EFFECT OF HEAT TREATMENT ON THE NUTRITIVE VALUE AND RESIDUES OF SOME SYNTHETIC PESTICIDES IN FRESH BOLTI 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-δ 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 –chain poly unsaturated fatty acids those of the 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 Soylak 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.
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 Arab 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 100 gram basis on dry weight according to the AOAC (2000). Carbohydrates were determined by difference 100 - (moisture + crude protein + ether extract + ash). Total solids were calculated by the following equation:

\[ \text{Weight of fresh or grilled fish flesh} \times \frac{100}{ \text{its moisture content} } \]

\[ T.S = \text{Weight of fresh or grilled fish flesh} \times 100 \]

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: \( \alpha \)-HCH, \( \beta \)-HCH, \( \gamma \)-HCH, Heptachlor, Aldrin, Heptachlor-epoxide, Dieldrin, Endrin, p.p'-DDE, o,p'-DDT, p,p'-DDD and p,p'-DDT all at 1 ng/lµl, Endrin, at 2 ng/lµl, Meothrin, Tetramethrin, Cyhalothrin, Cypemethrin, Fenvelerate, Deltamethrin all at 5ng/lµl.

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 Microelectron capture detector (GC-ECD) fitted with HP-608 capillary column (30 mx0.53mm id x0.5µm film thickness). The column temperature was programmed as initial temperature 160°C for 2min then increased at the rate of 5°C/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.
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. Considering 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 2-10 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 females respectively basis on wet weight. 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'‐DDT, 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’‐DDT 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)

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

* 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

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


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 Nemr 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

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>Fresh</th>
<th>Grilled</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>α-HCH</td>
<td>ND</td>
<td>2.85</td>
</tr>
<tr>
<td>β-HCH</td>
<td>ND</td>
<td>1.06</td>
</tr>
<tr>
<td>γ-HCH</td>
<td>ND</td>
<td>0.79</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>ND</td>
<td>1.61</td>
</tr>
<tr>
<td>Aldrin</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Heptachlor epoxide</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>ND</td>
<td>1.92</td>
</tr>
<tr>
<td>P,P'–DDE</td>
<td>ND</td>
<td>6.28</td>
</tr>
<tr>
<td>Endrin</td>
<td>ND</td>
<td>2.02</td>
</tr>
<tr>
<td>O,P’–DDT</td>
<td>ND</td>
<td>0.79</td>
</tr>
<tr>
<td>P,P’–DDT</td>
<td>ND</td>
<td>4.04</td>
</tr>
<tr>
<td>P,P’–DDT</td>
<td>ND</td>
<td>0.27</td>
</tr>
<tr>
<td>Meothrin</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Tetramethrin</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cyhalothrin</td>
<td>ND</td>
<td>0.92</td>
</tr>
<tr>
<td>Permethrin</td>
<td>ND</td>
<td>0.81</td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Fenvelerate</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Deltamethrin</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

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.

REFERENCES


