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Seasonal Differences in Organo Chlorine Pesticide Residues in Southern Iraqi Marsh Fish

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Abstract. The contamination of two fish species (Oreochromis niloticu and Liza abu) by organochlorine pesticides in southern Iraqi wetlands between the winter of 2021 and the fall of 2022 during several seasons is the subject of this study, To ascertain these OCP, mussel samples of these fish have been collected and extracted. Analysis of organochlorine pesticides was done by using gas chromatography-mass spectrometry (GC-MS). It was discovered that each of these species contained varied concentrations of 14 different kinds of chlorine pesticides. Seasonal variation of these OCPs has been studied, as have the levels of alpha-, delta-, lindane, lindane, hexachlor, aldrin, epoxyheptachlor, D.D.E, dieldrin, D.D.D , endrin aldehyde, endrin ketone, methyl chloride, endrin, and endosulfan. Oreochromis niloticu had mean pesticide concentrations ranging from 0.15 to 1.6 ng/g dry weight in the winter and summer, respectively, while Liza abu had mean pesticide concentrations ranging from 0.13 to 0.7% ng/g dry weight in the winter and summer, respectively. Considering the data at hand, this study—"the first of its kind in the area".

Highlights:

1. Organochlorine pesticide contamination in Oreochromis niloticus and Liza abu.
2. Seasonal GC-MS analysis of 14 pesticide types (2021–2022).
3. Pesticide concentrations ranged 0.13–1.6 ng/g; first study in area.

Keywords: Iraq marshes, GC/MS, pesticides, fish, pollution, accumulation.

اهتمت الدراسة الحالي بتحديد تلوث نوعين من الأسماك الاقتصادية المتواجدة في بيئة الدراسة (Oreochromis niloticus و Liza abu) بالمبيدات العضوية الكلورية في (اهوار) جنوب العراق، تم أخذ عينات فصلية من عضلات الأسماك لتحديد المبيدات الكلورية العضوية . تم إجراء تحليل المبيدات العضوية الكلورية باستخدام جهاز كروماتوغرافيا الغاز-/طيف الكتلة (GC-MS). تم تسجيل 14 نوعًا من المبيدات الكلورية في كلا النوعين بتركيزات مختلفة وهي ألفا ليندين، ليندين، دلتا ليندين، هيبتاكلور، ألدرين، إيبوكسيهيبتاكلور، D.D.E، ديلدرين، D.D.D، إندرينألدهيد، إندرينكيتون، ميثوكسي كلور، إندرين، إندوسولفان ومستوياتها المتفاوتة خلال الفصول المختلفة(الشتاء,الصيف,الربيع,الخريف)، كما تمت دراسة التباين الموسمي المبيدات العضوية الكلورية. حيث تراوحت متوسط تركيزات المبيدات في سمك البلطي النيلي بين (0.15-1.6) نانوغرام/غرام من الوزن الجاف خلال فصلي الشتاء والصيف على التوالي. وتراوح متوسط تركيزات المبيدات في سمك البلطي النيلي بين (0.13-0.7) نانوغرام/غرام من الوزن الجاف خلال فصلي الشتاء والصيف على التوالي. وعلى أساس الفترة الممتدة من شتاء 2021 إلى خريف 2022، تعد هذه الدراسة الأولى من نوعها في المنطقة .

Introduction

environment and tend to be toxic in higher organisms with potential risks to human health [1]. Consequently, the production and usage of these compounds have been

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banned or severely restricted in many countries throughout the world. However, due to their striking resistance to biotic and abiotic degradation, and their ability to migrate through several environmental compartments, they have continued to pose a significant threat to the food chain [2]. Since fish are a vital protein source in Iraq, the presence and fate of these agricultural staples are areas of concern. Thus, monitoring and regulating the amount of pesticides that may end up in fish and move through the food chain, leading to accumulation and biomagnification in consumers, are crucial approaches to food control and public health [3].

Organochlorine pesticides were among the first products used as a defence against insect pests. Having a common point of application representing that plants were sprayed or dusted with these chemicals, the production capacity of these synthetic substances, rather low yields, greatly increased [4].

The selection and improvements of agrochemicals for the control of pests was the drive that gave rise to the highest yield synthesis of organochlorine compounds which were also the ones with the largest global spread among the pesticides registered in the 1960s. Lindane is the exception because of its high efficacy as a delouser in the treatment of head lice and mite-infecting scabies[5]. Dieldrin, aldrin, and endrin are cyclodienes, whereas lindane are hexachlorocyclohexanes. The gamma-isomer is a pure insecticide scheme, of which the exotic simultaneous isomer exerts an antagonistic action to the other gamma-enantiomer in the central nervous system of the insect pests. The potency and rather broad-spectrum toxicity of DDT, together with its long half-life, led it to be widely used as an insecticide in agriculture as well as in the protection of communities against vector pests [6]. Furthermore, also some of these OCPs were used by some people in the marshes to catchfish which affects these organisms in the marshes [7].

Methods

Region of study

Al-Hammar Marsh is one of the largest wetlands in southern Iraq, part of the Mesopotamian Marshes. It is located near the Euphrates River and covers an extensive area of interconnected lakes, reed beds, and seasonal floodplains. This marsh is a significant ecosystem, supporting a wide variety of plant and animal species, including

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several endangered ones. It is also home to the Marsh Arabs, who have a unique culture and lifestyle adapted to the wetland environment [8].

The marsh plays a critical role in biodiversity conservation, water filtration, and as a natural flood buffer. However, it has faced challenges like drainage, pollution, and climate change, which have threatened its ecological balance. Restoration efforts in recent years aim to preserve this vital habitat [9].

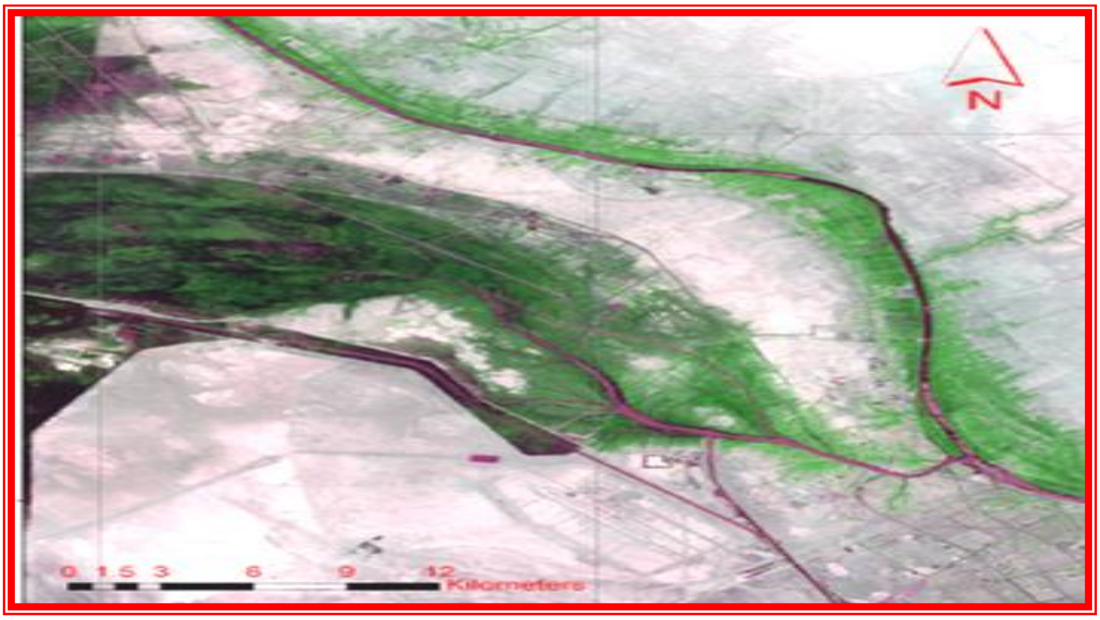

Fig (1) sample Locations of Study region

Fish samples:

Tow fish samples (Oreochromis niloticu and Liza abu) as shown in the picture (Fig 2 and 3) were collected from study region using gillnets and a cast net. They were placed in a cork box containing crushed ice to reduce their deterioration and preserve their tissues after death. Samples transferred to the lab(in marine science center) and were stored for the period extending from the winter of 2021 to the fall of 2022d inside ice-box until reached the lab. Samples of mussel tissues were taken and frozen. the samples of fish were grinding and sieving through a63 um mesh sieve. 25 gm wereextracted accordingto [10].

1. 25 gm of dried samples were weighed. They were placed in an extraction thimble and placed in the extraction apparatus.

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2- Using a dichloromethane solvent and a Soxhlet extraction apparatus, the material was continuously extracted for 24 hours.

3- The sample was evaporated to near dryness"using a rotary evaporator and the sample was preserved for the next step for purification and then analysis by using GC/MS.

Fig (2):Oreochromis niloticus

Fig (3):Liza abu

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Statistical Analysis

The statistical program (SPSS-22) Statistical Package for Social Science was used in the statistical analysis of the results of this study using Analysis of Variance (AVOVA) under a significant level of 0.05 and the Least Significant Difference (LSD) test.

Result and Discussion

1-Pesticide in O . niloticus:

Oreochromis niloticus had the lowest concentration of pesticide DDD (0.03 ng/g d.w.) in the spring and winter, and the highest concentration of pesticide aldrine (7.2 ng/g d.w.) in the winter, according to the results(Table 1). The average pesticide concentrations were 1.6 ng/g d.w. in the winter and 0.15 ng/g d.w. in the summer, as shown in (Table 1, Figure 4a, and Figure 4b).

Table 1: The pesticide kinds and concentrations (ng/g d.w.) in Oreochromis niloticus

Compound name"	Winter"	''spring	''summer	Autumn"
alpha-l"indane	0.3′	0.4′	0.06′	0.′13′
Lindane′	0.′4	‵0.1	0.23′	0. ‵20′
delta-lindane′	2′	1′.5	0.3′	0.1′7′
Heptachlore′	2.9′	2′	0.28′	0.22"
Aldrine′	7.2′	0.′3	0.′19	0.15"
Epoxyheptach′lor	6.3′	1.3′	0′	1.27"
D.D.E′	0.2′	0.2′	0′	0.21"
Dieldrin"	0.′6	0.8′	0"	0.8"
D.D.D"	0′	0′	0.′03	0.14‴
endrin aldhyde′	0.1′	0."4	0′	0.74′
endrin ketone′	0.4′	1.3′	0	0.25"
metoxy chlor′	0.6′	1.2′	0′	1.35‴
Endrin′	0.7′	1"	0"	1.28′
Endosulfan′	0′	0′	0′	0.16"
Totel′	21′.8	10′.5	‵1.11	7.07‴

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Mean'	'1.6	0.8'	'0.15	0.505'

0 =Not detected

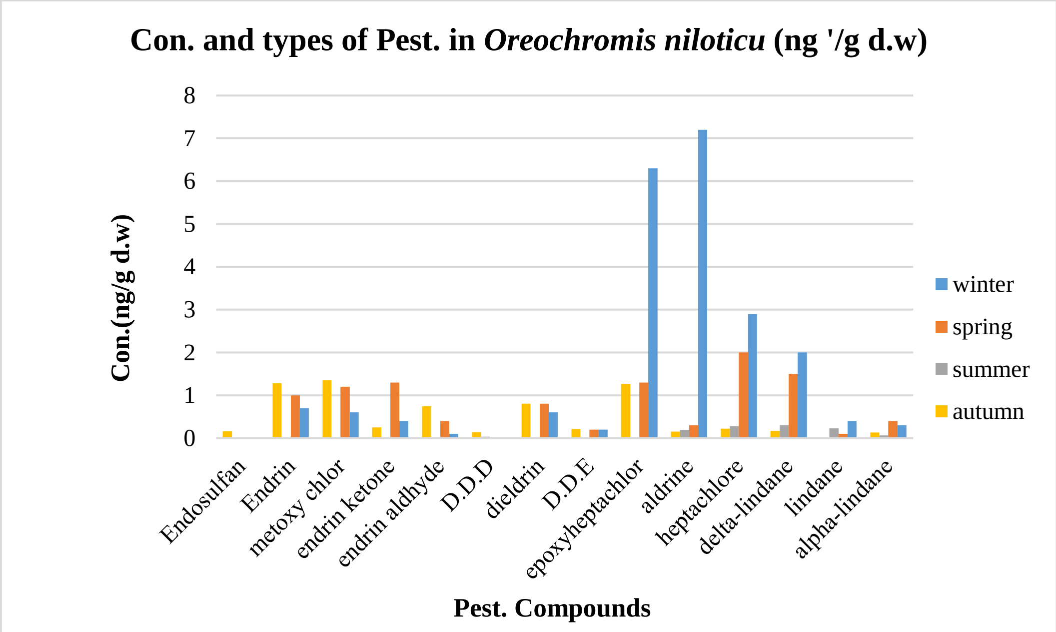

Figure (4a): O . niloticu's pesticide concentration and types (ng/g d.w.) during the study period.

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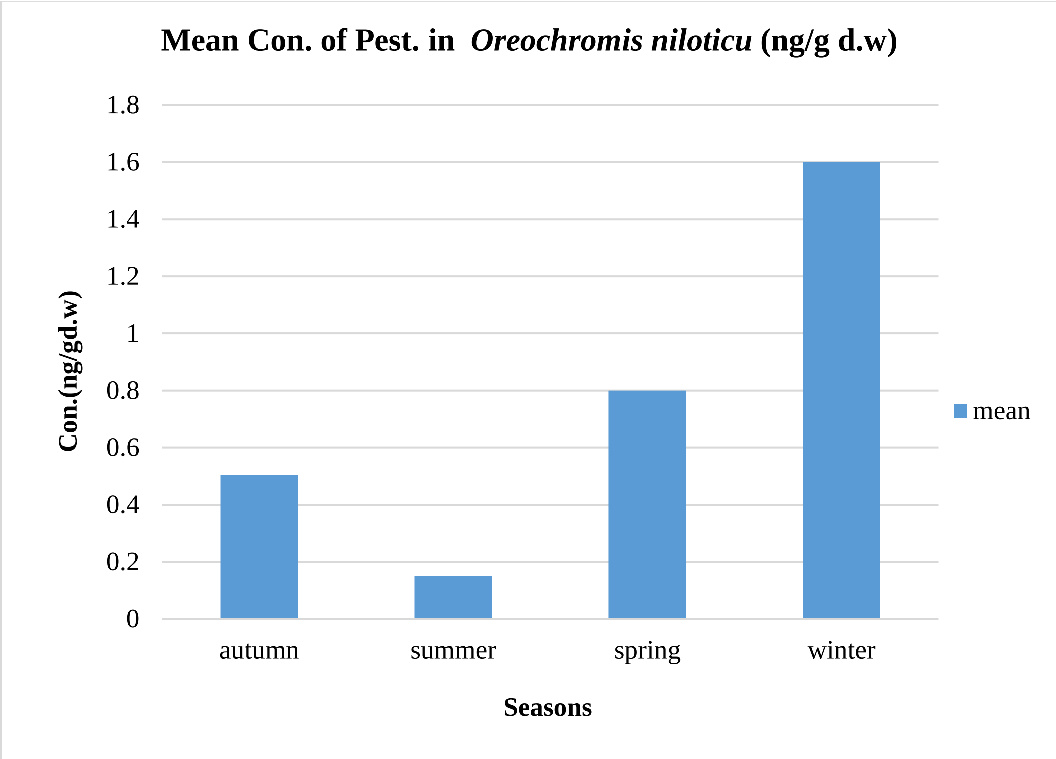

Figure (4b): Oreochromis niloticu's Mean Pesticide Concentrations (ng/g d.w.) During the Study Period.

Liza Abu Pesticide:

The results showed that Liza abu's pesticide content varied from 0.02 to 3.8 ng/g d.w., with winter time seeing the greatest concentrations of the pesticide Endrin. The average pesticide concentrations were 0.7 ng/g d.w. in the winter and 0.1 ng/g d.w. in the summer, as shown in (Table 2) and (Figure 5a, and Figure 5a.).

Table (2): The types of pesticides and their concentrations (ng/g d.w.) in Liza abu

Compound name’	Winter’	Spring’’	Summer’	‘’autumn
alpha-lindane’	0.2’	‘0.1	‘0.04	0.33’
Lindane’	0.1’	0’	0’.15	0.3’
delta-lind’ane	1.2	0.’1	0.’19	0.18’
Heptachlor’e	1.’’3	0.9’	0.2’4	0.48’
Aldrine’’	0.2’	0.’6	0.24’	0.43’

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Epoxyhep'tachlor	1'	0.1"	0'	0.39'
D.D.E'	0.2'	0.4	0.02"	0.27'
Dieldri'n	0.3"	0.1'	0'	0.93'
D.D.D'	0.1"	0'	0.'1	0.24'
endrin aldhyde'	0.'2	0."1	0.0'2	0.25'
endrin ketone'	0.8	0.1'	0.02'	0.08'
metoxy chlor'	1'	0.3'	0'	0.22'
Endrin'	3."8	0.6'	0'	0.05'
Endosulfan'	0'	0'	0'	0.56'
Totel'	10.4'	3.3'	.1'01	4.71'
Mean'	0.7'	0.2'	0.1'3	0.336'

0=Not detected

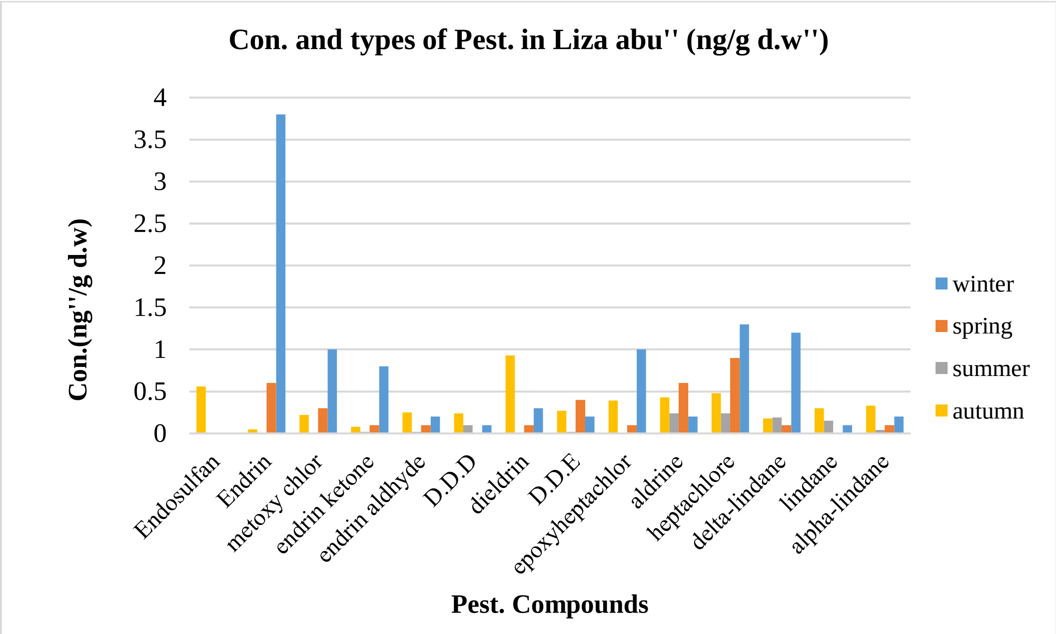

Figure (5a) Liza abu's pesticide concentration and types (ng/g d.w.) during the study period.

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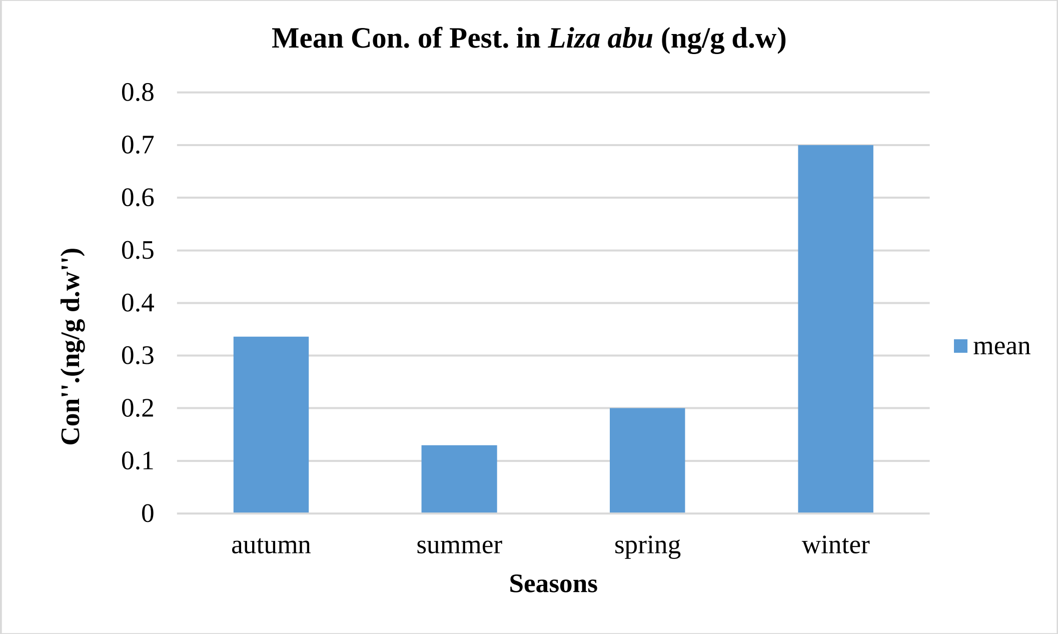

Figure (5b) :Liza abu's mean pesticide concentrations (ng/g d.w.)

As seen in Figure (6), the results indicated that Liza abu had the lowest mean of pesticide (1.36ng/g d.w.) and Oreochromis niloticu had the greatest mean (3.05ng/g d.w.).

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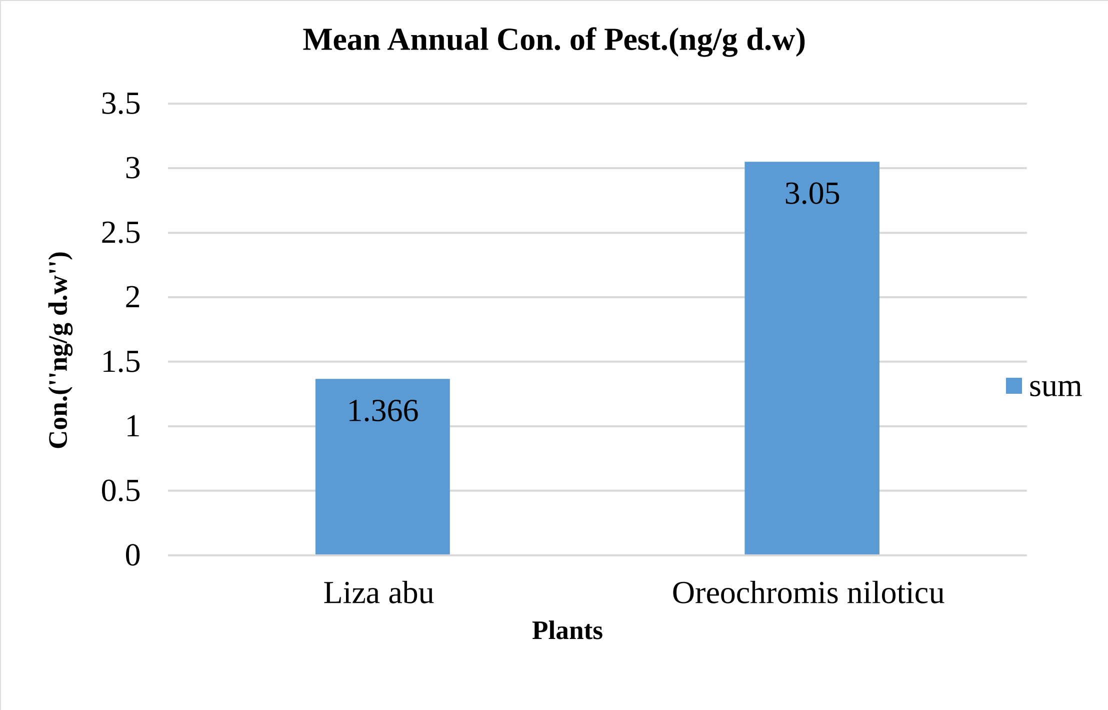

Figure (6): The average annual concentrations of pesticide chemicals (ng/g d.w.) for the fish studied

Fish are major bioindicators of environmental contamination, according to the statistical analysis's findings, which also revealed no significant differences ($p > 0.05$) between the seasons and substantial differences ($p < 0.05$) between the two species. It is regarded as one of the aquatic resources and plays a significant role in the population's nutrition. These fish species are among the freshwater fish that locals eat. But Concern over the potential health effects of eating fish tainted with chemicals is growing. Since pesticides from the environment can biomagnify in a variety of creatures, pesticides in the tissues of edible fish pose a serious risk to human health if the fish are exposed to the chemicals through food and water. Higher pesticide concentrations are found in fish samples because the organisms' feeding state, age, and mobility determine the quantities and occurrence of residues [11].

Because Oreochromis niloticu fish prey on various aquatic invertebrates and other smaller fish, their concentrations were larger than those of Liza abu. "Because it consumes pieces of aquatic plants or phytoplankton from diatoms and green algae," the Liza abu fish is classified as a herbivorous fish."It may be more common than most

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people think for fish and other aquatic species to be exposed to pesticides. The majority of fish kills caused by pesticides are not reported, and in those that are, the number of fish killed is frequently underreported. Accurate counts are hampered by unfavorable aquatic environment factors, such as water depth and transparency, as well as the small size and camouflage coloring of many fish, particularly youngsters. Carcasses are swiftly removed from a kill site by scavengers. Fish that are anxious and dying may hide in thick vegetation or completely abandon the region. Get in touch with the Fish and Wildlife Service or your local game warden right away if you know of any dead or sick fish or aquatic life that you believe may have been contaminated by pesticides. Details regarding possible pesticides that could harm fish and other aquatic life [12]. [13]They found Insecticides cause reproductive problems and a slowdown in growth. Other biological markers include spinal abnormalities, histological alterations in the gills, liver, hematological tissue (including the spleen, head of the kidney, and renal tubules), endocrine tissues, and brain, neurological, behavioral, and genetic defects. of pesticide exposure. Fish are very vulnerable to water contamination from the environment. [14] study the Fish inhabiting rice fields: Bioaccumulation, oxidative stress and neurotoxic effects after pesticides application, Overall, the findings demonstrated that the antioxidant systems were unable to stop oxidative damage in M. nigripinnis's liver and gills following the administration of the pesticide mixture. A. lacustris, on the other hand, responded differently, exhibiting a suppression of antioxidant defenses without oxidative damage to tissue lipids. Additionally, the brain and muscle tissues of A. lacustris and the brain of M. nigripinnis showed a considerable decrease in acetylcholinesterase activity following spraying. Our findings demonstrate that native fish populations living in rice fields are at risk for health problems due to current-use herbicides such as glyphosate, BF, AZ, and CYP.

Conclusion

1-Among the 14 types of chlorine pesticide residues found in the study region with varying concentrations in the samples examined are alpha-lindane, lindane, delta-lindane, heptachlor, aldrin, epoxy heptachlor, D.D.E, dieldrin, D.D.D, endrin aldehyde, endrin ketone, methoxy chlor, Endrin, and endosulfan.

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2- Because of their different feeding patterns, Oreochromis niloticus tends to acquire more pesticide than Liza abu

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