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A comparative study on the effect of pesticides used in agriculture on catfish in some Nile Delta governorates

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ABSTRACT

The increased usage of chemicals and other harmful compounds has contaminated air, water, soil, and food, endangering life. This threat has grown with fast industrialization and exponential population expansion. Because agricultural runoffs contain pesticide and fertilizer residues, they have a negative impact on the quality of surface and ground water. The goal of the current article is to gather data on pesticide pollution in aquatic environments and its potential impacts on fish and human health. Because pesticide pollution causes acute toxicity in fish which has a harmful effect on human health, with results in abrupt and intense mortality, it is a serious concern. Due to some outlawed pesticides are still used in agricultural settings and have detrimental effects on organisms, Samples of catfish (***Clarias sp***) and water were collected from four governorates in the Delta region (El-Behera, El-Gharbia, El-Qalyubia, and El-Dakahlia). The results demonstrated that the catfish from the four governorates had endosulfan, heptachlor, aldrin, pp-DDT, and diazinon detected. However, dicofol was detected in EI-Behera & El-Gharbia. Chlorpyrifos was not detected in El-Gharbia. The catfish gathered from four governorates did not have an estimated daily intake (EDI) greater than the PDI. Ultimately, the findings indicated that the Target Hazard Quotient (THQ) was validated in four governorates where the mean score was less than one. When the THQ is less than 1, the exposed populace is not obviously in danger to their health. The hazard index (HI) for catfish taken from the Nile River in three governorates is less than one. In El- Behera governorate, a higher than 1 hazard index (HI) suggests a possible risk to human health because consuming contaminated fish may result in long-term pesticide accumulation in the body. Finally, coordinated efforts, combined with sensible pesticide application and integrated pest management are thought to be the primary methods of reducing pesticide pollution in aquatic systems.

Key words: Pesticides, Catfish, Nile Delta governorates.

1. Introduction

At Cairo, the River Nile splits into the Damietta and Rasheed branches, the Nile delta being formed by both of them. Due to population expansion, increasing urbanization, industrialization, and agriculture, there is a constant demand for water resources on both branches for irrigation, home water supply, and industrial applications (Jiries *et al*., 2002). At the same time, runoff from agriculture and home and industrial wastewater sources is degrading the water quality of the area (Baraka *et al*., 2013). As a result, pollution is a serious problem that affects both human health and the environment (Hogsette *et al*., 2006: Shaaban *et al*., 2021).

Pollution from the Nile branches must be monitored in order to provide quantitative information on the most prevalent organic micropollutants, to pinpoint their sources, to comprehend their fate, to comply with regulations, to understand the implications for human ecological health and to better target advanced treatment technologies. The use of innovative remediation technologies and the creation of management plans are hampered by the absence of baseline information regarding pollution and its impacts in the Nile (Edris *et al*., 2017; Hassan *et al*., 2019).

In addition to endangering human health by contaminating the water and food supplies, pollutants in waters of the Nile also pose a hazard to aquatic life in general. Due to their skin, gills, and food, fish are among the most impacted species since they are constantly coming into contact with contaminants in the aquatic environment. Since pollutants can enter aquatic species' tissues and eventually bioaccumulate in fish over time, the biggest issue affecting the quality of fish production in their native habitat is really water pollution (Botaro *et al.*, 2011).

Egypt is a major consumer of catfish since it is widely available and reasonabl y priced.Typically, catfish live in dirty, murky waterways.It is more exposed to several types of environmental pollu tion than other fish species.Because catfish flesh has a relatively high fat content, it is more likel y to contain fatsoluble environmental pollutants such as pesticides Furthermore, the recent use of pesticides in agriculture raises the possibility tha t catfish meat is contaminated(Holtan, 1998; Abbassy et al., 2021).

Pesticides are many kinds, including carbamates, ureas, pyrethroids, organochlorine, and organophosphorus, are used in Egypt. These pesticides can be divided into four main categories: herbicides, bactericides, fungicides, and insecticides. Organophosphorus insecticides are becoming more important in the fight against pests, and they are replacing organochlorine pesticides. More than 80% of the insecticides used are organophosphorus products. The bulk of applications are used in agriculture. Less than 4% of pesticides used in Egypt are herbicides. In some Egyptian governorates, the residue levels of pesticides were found in fish, sediment, and water samples taken from lakes, irrigation canals, drains, and the River Nile. (Bonner, *et al*., 2017; Polanco Rodríguez *et al*., 2017).

Chronic exposure to pollutants and Pesticides exceeding safe thresholds in humans can have deleterious effects, including non-carcinogenic risks including hepato-renal dysfunction and neurologic changes (Hassan *et al*., 2020; Shaaban *et al*., 2021; Saad *et al.*, 2022).It is normal practice to evaluate the possible non-carcinogenic health risks associated with long-term exposure to a range of pollutants via fish intake using the target hazard quotient (THQ), set by the US EPA (EPA, 1996)

Aim of work

In this context, the study's goals were to track the presence of pesticides in catfish samples along Egypt's two Nile branches in 4 governorates in the Delta (El-Behera, El-Gharbia, El-Qalyubia, and El-Dakahlia) and evaluate the possible health risks to the local populace from consuming tainted catfish for their lives.

Ethical approval

This study received ethical approval from the Faculty of Science, Damanhur University, Egypt (3-5-2024)

2. Materials and Methods

Sampling

The governorates in the heart of the Delta that have agricultural operations are El-Behera, El-Gharbia, El-Qalyubia, and El-Dakahlia. These are the locations of the sampling sites. The study included 40 catfish in total, which were taken from the four Egyptian cities. For the purpose to identify and quantify the amount of pesticides present, we examined the fish. An individual fish typically weighs 700- 1000 g.

After being quickly transported to the lab into an ice chest, fish samples were chilled for 2 days at -4 °C in order to prepare them for extraction and analysis. The samples were collected and immediately placed in spotless glass containers that had big mouths & covered. Fish muscle was used to measure the average concentrations of pesticide residues, which were recorded as concentrations ± SD

Sample extraction

Just 3 ml of H_2O &10 g of fish muscle samples were put into a centrifuge tube for a minute, the mixture vortexed. 20 milliliters of acetonitrile were added, and the mixture was vortexed for 15 minutes. Centrifuging for five minutes at 4000 rpm & vortexing for an extra 2 minutes were done followed adding 5 g of sodium chloride to the liquid. After 10 mL of the extraction solution was added to a 100 mL flask, it was frozen for 20 minutes at −24 °C. Cold extracts at -24 °C were quickly filtered using filter paper to remove the frozen lipids. The filtered extract was concentrated to 1 milliliter by rotating evaporation (Chen *et al*., 2009).

GC analysis

One microliter of extract was injected using gas chromatographic system (Agilent Technologies, USA). For analysis, a J & W Scientific DB-1701 capillary column was employed. Throughout the experiment, the temperatures of the oven, detector, and injection were varied from 150 to 270 ºC & 260 ºC, respectively. One milliliter of helium / minute used as carrier gas. Pesticide residues were identified by comparing peak relative retention durations of the samples with standard values. Area of the sample's equivalent peak & the reference peak measured and compared

Water samples analysis

The water samples were run through What-man 0.45 µm filter mesh filters to remove suspended pollutants. The collected water samples were stored in 500 mL containers. Glass jars with black interiors held the samples to GC analysis. Samples of water were analyzed. Using **Edgell & Wesselman's (1989)** aqueous matrix extraction process, pesticides were removed from the water samples, enabling the study of non-volatile & semi-volatile organic compounds

Assessment of human risk

The estimate daily (EDI) of pesticides using fish consumption examined by the equations:

$$EDI = \frac{(CM \times IR)}{BW}$$

BW indicates body weight = 70 kg in adults, IR indicates daily intake for fish = 62.25 g/person/day, & Cm indicates concentration of pesticide in samples (µg/g-ww). (EPA, 1996)

THQ values indicate the potential health risk associated with the pesticides.

Evaluation of human risk Using that equation to determine the target hazard quotient (THQ), possible non-carcinogenic health risks related to eating catfish contaminated with pollutants were assessed.

$$THQ = \left(\frac{(EF * ED * IR * C)}{(RFD * BW * AT)}\right) * 10^{-3}$$

There may be no risk when THQ <1, but there is when THQ ≥ 1.

EF defines exposure frequency =365 days/year, ED represents exposure duration =70 years , IR defines fish ingestion rate =38.14 g/person/day ,C represents contaminant concentration in catfish (mg/kg), RfD known as oral reference dose for endosulfan, heptochlor, dicofol, DDT, aldrin, and chlorpyrifos is 0.006, 0.0005, 0.0004, 0.0005, 0.001 and 0.0025., BW defines body weight average = 70 kg/person, AT known as average time for non-carcinogens =365 days/ year × ED (Taghizadeh *et al* ., 2.019)

The hazard index (HI) used to evaluate the potential risk that organo-chlorine &organo-phosphorus substances provide to human health. According to the equation, the HI is the total THQ for different exposures to organo-chlorine and organo-phosphorus chemicals.

HI = Σ TTHQs = THQ endosulfan + THQ heptachlor + THQ dicofol + THQ DDT+ THQ aldrin + THQ chlorpyrifos

ΣTTHQs represents the target hazard quotients for all organo-chlorine + organo-phosphorus chemicals; a potential harm to human health is expected when the hazard index rises above 1. (Huang *et al.*, 2008)

Statistical analysis:

All the present data were expressed as mean values accompanied by the stander division and the statistical analysis (The mean differences between the groups) was performed by using one -way analysis of variance (ANOVA).the statistical tests were performed by using the statistical package for the social science (spss) program(version 25.0). Values were considered statistically significant when p- value was less than 0.05. Means with different superscript letters (a, b, and c) are significantly different - Post Hoc Test (Tukey HSD) / P ≤ (0.05). n=3

4. Results

Fish species weight and length were measured in this study; mean ± SD

In this study, the fish samples were collected from four governorates in the Delta region (El-Behera, El-Gharbia, El-Qalyubia, and El-Dakahlia). (Table 1), the fish samples mean weight in El-Behera was 923.73g ±75.2, in El-Gharbia was 865.53g ±83.82, in El-Qalyubia was 925.83 g±101.7 and in El-Dakahlia was 756.53 g ±78.04. The fish samples mean length in El-Behera was 48.36 cm ±5.24, in El-Gharbia was 46.56 cm ± 4.38, in El-Qalyubia was 52.03 cm ± 6.43 and in El-Dakahlia was 41.23 cm ± 2.96. The fish samples show insignificant difference between the four governorates in weight and length.

Table 1. Fish weight and length were measured in this study; mean ±SD

Catfish		Mean ± SD	F value
weight(g)	El-Behera	923.73 ± 75.20	2.416
	El-Gharbia	865.53 ± 83.82	
	El-Qalyubia	925.83 ± 101.74	
	El-Dakahlia	756.53 ± 78.04	
Length (cm)	El-Behera	48.36 ± 5.24	2.506
	El-Gharbia	46.56 ± 4.38	
	El-Qalyubia	52.03 ± 6.43	
	El-Dakahlia	41.23 ± 2.96	

The Data were expressed as Mean ± SD. There is insignificantly different between means. Post Hoc Test (Tukey HSD) / P ≤ (0.05). n=3

The chemicals recognized as organo-phosphorus and organo-chlorous in water samples

Table 2 presents the findings from the water samples collected from the 4 governorates for this study, the endosulfan not detected in 2 governorates El-Gharbia and El- Qalyubia but in El-Behera was 35.50 ±5.56 and in El-Dakahlia was 16.26±2.6 ppb.

The heptachlor in El-Behera was18.6 ± 2.02, in El-Gharbia was 15.12 ± 1.73, in El- Qalyubia was 4.00 ± 1.0 and in El-Dakahlia was 2.30 ± 0.52 ppb.

Dicofol in El-Behera was12.8 ± 1.60, in El-Gharbia was 5.21 ± 0.70 ppb and in both El-Qalyubia& El-Dakahlia dicofol not detected.

p,p′-DDT not detected in 2 governorates El-Behera & El-Dakahlia , in El- Qalyubia the mean value was 13.83 ±2.57 and in El- Qalyubia was 8.9± 2.00 ppb.

Aldrin mean value in El-Gharbia was 20.16 ± 3.7 ppb but in the 3 governorates El-Behera, El-Qalyubia and El-Dakahlia not detected.

Chloropyrifos level in El-Behera was 2.25 ± 0.44, in El- Qalyubia was 11.46 ±1.4 and in El-Dakahlia was 7.10 ± 2.49 ppb in El-Gharbia was not detected.

Diazinon not detected in 3 governorates El-Gharbia, El- Qalyubia and El-Dakahlia but in El-Behera the mean value was 21.80 ± 3.4 ppb.

As shown in Table 2, GC analysis results revealed significant differences in organo-chlorine, and organo-phosphorus in water samples among various governorates. Endosulfan(ppb) in El-Behera show a highly significant increase (p≤0.05) in compared to Endosulfan(ppb) in El-Gharbia, El-Dakahlia, and El- Qalyubia. also Endosulfan(ppb) in El-Dakahlia show a significant increase (p≤0.05) in compared to El-Gharbia, El-Behera, and El-Qalyubia governorates.

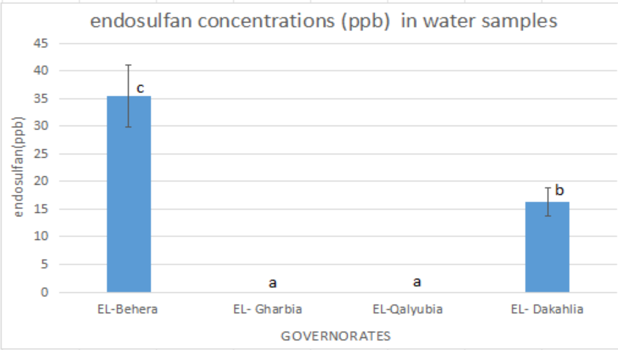
However, no significant changes were observed in Heptachlor (ppb) in El-Behera compared to El-Gharbia, or in El-Dakahlia, compared to El- Qalyubia. Heptachlor and Dicofol in El-Behera and El-Gharbia show a significant increase (p≤0.05) in compared to El-Dakahlia, and El- Qalyubia governorates.

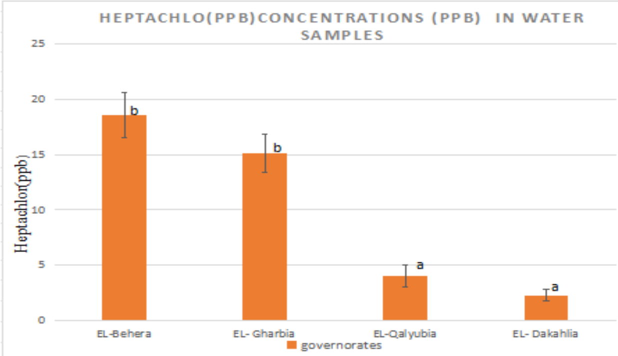
The analysis of pp-DDT also exhibited a highly significant increase ($p \leq 0.05$) in El-Gharbia, and El- Qalyubia when compared to El-Dakahlia, and El-Behera, while in contrast there were no significant difference between El-Dakahlia, and El-Behera changes observed in Aldrin levels in El-Gharbia compared to the other three governorates was significant. Regarding Chloropyrifos levels, the results demonstrated a significant decrease ($p \leq 0.05$) in El-Gharbia, and El-Behera compared to the other two governorates, whereas El-Behera group show a significant changes in Diazinon level when compared to the El-Gharbia, El-Dakahlia, and El- Qalyubia governorates.

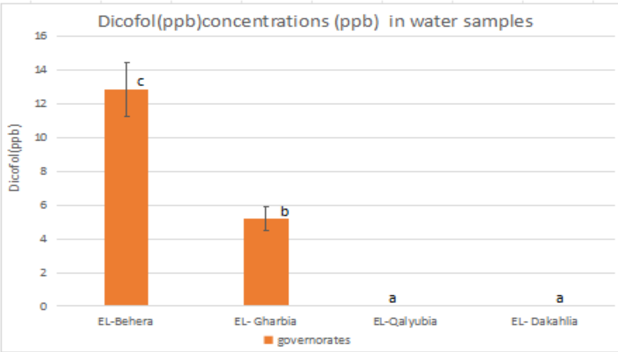
Table 2. Pesticide concentrations (ppb) of organo-chlorine, organo-phosphorus in water samples from four governorates (n=3).

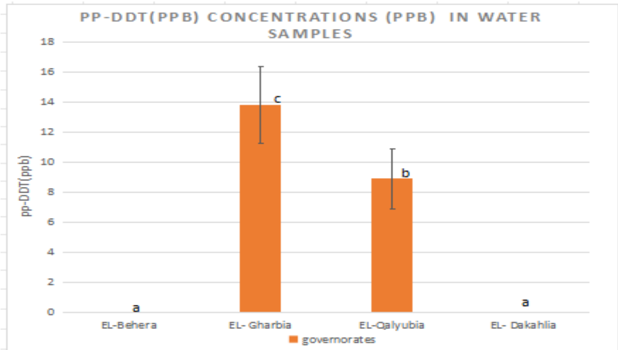
Pesticide	Governorate	Concentration (ppb)	F-Value
Endosulfan	El-Behera	35.50 ± 5.56^{c}	90.006
	El-Gharbia	0^{a}	
	El-Qalyubia	0^{a}	
	El-Dakahlia	16.26 ± 2.6^{b}	
Heptachlor	El-Behera	18.6 ± 2.02^{b}	72.365
	El-Gharbia	15.12 ± 1.73^{b}	
	El-Qalyubia	4.00 ± 1.00^{a}	
	El-Dakahlia	2.30 ± 0.52^{a}	
Dicofol	El-Behera	12.8 ± 1.60^{c}	142.613
	El-Gharbia	5.21 ± 0.70^{b}	
	El-Qalyubia	0^{a}	
	El-Dakahlia	0^{a}	
pp-DDT	El-Behera	0^{a}	53.130
	El-Gharbia	13.83 ± 2.57^{c}	
	El-Qalyubia	8.90 ± 2.00^{b}	
	El-Dakahlia	0^{a}	
Aldrin	El-Behera	0^{a}	88.776
	El-Gharbia	20.16 ± 3.7^{b}	
	El-Qalyubia	0^{a}	
	El-Dakahlia	0^{a}	
Chloropyrifos	El-Behera	2.25 ± 0.44^{a}	37.436
	El-Gharbia	0^{a}	
	El-Qalyubia	11.46 ± 1.4^{c}	
	El-Dakahlia	7.10 ± 2.49^{b}	
Diazinon	El-Behera	21.80 ± 3.4^{b}	119.108
	El-Gharbia	0^{a}	
	El-Qalyubia	0^{a}	
	El-Dakahlia	0^{a}	

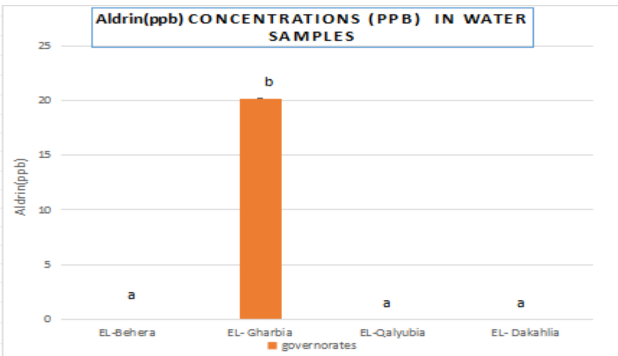
The Data were expressed as Mean ±SD.- Means with different superscript letters (a, b, and c) are significantly different -Post Hoc Test (Tukey HSD) / P ≤ (0.05). n=3

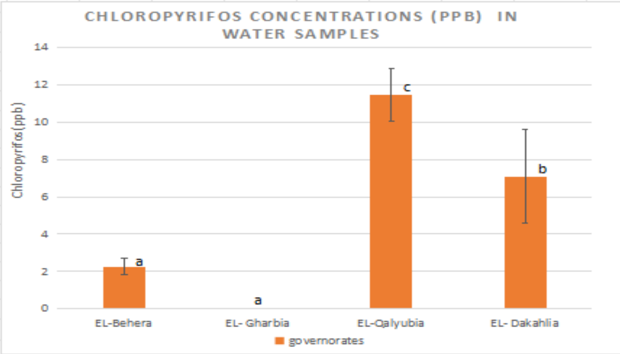












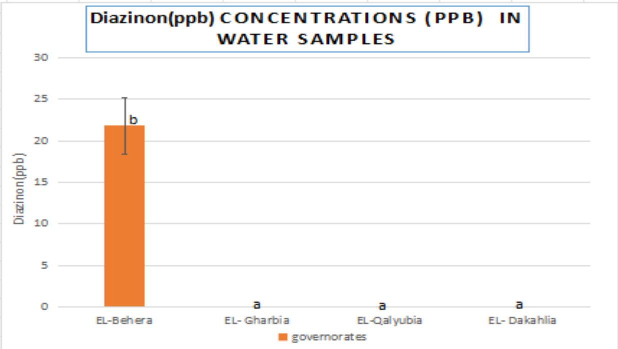


Figure 1 Column chart of Pesticide concentrations (ppb) of organo-chlorine, organo-phosphorus in water samples from four governorates (n=3).

The Pesticide in muscles catfish samples

Table 3 shows that the analyzed muscle samples of catfish contained pesticide residues. Seven detected Pesticide include endosulfan, heptachlor, dicofol, p,p′-DDT , aldrin, chlorpyrifos and diazinon were detected. In the El-Behera governorate, The mean values of these 7 pesticides were 48.16 ± 2.11, 12.86 ± 1.42, 10.43 ± 0.90, 19.73± 1.90, 14.30± 2.16, 24.43 ± 1.1 and 14.80 ± 3.45 ppb, respectively. In El-Gharbia governorate mean values of these 7 pesticides were 32.36± 3.06 ,12.16 ± 1.48, 6.26 ±0.80, 12.16 ±3.03, 16.93 ±1.81, ND and 14.46 ± 1.81 ppb, respectively. In El- Qalyubia governorate The mean values of these 7 pesticides were 14.93 ± 2.49,4.63 ± 0.55, ND, 5.90 ± 0.15,15.23 ±2.37, 3.80 ± 0.36 and 16.16 ± 3.59 ppb, respectively. In El-Dakahlia governorate The mean values of these 7 pesticides wer12.26 ± 1.68, 3.46 ±0.72, ND, 5.33±0.68, 12.46 ±0.81 ,3.43 ± 0.17 and 7.53 ± 0.81 ppb, respectively

GC analysis results show that Endosulfan in El-Behera has significant increase (p≤0.05) in compared to Endosulfan in El-Gharbia , El-Dakahlia, and El-Qalyubia. also Endosulfan in El-Gharbia show a significant difference (p≤0.05) in compared to El-Behera , El-Dakahlia , and El- Qalyubia governorates. However, no significant changes were observed in Heptachlor in El-Behera compared to El-Gharbia, or in El-Dakahlia, compared to El- Qalyubia Dicofol in El-Behera and El-Gharbia show a significant increase (p≤0.05) in compared to El-Dakahlia, and El-Qalyubia governorates.

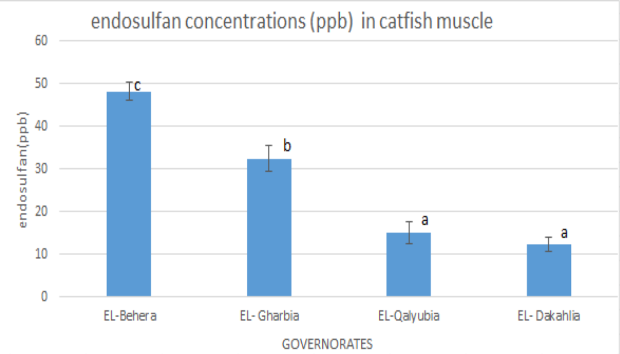
The analysis of pp-DDT also exhibited significant increase (p≤0.05) in El-Behera when compared to El-Dakahlia, El-Gharbia , and El-Qalyubia while in contrast there were no significant difference between El-Dakahlia, and El- Qalyubia. The Aldrin did not show any significant differences between various governorates. in contrast Chloropyrifos showed a significant decrease (p≤0.05) in El-Dakahlia, El-Gharbia, and and El- Qalyubia compared to El-Behera governorate, whereas the result indicated a significant decrease for Diazinon level in El-Dakahlia when compared to the El-Gharbia, El-Behera, and El- Qalyubia governorates

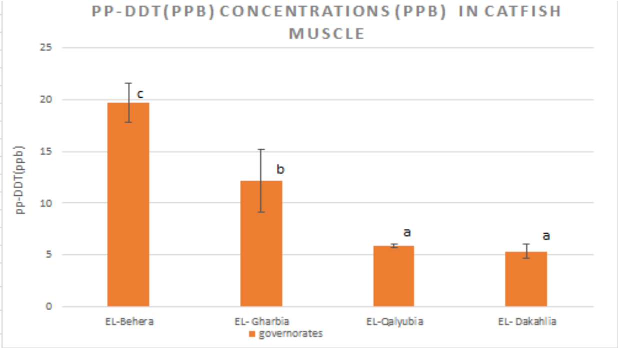
Table 3. The concentrations of pesticides (ppb) of in catfish muscle throughout four governorates

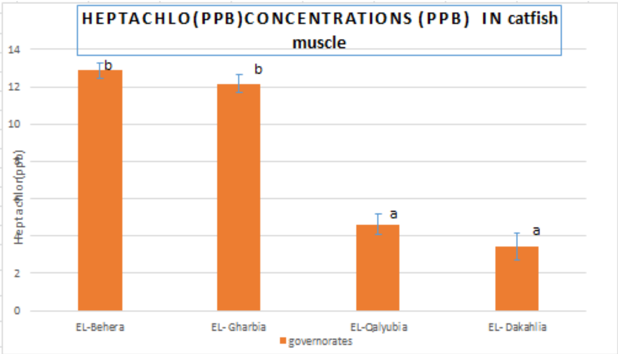
Pesticide	Governorate	Concentration (ppb)	F-value	Permitted levels			
				FAO	USFDA	CFLA	FSANZ
Endosulfan	El-Behera	48.16 ±2.11[C]	146.427	100-200	---------	---------	---------
	El-Gharbia	32.36 ±3.06[b]					
	El-Qalyubia	14.93 ± 2.49[a]					
	El-Dakahlia	12.26 ±1.68[a]					
Heptachlor	El-Behera	12.86 ±1.42[b]	30.244	200	300	5	5
	El-Gharbia	12.16 ±1.48[b]					
	El-Qalyubia	4.63 ± 0.55[a]					
	El-Dakahlia	3.46 ± 0.72[a]					
Dicofol	El-Behera	10.43 ± 0.90[c]	213.827	---------	---------	---------	---------
	El-Gharbia	6.26 ± 0.80[b]					
	El-Qalyubia	0[a]					
	El-Dakahlia	0[a]					

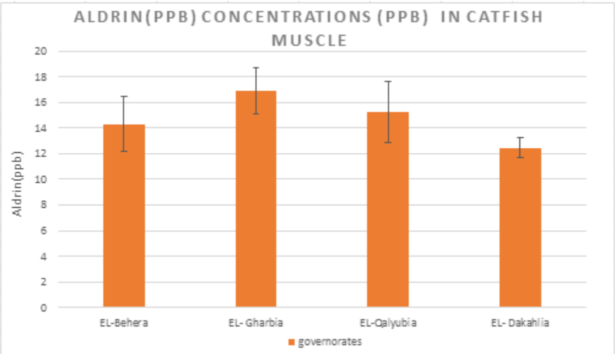
p,p-DDT	El-Behera	19.73 ±1.90^{c}	37.090	500	300	5000	1000
	El-Gharbia	12.16 ±3.03^{b}					
	El-Qalyubia	5.90 ± 0.15^{a}					
	El-Dakahlia	5.33 ±0.68^{a}					
Aldrin	El-Behera	14.30 ±2.16^{a}	2.915	200	300	100	100
	El-Gharbia	16.93 ±1.81^{a}					
	El-Qalyubia	15.23 ±2.37^{a}					
	El-Dakahlia	12.46 ±0.81^{a}					
Chloropyrifos	El-Behera	24.43 ±1.21^{c}	503.423	1000	---------	---------	---------
	El-Gharbia	0^{a}					
	El-Qalyubia	3.80 ±0.36^{b}					
	El-Dakahlia	3.43 ±0.17^{b}					
Diazinon	El-Behera	14.80 ±3.45^{b}	6.253	200	---------	500	500
	El-Gharbia	14.46 ± 1.81^{ab}					
	El-Qalyubia	16.16± 3.59^{b}					
	El-Dakahlia	7.53 ±0.81^{a}					

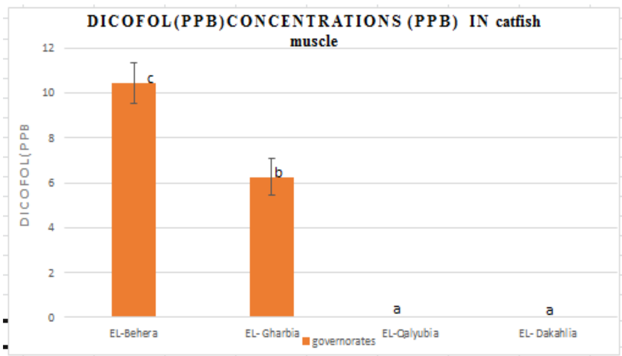
The Data were expressed as Mean ±SD. Means with different superscript letters (a, b, and c) are significantly different, Post Hoc Test (Tukey HSD) / P ≤ (0.05). n=3

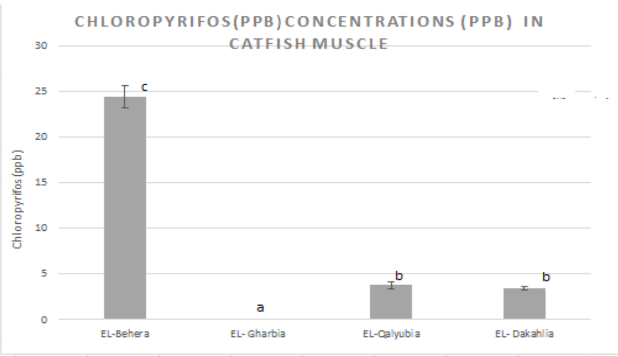












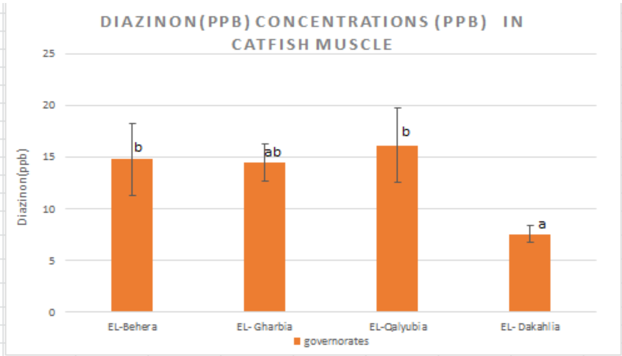


Figure 2. Column chart of Pesticide concentrations (ppb) of organo-chlorine, organo-phosphorus in muscles samples from four governorates (n=3).

Estimated daily intake of organo-chlorine and organo-phosphorus pesticides (µg/kg BW/day) in adult person:

From the data shown in Table 4, the EDI endosulfan is (0.042) in El-Behera, (0.0287) in El-Gharbia, (0.0132) in El-Qalyubia and (0.0109) in El-Dakahlia. The EDI of heptachlor (0.0114) in El-Behera, (0.0108) in El-Gharbia, (0.004) in El-Qalyubia and (0.003) El-Dakahlia. The EDI of dicofol (0.009) in El-Behera and (0.005) in El-Gharbia. The EDI of p,p′-DDT (0.017) in El-Behera, (0.011) in El-Gharbia(0.005) in El-Qalyubia and(0.004) El-Dakahlia. The EDI of aldrin (0.012) in El-Behera, (0.015) in El-Gharbia, (0.013) in El-Qalyubia and (0.011) in El-Dakahlia. The EDI of chlorpyrifos (0.021) in El-Behera, (0.003) in both El-Qalyubia and in El-Dakahlia. The EDI of diazinon (0.013) in El-Behera, (0.012) in El-Gharbia, (0.014) in El-Qalyubia and (0.006) in El-Dakahlia

Table 4. EDI of pesticides (µg/kg BW/day) in adult humans (70 kg/person) from all four governorates in catfish. Permissible daily intake, as per Codex Alimentarius, is PDI (1) (µg/kg bwt). The FDA's tolerance or critical limit for fish consumption by humans is the PDI (2).

Governorates	Endosulfan	Heptachlor	Dicofol	p,p′-DDT	Aldrin	Chlorpyrifos	Diazinon
El-Behera	0.042	0.0114	0.009	0.017	0.012	0.021	0.013
El-Gharbia	0.0287	0.0108	0.005	0.011	0.015	ND	0.012
El-Qalyubia	0.0132	0.004	ND	0.005	0.013	0.003	0.014
El-Dakahlia	0.0109	0.003	ND	0.004	0.011	0.003	0.006
Permitted levels							
PDI(1)	6	0.1		100	0.1		
PDI(2)		300			300		

Target hazard quotient (THQ):

The target hazard quotients (THQ) values—a value larger than one denotes a danger to health—indicate the possible health risk associated with pesticides. The THQ for catfish in our analysis was less than 1.00 for all detected organo-chlorine, organo-phosphorus compounds that were collected from four governorates in the Delta area (Table 5). Moreover, the hazard index (HI) for every organo-chlorine and every organo-phosphorus chemical in catfish was less than one in three governorates: El-Gharbia, El-Qalyubia, and El-Dakahlia. There are several entries in El-Behera governorate on the Hazard Index (HI) that point to a possible health risk connected to pesticide usage.

Table 5. THQ for pesticides in catfish from 4 governorates.

Governorate	Target Hazard Quotient (THQ)							HI =ΣTTHQs	Human risk
	Endosulfan	Heptachlor	Dicofol	p,p′-DDT	Aldrin	Chlorpyrifos	Diazinon		
El-Behera	0.050	0.163	0.166	0.250	0.090	0.38	0.037	1.136	yes
El-Gharbia	0.034	0.154	0.099	0.154	0.108	ND	0.036	0.585	N0
El-Qalyubia	0.016	0.059	ND	0.075	0.097	0.009	0.041	0.297	N0
El-Dakahlia	0.013	0.044	ND	0.068	0.079	0.008	0.019	0.231	N0

5. Discussion

The study's goals were to track the presence of 7 pesticides (Endosulfan, Heptachlor, Dicofol, p,p′-DDT, Aldrin, Chlorpyrifos and Diazinon) in catfish samples along Egypt's two Nile branches in 4 governorates in the Delta (El-Behera, El-Gharbia, El-Qalyubia, and El-Dakahlia)

Endosulfan is an organo-chlorine insecticide whose use is being phased out worldwide. It has become a very controversial agrochemical due to its endocrine properties, acute toxicity and potential for bioaccumulation. In April 2011, negotiations under the Stockholm Convention led to a global ban on the production and use of endosulfan due to the risks it poses to human health and the environment. More than 80 nations, including the US, the European Union, Australia, New Zealand, and many West African countries. By the time the Stockholm Convention prohibition was agreed upon, Brazil, Canada, and other countries had already declared phase-outs or outlawed it. dosulfan in India, while supplies last.China and India still utilize it widely even though there are laws prohibiting it. It is utilized in a few other nations as well. The Israeli company Makhteshim Agan produces it, along with a number of Chinese and Indian firms. The manufacturing and distribution of endosulfan in India were prohibited by the India Supreme Court on May 13, 2011, with an indefinite prohibition in place. (Weber, *et al* ., 2010; Menezes, *et al* ., 2017)

Although heptachlor was once employed as an insecticide, almost all of its registered uses have been revoked. Oral research has shown that acute (short-term) exposure to heptachlor can have effects on the gastrointestinal tract in addition to nervous system effects. Oral exposure has been shown to have effects on the liver and central nervous system in animal experiments. Humans who inhale orally over an extended period of time may experience neurological side effects such as irritation, salivation, and dizziness; oral exposure may also have effects on the blood. Studies on humans and heptachlor and cancer are not definitive. Liver tumors have been detected in animal oral studies. Heptachlor is a Group B2 probable human carcinogen according to the EPA.(Xiao, *et al* ., 2011; Manimekala, *et al* ., 2022)

Insecticide dicofol is an organo-chlorine that shares chemical similarities with DDT. One miticide that works very well against spider mites is dicofol. International law prohibits its use and manufacturing, as stated in the Stockholm Convention. DDT is one of the intermediates utilized in its manufacturing. Many environmentalists have criticized this, however dicofol is classified by the World Health Organization as a Level II, "moderately hazardous" pesticide. It is known to be toxic to aquatic life, and it can weaken the eggshells of many bird species. (Lu, *et al* ., 2019; Wang, *et al* ., 2022).

The primary application of p,p'dichlorodi-phenyltrichloroethane (p,p'-DDT) in agricultural crops has been as an insecticide. It is a crystalline chemical compound that is tasteless, colorless, and nearly odorless. It was first created as an insecticide, but its effects on the ecosystem led to its notoriety. Austrian scientist Othmar Zeidler created DDT for the first time in 1874. The Swiss chemist Paul Hermann Müller discovered the insecticidal properties of DDT in 1939. During the latter half of World War II, DDT was employed to stop the development of typhus and malaria among soldiers and civilians, two diseases carried by insects. There is mounting evidence in the contemporary literature linking exposure to DDT and its breakdown product DDE to negative health consequences such diabetes, breast cancer, low-quality semen, spontaneous miscarriage, and poor neuro development. (Cano-Sancho , *et al* ., 2017; Hernández-Mariano *et al* ., 2022).

Aldrin is an organo-chlorine insecticide that was widely used until the 1990s and was subsequently banned in most countries. Poisoning in humans caused by aldrin and dieldrin is characterized by severe motor convulsions. Other effects include malaise, coordination problems, headache, dizziness, and gastrointestinal disorders. These attacks occur with or without other symptoms of poisoning. (Zitko, 2003; Pang *et al* ., 2022).

Chlorpyrifos (CPS), also known as chlorpyrifos, is an organophosphorus pesticide used on crops, animals, buildings, and other environments to kill a variety of pests, including insects and worms. It acts on the nervous system of insects by inhibiting acetylcholinesterase. Based on the 1999 acute toxicity information, the World Health Organization classified chlorpyrifos as a substance of moderate hazard to humans (Class II). Exposures above the recommended limits have been associated with neurological effects, persistent developmental disorders, and autoimmune diseases. Exposure to the substance during pregnancy can impair the intellectual development of children. (Feng et al., 2020; Ma et al., 2020)

Diazinon is a non-systemic organophosphate insecticide formerly used to control cockroaches, silverfish, ants, and fleas in non-food residential areas. Diazinon was widely used for general garden purposes and indoor pest control in the 1970s and early 1980s. In the western United States, a bait has been used to control carrion wasps. In Australia and New Zealand, diazinon is used in flea collars for pets. Diazinon is the main ingredient in Golden Fleece brand sheep bath. The United States banned the use of diazinon in residential areas in 2004 due to risks to human health. However, it is still allowed for agricultural uses. Diazinon can be exposed through inhalation, ingestion, or skin contact. Negative health effects of exposure to diazinon include watery eyes, salivation or runny nose, loss of appetite, vomiting, severe coughing, abdominal pain, and even various muscle stiffness/paralysis. Headaches also pose health risks. Some other physiological effects include pinhead-sized pupils, increased heart rate, seizures, and even coma. Exposure to more diazinon may bring these risks. With less exposure, symptoms may be less severe, such as B. just a runny nose or watery eyes. It should be noted that while diazinon poses many different health risks, the EPA has not classified it as a carcinogen. (Larkin J. & Tjeerdema, 2000; Moussavi *et al.,* 2013).

It is widely believed that pesticide exposure mainly results in serious illnesses. Pervious researches have also demonstrated a strong correlation between pesticide use & the development of cancer in both adults and children. A number of cancers, including neuroblastoma, soft tissue sarcoma, leukemia, Burkitt lymphoma, Wilm's tumor, non-Hodgkin lymphoma, lung cancer, rectum cancer, and ovarian cancer, have been linked to persons who were closely exposed to pesticides (Nie *et al*., 2015; Bonner, *et al*., 2017; Polanco Rodríguez *et al*., 2017).

Numerous clinical and epidemiological investigations have established a connection between pesticide poisoning and asthma and bronchial hyperreactivity symptoms. Asthma flare-ups can result from pesticide exposure due to irritation, inflammation, or immunosuppression (Amaral, 2014; Hernández, *et al*., 2011). Numerous findings in science suggested that diabetes could be brought on by exposure to environmental toxins. There is evidence that a significant risk of type 2 diabetes and its complications is associated with pesticide exposure, particularly with regard to organochlorines and their metabolites (Hernández, *et al* ., 2011).

Epidemiological research examined the effect that environmental factors, such as pesticides, have in the onset of Parkinson's disease (PD). The majority of research was done to look for a link between PD and pesticide exposure. The results indicated a strong positive correlation between them. It was discovered that rotating crops may increase the chance of Parkinson's disease. Moreover, it was established that paraquat and the elevated risk of Parkinson's disease were strongly connected. A correlation between Parkinson's disease (PD) and the use of some pesticides, including herbicides like paraquat, insecticides like organophosphate and rotenone, and fungicides like cyprodinil, fenhexamid, and trimethoprim-methyl, has been reported by Freire & Koifman (2012) and Brouwer *et al*., (2017). At sufficient dosages, exposure to these chemicals may raise the risk of sperm abnormalities, fetal growth retardation, aberrant fertility, abortions, and birth malformations (Frazier, 2007). Most pesticides, especially those containing organo-phosphorus chemicals, affect the male reproductive system by suppressing spermatogenesis, lowering testis weights, compromising sperm DNA, and lowering sperm activities (such as counts, viability, density, and motility) (Mehrpour, *et al*., 2014) . Research using observational studies of employees exposed to pesticides and animal models in the lab has shown how these substances have harmful impacts on human health. However, it is crucial to comprehend the chemical process by which pesticides affect human health. Pesticides reduce fertility and result in abnormalities of the genital system in both males and females by imitating, blocking, or releasing time-releasing endocrine hormones (Kabir *et al*, 2015) They also induce several types of cancer and compromised immune function at the same time (Garry,2004)

Pesticide-induced genetic disruption can be broadly categorized into three classes: (i) pre-mutagenic damages such as DNA strand breaks (Grover, *et al.*, 2003) DNA adducts (Peluso *et al* ., 1996) (ii) gene mutations, including insertions, deletions, inversions, and translocations (Edwards & Myers , 2007) (iii) chromosomal aberrations, including aneuploidy (loss or gain of an entire chromosome), chromosomal rearrangements (Carbonell *et al*., 1993) and deletions or breaks (clastogenicity). Pesticide exposure-related genetic alterations that result in polymorphisms that modify the ligand's affinity or the expression of downstream target genes (Dong *et al*., 2008).

In this study's the water and fish samples that were examined in 4 governorates, all of the reported organo-chlorine and organo-phosphorus levels in fish and water samples are displayed in Tables 2 &3, respectively. There is not a serious risk to human health from the pesticide levels discovered throughout this examination .

In the fish muscle sample, according to FAO (1999) endosulfan had greater pesticide levels which is within allowed limits. The detected heptachlor level is within the permitted values as reported by the FAO (1999) & USFDA (2001), however it is over the authorized quantities as reported by the CFIA (2005) & FSANZ (2006). FAO (1999), USFDA (2001), CFIA (2005), and FSANZ (2006) all state that the levels of p,p′-DDT& Aldrin found have been found to be within allowed limits. Diazinon which the FAO (1999), CFIA (2005), and FSANZ (2006) all deem safe, and chlorpyrifos, which the FAO (1999) believes to be at a safe level.

Amounts of organo-chlorine and organo-phosphorus accumulate into water sources as a result of pesticide spraying on food crops, agricultural runoff, leaching from contaminated soil, and negligent pesticide container disposal (Sathish Kumar *et al*., 2024). In comparison to the dry season, several organo-chlorine and organo-phosphorus were greater in the water, gills, and muscle during the rainy season. Since farming is one of the main jobs of the people who reside near the water body, this could be the result of increased farming activity during the wet season. As mentioned before, Sadauki *et al.* (2022) reported that cropland is irrigated with the water. As a result, runoff from farms may contaminate it greatly, with an increase in the event of a rainy and farming season.

Table 4& 5 presents the findings of the risk analysis of organo-chlorine and organo-phosphorus. Risk Assessment for Human Health. Based on the anticipated daily intakes of identified pesticides from fish samples, the hazards to human health were evaluated. The observed pesticide residual concentrations were compared. The Health Risk Index (HI) & estimated daily intake (EDI) were used to calculate the exposure dose. Both the organo-chlorine and organo-phosphorus residue concentrations were found in catfish harvested from the Nile River had an EDI that was not higher than the PDI. Furthermore, data from the FDA (2011) and CAC (2009) indicate that the PDI (µg/kg bwt) of catfish collected from four governorates in the Delta region is greater than the EDI.

The EDI and ADI values were used to calculate the HI values. As is well known, there is risk associated with consuming fish when the index value is greater than 1, and there is no risk when the value is less than 1. Fish samples from the four governorates were analyzed for the current study, and the results showed that the HI values were less than 1 except in EL- Behera governorate. Based on the available data, it is predicted that there is very little exposure to both organo-chlorine and organo-phosphorus, and that long-term exposure will not pose a significant risk to human health. The results are in line with those of Barakat *et al*. (2017), Shalaby *et al*. (2018), and Abbassy *et al.* (2021), who found no signs of pesticide toxicity in fish obtained from the Nile in Cairo, lake Qarun, and

Edko Lake, respectively. Long-term pesticide accumulation in human body tissues brought on by consuming tainted fish frequently results in health consequences.

Conclusion

The results indicated the presence of endosulfan, heptachlor, dicofol, p,p′-DDT, aldrin, chlorpyrifos, and diazinon in four governorates in the Egyptian Delta region: El-Behera, El-Gharbia , El-Qalyubia , and . El-Dakahlia. It is notable that large amounts of compounds called organo-chlorine and organo-phosphorus have been identified in the Nile. The predicted daily intakes for all identified organo-chlorine and organo-phosphorus compounds were less than the acceptable daily intake allowed for catfish. Furthermore, the results confirmed that, with the exception of El-Behera, there is no risk index for consuming catfish. However, it is recommended that future studies validate the results by considering the inclusion of additional sample locations across the Delta region.

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