m, 0.32mm, 0.25μm). Helium gas at flow rate of 1.8mL/min was used as carrier gas at injection temperature of 2800C. Injection method was spitless mode at volume 1.0 μL. The analyses were operated in SIM mode at transfer line temperature of 2800°C.

RESULTS AND DISCUSSION

Six components of the organochlorinated pesticides residues were detected in the muscle tissue of Atlantic herring (*C. harengus*) obtained in February as shown in Figure 1. These included a-HCH with a minimum and maximum concentration range of 821.25 - 1916.22ng/g (mean 1368.74 ± 47.49 ng/g), d-HCH was the second component detected and ranged from 0.30 ng/g - 0.75 ng/g (mean 0.52 ± 0.23 ng/g), Aldrin ranged from 5.46 ng/g - 12.75 ng/g (mean 9.11 ± 3.65 ng/g), Heptachlor epoxide ranged from 23.70 - 55.26 ng/g (mean 39.48 ± 15.78 ng/g), Endrin aldehyde ranged from 25.26 -

58.89 ng/g (mean 42.08 ± 16.82 ng/g). The last detected component Methoxychlor ranged from 0.66 -1.59 ng/g (mean 1.12 ± 0.47ng/g). Nine components were absent and d-HCH had the lowest value range detected.

In March, four components were detected namely: a-HCH with minimum and maximum range of 327.63 ± 764.52 ng/g (mean 546.07 ± 18.45 ng/g), Heptachlor epoxide had minimum and maximum of 3.69 - 8.61 ng/g (mean 6.15± 2.46 ng/g), p,p'-DDT ranged 0.09 - 0.21 ng/g (mean 0.14 ± 0.06 ng/g), Methoxychlor 0.24 - 0.51 ng/g (mean 0.38 ± 0.14 ng/g) (Figure 2). In fish samples for April as shown in Figure 3, five components were detected and ten were absent. The five detected were: a-HCH with minimum and maximum range of 473.04 - 1103.76 ng/g (mean 788.40 ± 35.36 ng/g), b-HCH ranged from 0.21- 0.51 ng/g (mean 0.36 ± 0.15 ng/g), d-HCH from 0.12 - 0.27 ng/g (mean 0.20 ± 0.08 ng/g), Heptachlor epoxide from 1.26 - 2.97 ng/g (mean 2.11 ± 0.86 ng/g), and Methoxychlor with a range of 0.09 - 0.21 ng/g (mean 0.25 ± 0.06 ng/g). As indicated in Figure 1, 2 and 3, longer error bars indicate higher variability, while shorter error bars indicate more consistent measurements. Components with mean concentrations of 0 or close to 0 are likely not detected in some months. These components have very short bars or no bars.

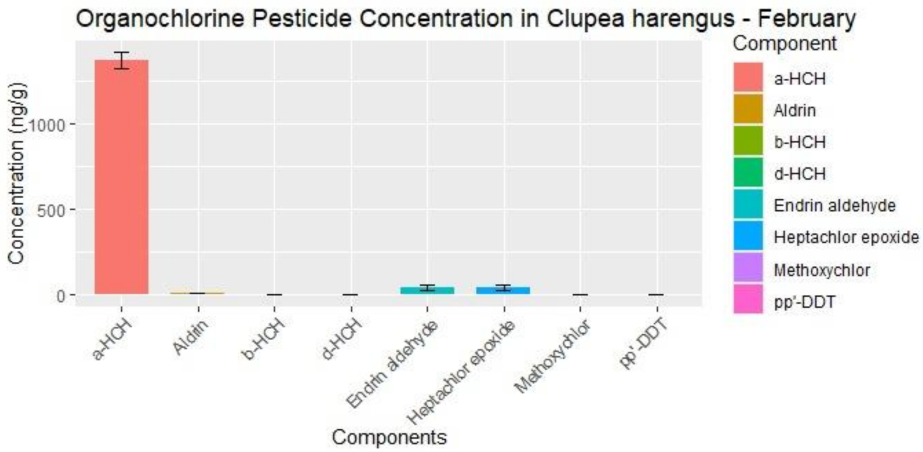

Figure 1. Organochlorine pesticide concentration (ng/g) in *Clupea harengus* for the month of February.

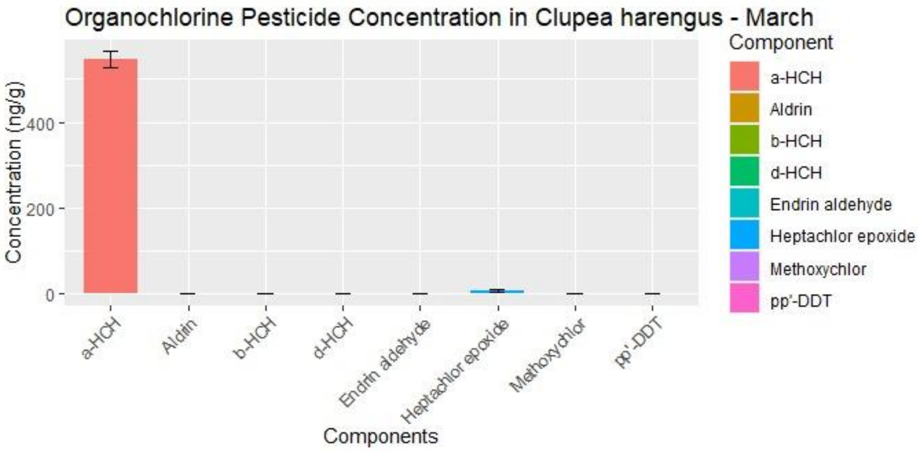

Figure 2. Organochlorine pesticide concentration (ng/g) in *Clupea harengus* for the month of March.

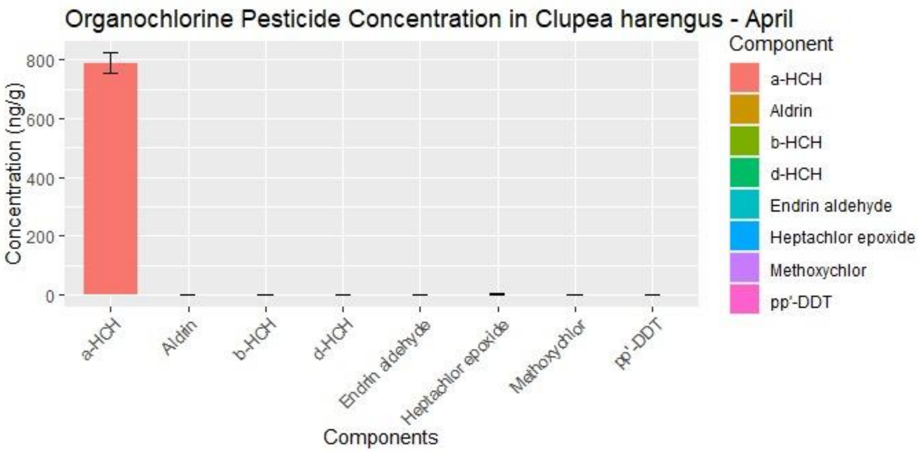

Figure 3. Organochlorine pesticide concentration (ng/g) in *Clupea harengus* for the month of April.

As shown in Table 1, the mean concentration of a-HcH and Heptachlor epoxide were significantly different ($p<0.05$) for the three months of February, March and April in the fish samples examined. Methoxychlor mean concentration for February was significantly different ($p<0.05$) from both March and April. However, there is no significant difference ($p>0.05$) in the mean concentration of d-HcH in fish muscle for February and April. b-HcH was only detected in the month of April; Aldrin and Endrin aldehyde detected in February only while p,p'-DDT was also detected only in the month of March. The summation of the mean concentration in all the months; February, March and April were ∑243.51±14.07, ∑138.19±5.27 and ∑158.26±7.30 respectively.

Table 1. Mean concentration and Standard deviation of OCPs (ng/g) for the month of February, March and April

Components	February	March	April
	Mean±SD	Mean±SD	Mean±SD
a-HCH	1368.74±47.49 [c]	546.07±18.45[a]	788.40±35.36 [b]
b-HCH	ND	ND	0.36±0.15
d-HCH	0.52±0.23 [b]	0.00±0.00 [a]	0.20±0.08 [b]
Heptachlor	ND	ND	ND
Aldrin	9.11±3.65 [a]	ND	ND
Heptachlor epoxide	39.48±15.78 [c]	6.15±2.46 [b]	2.11±0.86 [a]
Endosulfan I	ND	ND	ND
p,p'-DDE	ND	ND	ND
Dieldrin	ND	ND	ND
Endrin	ND	ND	ND
Endosulfan II	ND	ND	ND
p,p'-DDD	ND	ND	ND
Endrin aldehyde	42.08±16.82 [a]	ND	ND
p,p'-DDT	ND	0.14±0.06	ND
Methoxychlor	1.12±0.47 [b]	0.38±0.14 [a]	0.25±0.06 [a]
Mean of OCPs	∑243.51±14.07	∑138.19±5.27	∑158.26±7.30

*Mean with same superscript along the columns are not significantly different at p>0.05
ND = Not detected

This study examined the concentrations of organochlorinated pesticides in the muscle tissues of Atlantic herring (*Clupea harengus*). Organochlorinated pesticides are harmful substances that can accumulate in the muscles of fish, posing risks to human consumption. These chemicals according to Massone et al., (2023) are highly toxic and can persist in the environment for many years, accumulating in the food chain and posing risks to human and animal health. The isomers of

Hexachlorocyclohexane, a-HCH was detected in all the samples in all months followed by d-HCH while b-HCH was only found in the month of April. The concentration of this pesticides in all the fish samples were much higher than the FAO/WHO (2009) set Maximum residue Limits (MRLs) of 0.01 ng/g (Shoiful et al., 2013). According to El-Badaoui et al., (2021), lindane (d-HCH) concentration values of 0.7-0.72ng/g and 0.003-0.044ng/g values of pp'-DDT and its metabolites (p,p'-DDE) were recorded in four fish species of *Cyprinus carpio*, *Barbus barbus*, *Hypophthalmichthys nolitrix* and *Rutilus rutilus*. Aldrin was only detected in the muscles of *C. harengus* collected in February. Fish mortality due to pesticides like Aldrin groups of chemicals are on the record (Sebra and Mehana, 2015; Jayaraj et al., 2016).

The absence of Dieldrin but with detected concentrations of Aldrin may indicate that Aldrin had not undergone photolysis to produce Dieldrin as a metabolite as observed by Agency for Toxic Substances and Disease Registry (ATSDR) of The United States Department of Health and Human Services (1993). Saha et al., 2017 recorded Aldrin (0.187±0.05mg/kg) and heptachlor (0.272±0.054 mg/kg residues in fish samples offer for sale in West Bangal India. Akan et al., 2014 also extracted 6.76mg/kg Aldrin in fish samples harvested in Lake Chad. The sale of Dieldrin and Aldrin has been banned by National Agency for Food and Drug Administration and Control (NAFDAC) because of their toxicity and persistence in the environment (Akan et al., 2013). The concentration of aldrin in *C. harengus* was much higher than FAO/WHO (2009) set Maximum Residue Limit (MRL) of 0.2ng/g. Heptachlor was not detected but Heptachlor epoxide was found in fish samples. The highest concentration was in February, followed by March and then April samples. The concentration of 0.003ng/g present in the fish samples was higher than recommended Maximum Residue Limits for Heptachlor epoxide by FAO/WHO (2009) in the fish samples (Shoiful et al., 2013). The maximum concentration of methoxyclor was detected in muscle of *C. harengus* sample in month of February while the least value was detected in fish samples in April. The amount of methoxyclor in the environment changed seasonally due to its use in farming. It does not dissolve readily in water - its degradation may take many months. The mean concentration of methoxyclor in this study was a bit higher than the lowest value of 0.20ng/g calculated from the three months samples, set by FAO/WHO (2009). p,p'-DDT was only detected in C. harengus sample collected in the month of February. The concentration of p,p'-

DDT was low compared to the set Maximum Residue Limits of 1.0ng/g by FAO/WHO (2009). In a similar work by Hassan et al., 2009, organo chlorinated pesticides residues recorded in fish tissue obtained from private fish farms in Egypt included Lindane (d-HCH) and pp'-DDT. Also, Reindl et al., 2013 discovered in the fish muscle of salmon, carp, herring and cod the presence of p,p'-DDT, endrin, diedrin and methoxyclor.

Endrin aldehyde in samples from February had a high mean concentration and absent in other samples. The concentration in fish sample was much higher than the 0.20ng/g set standard by FAO/WHO (2009). It is an established fact that all pesticides are potentially lethal to the fishes even at relatively low concentration (Ullah and Zorrienhzahra, 2015).

CONCLUSION

The contamination of the fish samples does not originate primarily from the market itself. The levels of detected pesticide residues in the fish samples imported into the country and sold in the markets exceeded the Maximum Residue Limits (MRLs), indicating potential risks to human health.

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