



EFFECT OF HEAT TREATMENT ON THE NUTRITIVE VALUE AND RESIDUES OF SOME SYNTHETIC PESTICIDES IN FRESH BOLTİ FISH

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ABSTRACT

Fresh Bolti fish (*Tilapia nilotica*) collected randomly from 9 different markets in Ismailia Governorate for evaluation the effect of grilled fish by the method used in grillrooms and houses on the concentration of pesticide residues found and the nutritive value. Results revealed that decrease in the estimated parameters i.e. moisture, crude protein, fat and ash by grilling, this decrease were 6.07, 2.63, 4.07 and 1.56%, respectively. On the contrary, carbohydrates behaved another behavior that there was an obvious increase ranged from 1.98% to 2.92%.

Fresh and grilled fish were analyzed to detect 12 organochlorine (OC) and 7 synthetic pyrethroid (SP) pesticides with a mean level on a lipid basis. Gas Liquid Chromatography equipped with Electron Capture Detector GC-ECD was used to detect the contamination in the samples.

The results showed that p,p'-DDE isomer was dominated over the other isomers in all analyzed fish samples, followed by α -isomer of hexachlorocyclohexane. The concentrations of OC residues were higher than SP pesticides in all fish muscles. Also, the fresh fish muscle recorded higher concentrations of the evaluated pesticides than the grilled one.

INTRODUCTION

Ismailia, a medium-size Egyptian city, has a population of 270,000 and an annual growth rate of

3.8%. it is considered the East gate for Egypt to Asia continental and Arab countries (Zahran 2010). Fish has been recognized as a high quality protein and fat that are completely digested and assimilated in body than that of any other protein and fat. Fish oils are a rich natural sources of long ω -3 series. Beneficial health effects of ω -3 are well demonstrated and include the prevention of a number of disease, such as coronary heart diseases, inflammation, hypotriglyceridemic effect, allergies, hypertension, arthritis, autoimmune disorders, and cancer (Sahena et al 2010). Fish are constantly exposed to chemicals in polluted and contaminated waters as a good indicator of contaminants in aquatic systems (Tuzen and Soyak 2007). Fish exposed to pesticides in four primary ways (1) dermally, direct absorption through the skin by swimming in pesticide-contaminated waters, (2) breathing, by direct uptake of pesticides through the gills during respiration, (3) orally, by drinking pesticide-contaminated water and (4) feeding on dead insects which poisoned by insecticides or contaminated prey (Louis et al 2009). Governments in developing countries do their best to cover malnutrition in animal protein by increasing fish production from rivers and aquaculture (farmed). Twenty percent from protein requirements in Egypt come from sea. The production of fish in Egypt as recorded by the annual report of organization for aquarium development Nasr City, Cairo, for the Nile, Lake and farm fish, Bolti fish represents about 38.20% of total fish products in Egypt (Ammar 2004). The nutritive value of fish can be affected by grilling as one of the most easy home-made consumed cooking method. OC and SP are non-systemic with high solubility in fats

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present in fish muscles. In Egypt, OC pesticides were used from the 1950s until 1981. This class of pesticides is characterized by persistence in the environment and the tendency to accumulate in aquatic organisms. Residues and metabolites of many OC are very stable with long half lives in the environment (Abou-Arab, 1999 & UNEP 2002). SP pesticides are a class of lipophilic insecticide very easily degraded in the natural environment, sensitive to sunlight and relatively low toxicity as compared with OC, we have to consider the less cost of OC and SP than any other pesticides (Demoute 2006 & Miyamoto *et al* 1981). Although Egypt is the largest pesticide market in Arabian countries and the fourth largest importer of pesticides among developing countries, there are no regular monitoring programs for identification and determination of pesticides in the environment (Abou-Arab, 1999; El Nemr and Abd-Allah 2004 & Yamashita *et al* 2000). The pesticides applied on land eventually find their way to the aquatic environment, thus contamination occurred and subsequently get accumulated in Fish (Kaur *et al* 2008) in which we are interested in.

The main objectives of the present study was to evaluate:

- 1- The gross chemical composition in fish (fresh and grilled bolti fish) including moisture, crude protein, fat, ash contents and carbohydrates.
- 2-The daily requirements for the illustrated estimates for children and adults.
- 3- Determination of the presence of OC and SP pesticide residues in fresh fish muscles.
- 4- Studying the effect of grilling on residues determined.

MATERIALS AND METHODS

Fish Sampling

Fish samples were collected from 9 different local markets at Ismailia governorate and then individually placed into numbered clean polyethylene bags.

The mean weight and length of fish were 301.56 ± 45.64 g and 22.24 ± 2.11 cm respectively.

Technological Method

Fish samples are subjected to the grilling process which was carried out with an electrically operated grill at 180°C for 30 min.

1- Chemical composition analysis of fish contents

Fish flesh of each fresh and grilled fish were minced using meat mincer and were chemically analyzed for moisture, crude protein, ash and ether extract content per 100gram basis on dry weight according to the AOAC (2000). Carbohydrates were determined by difference $100 - (\text{moisture} + \text{crud protein} + \text{ether extract} + \text{ash})$. Total solids were calculated by the following equation:

$$T.S = \frac{\text{Weight of fresh or grilled fish flesh} - \text{its moisture content}}{\text{Weight of fresh or grilled fish flesh}} \times 100$$

2- Analysis of pesticide residue in fish samples

2-1 Standard Pesticides Used

All samples were analyzed for 12 organochlorine and 7 pyrethroid pesticides. Pesticides standard solution prepared in n-hexane : α -HCH, β -HCH, γ -HCH, Heptachlor, Aldrin, Heptachlor-epoxide, Dieldrin, Endrin, p,p'-DDE, o,p'-DDT, p,p'-DDD and p,p'-DDT all at 1 ng/ μ l, Endrin, at 2 ng/ μ l, Meothrin, Tetramethrin, Cyhalothrin, Cypermethrin, Fenvelerate, Deltamethrin all at 5ng/ μ l.

2-2 Extraction and Clean up

Extraction and clean up in fish muscles to determine pesticide residues were carried out using the method applied by UNEP/IOC/IAEA, (1989, 1991); IOC (1993), Khaled *et al* (2004), Nasr *et al* (2009) and Bordet *et al* (2002).

All solvents were of pesticide residue analysis grade and the purity of all reagents was carefully checked.

2-3 Determination

Analysis of OC and SP pesticides in fish muscle fat were carried out with an Agilent Gas Chromatograph, model 7890 equipped with Micro-electron capture detector (GC-ECD) fitted with HP-608 capillary column (30 m x 0.53mm id x 0.5 μ m film thickness). The column temperature was programmed as initial temperature 160°C for 2min then increased at the rate of $5^{\circ}\text{C}/\text{min}$, till 260°C then hold 2 min. The detector and injector temperatures were maintained at 320°C and 260°C , respectively, with nitrogen carrier gas flow rate of 3 ml /min.

2-4 Recovery Tests

Recovery analyses were carried out on samples fortified using 0.5, 1 and 1.5 of the permitted limit each. The mean recovery of all pesticides used were tabulated in **Table (1)**.

Table 1. Average recovery percentage, standard deviation, retention times and method detection limits

Pesticides	% Recovery± SD	Retention times (Rt) (min)	LOD (ng g ⁻¹)
α-HCH	86.52±0.73	5.41	0.03
β-HCH	82.12±0.82	7.04	0.04
γ-HCH	81.01±1.12	8.08	0.05
Heptachlor	85.52±0.65	9.28	0.06
Aldrin	83.87±0.59	10.84	0.06
Heptachlor epoxide	81.94±1.12	13.04	0.03
Dieldrin	80.23±1.84	16.15	0.03
P,P'-DDE	82.01±1.35	17.18	0.06
Endrin	91.86±0.76	18.35	0.03
O,P'-DDT	87.34±0.33	20.24	0.03
P,P'-DDD	90.27±1.06	21.21	0.02
P,P'-DDT	93.79±1.19	25.75	0.01
Meothrin	94.26±0.34	26.17	0.03
Tetramethrin	95.22±0.83	29.59	0.02
Cyhalothrin	93.48±0.37	30.21	0.02
Permethrin	94.05±0.67	30.72	0.03
Cypermethrin	92.98±0.52	34.76	0.02
Fenvelerate	93.82±0.58	38.36	0.02
Deltamethrin	92.67±0.74	40.41	0.02

RESULTS AND DISCUSSION

1-The gross chemical composition

Gross chemical composition as percentage of both fresh and grilled Bolti fish are demonstrated in **Table (2)**. It could be observed from its analytical data that the sequence of the average values of moisture, ether extract, crude protein and ash contents are graded in reduction at considerable levels ranged from 76.88 to 70.81%, 8.33 to 4.26%, 80.49 to 77.86%, 7.28 to 5.72 and 1.98 to 2.92% respectively for the illustrated estimates. Consider-

ing the average value of total solids led to detect that the heat used in grilling has increased the total solids values from 23.13% in fresh samples to 29.07% in grilled samples. These results were in agreement with those of **Galhom, (2002)** who found that moisture content of some Egyptian water fish ranged from 70.00 to 79.00% and the Nile fishes had crude protein and ash contents at levels ranged from 15.20 to 21.50% and 1.38 to 1.62% as wet weight respectively.

Darweish and Shams El-Din, (1993), also stated that the ash content of Bolti fish were 4.73 and 1.05% basis as dry and wet weight respectively.

Table (3) presents data of the contribution of gross chemical composition of the grilled Bolti fish to the daily requirements as average values of protein, ash, fat and energy for both children from 7-10 years and adults. These data show that these estimates have contributed to the daily requirements for children at levels of 80.79, 92.78, 6.20 and 0.73% respectively basis on wet weight. The same estimates achieved 35.91, 84.35, 8.27 and 0.54% of these contribution for adult males and 45.24, 87.90, 8.27 and 0.728% respectively as wet weight for adult females. The same table illustrated that the contribution of grilled fish to the daily requirements of energy for the adult males and females are negligible. The nutritive value was nearly in agreement with the work of **Amir (1972)**.

II- Detection of OC and SP pesticides in fish muscle

The concentrations of OC and SP pesticides in the fresh and grilled bolti fish collected from 9 markets in Ismailia governorate are presented in **Table (4)**. The results are expressed in ng g⁻¹ fish fat.

From **Table (4)**, the data proved that the high content of fats present in the fresh muscle, the increasing of the residues found. By grilling method, the fats drips away with the toxic chemicals dissolved in. p,p'-DDE, p,p'-DDD were the main metabolites of DDT detected with highest concentrations of 6.28, 4.04ng/g, respectively with 100% frequency percentage in case of p,p'-DDE and 25% of the other metabolite. The effect of grilling method decreased the residues to 1.83 and 1.34 with percentage reduction of 57.93 and 55.57%, respectively. Also α-HCH detected in high frequency percentage 75% with a mean value of 2.12 decreasing to 0.62 ng/g with reduction percentage of 70.75% after the grilling method. From **Table (4)** we notice that the grilling method

Table 2. Effect of Grilling on the Gross Chemical Composition of Bolti fish flesh. (g/100g dry weight)

Treatment	Range and average	Moisture	Ether extract	Crud protein	Ash	*Carbohydrates	Total Solids
Fresh flesh	Maximum	77.53	10.43	82.97	8.07	2.59	25.26
	Minimum	74.72	5.61	76.01	6.34	1.55	22.47
	Average	76.88	8.33	80.49	7.28	1.98	23.13
Grilled flesh	Maximum	72.77	5.11	80.25	6.38	3.48	31.07
	Minimum	68.27	3.28	76.37	5.00	2.65	27.23
	Average	70.81	4.26	77.86	5.72	2.92	29.07

* basis on dry weight

**Calculated by difference

Table 3. Contribution of protein, ash, fat and energy of grilled Bolti fish to the Daily nutritive requirement for children from (7-10 years) and adults

Component %	*Average value	Daily nutritive requirements for children (7-10) and adults					
		7-10 years (gm)	Contribution % per100gm	Males	Contribution % per100gm	Females	Contribution % per100gm
Protein	22.62	*28.00	80.79	63.00 gm	35.91	50.00gm	45.24
Ash	1.67	**1.80	92.78	1.98 gm	84.53	1.90 gm	87.90
Fat	1.24	***1.00	06.20	15.00 gm	8.27	15.00 gm	8.27
Carbohydrate	0.850	20.00	—	—	—	—	—
Energy(Kcal)	14.56	2000	00.73	2700 (Kcal)	0.54	2000	0.728

*Basis on wet weight

**Recommended Dietary Allowances, 10th Edition (1989).

***Recommended Dietary Allowances for Indian Swaminathan (1993).

eliminate the SP pesticides detected in the fresh fish muscle. We have to notice that none of the detected pesticides are exceed the permissible limit set by the international Commissions **FAO (1983)**.

The main reasons for the increasing presence of these OC in the environment are, first, the cheap and ready availability of chlorine gas on an industrial scale led to the production of chlorinated compounds of technological importance. Secondly, many of these polychlorinated organic compounds, cyclic in structure, and highly thermo-stable in character, which were resistant to biodegradation; and thirdly, the uncontrolled use and discharge of these chemicals resulted in methods for their detection led to the growing awareness of their increasing presence in the ecosystem (**Smith and Gangolli 2002**). Many literatures are found the

predominancy of p,p'-DDE over the other p,p'-isomers in all studied fish as **El Nembr and Abd Allah (2004)**, but they conclude that the level of organochlorine pesticides contamination in fish from the studied governorates is relatively low and should not pose a health risk to consumers. **Abou Arab et al (1995)** found that total DDT were predominant in fish samples in both seasons indicating the high stability of these compounds in the environment. **Nasr et al (2009)** found that p,p'-DDE residue were the most abundant in fish sample.

The cooking method as grilling led to non detectable of SP pesticides residues, this is may be due to the high temperature used in grilling (180°C), this statement agreed with **Lutnicka et al (1999)**.

Table 4. The minimum, maximum, standard deviation of the mean (ng g⁻¹ fish fat), frequency percentage in fresh and grilled fish

Pesticides	Fresh				Grilled				
	Min	Max	Mean ± SD	% Frequency	Min	Max	Mean ± SD	% Frequency	% Reduction
α-HCH	ND	2.85	2.12±0.92	75.00	ND	1.03	0.62 ± 0.120	25.00	70.75
β-HCH	ND	1.06	0.78±0.45	66.66	ND	0.82	0.42 ± 0.11	11.11	46.15
γ-HCH	ND	0.79	0.58±0.31	25.00	ND	ND	ND	0.00	>91.37*
Heptachlor	ND	1.61	1.49±0.72	25.00	ND	1.06	0.85 ± 0.21	16.66	42.95
Aldrin	ND	ND	ND	0.0	ND	ND	ND	0.0	--
Heptachlor epoxide	ND	ND	ND	0.0	ND	ND	ND	0.0	--
Dieldrin	ND	1.92	1.69±0.19	25.00	ND	0.52	0.66 ± 0.37	27.27	60.94
P,P'-DDE	ND	6.28	4.35±1.03	100.00	ND	2.45	1.83 ± 0.417	50.00	57.93
Endrin	ND	2.02	1.89±0.59	25.00	ND	0.93	0.71 ± 0.135	5.55	62.43
O,P'-DDT	ND	0.79	0.71±0.14	50.00	ND	0.48	0.43 ± 0.12	25.00	39.43
P,P'-DDD	ND	4.04	3.03±0.22	16.66	ND	2.95	1.34±0.0056	25.00	55.77
P,P'-DDT	ND	0.27	0.22±0.03	8.33	ND	0.14	0.12 ± 0.04	5.55	45.45
Meothrin	ND	ND	ND	0.0	ND	ND	ND	0.0	--
Tetramethrin	ND	ND	ND	0.0	ND	ND	ND	0.0	--
Cyhalothrin	ND	0.92	0.83±0.22	11.11	ND	ND	ND	0.0	>97.59*
Permethrin	ND	0.81	0.70±0.31	8.33	ND	ND	ND	0.0	>98.57*
Cypermethrin	ND	ND	ND	0.0	ND	ND	ND	0.0	--
Fenvelerate	ND	ND	ND	0.0	ND	ND	ND	0.0	--
Deltamethrin	ND	ND	ND	0.0	ND	ND	ND	0.0	--

ND: Not detectable (below the LOD)

*According to the LOD

Certain pyrethroids such as cyhalothrin and permethrin where the isobutenyl group attached to the cyclopropane moiety has been altered, are slightly more stable to sunlight than other pyrethroids which agreed with **U.S. Department of Health and Human Services (2003)**.

Conclusions

The grilling processes of fish basis on dry weight, showed significant decrease in its nutritive value for fat, crude protein and ash but showed fairly increase in the total solids and carbohydrates.

As the fats drips away by grilling cooking method, this will reduce toxic chemicals that have accumulated in fatty tissue. None of residues of OC or SP pesticides in fresh or grilled fish muscles exceed the permissible limits set by the FAO.

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