

## DETERMINATION OF SOME TOXIC TRACE ELEMENTS OF FRESH, FROZEN AND CANNED FISH SPECIES

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### ABSTRACT

In this study, fresh fish (*Otolithes ruber*, *Saurida tumbil*, *Pseudorhombus malayanus*, *Acanthopagrus latus*, *Hypophthalmichthys molitrix* and *Tenualosa ilisha*), imported frozen fish (*Megalaspis cordyla*, *Ctenopharyngodon idella*, *Labeo rohita* and *Acanthopagrus latus*) and imported canned fish species (sardines, mackerel and tuna) were used to detect and determine some toxic trace elements. All fish samples contained trace elements. The total concentrations mean for Cu, Zn, Pb, Ni, Co, Cd and Mn were between (1.73-11.93), (8.75-25.80), (ND-3.19), (0.11-0.31), (0.10-0.35), (0.23-3.00) and (0.11-1.86) mg/kg dry weight respectively in muscles of fresh fish, and between (13.21-53.74), (6.61-43.93), (0.35-2.10), (0.37-2.30), (0.20-0.54), (1.50-3.53) and (0.13-4.50) mg/kg dry weight respectively in the muscles of frozen fish species, and between (21.75-56.30), (5.21-82.84), (0.25-1.51), (0.33-1.96), (0.20-0.47), (0.51-2.22) and (0.13-0.81) mg/kg dry weight respectively in canned fish. Concentrations average of some trace elements were exceeded the permitted legal limits that set by the Food and Agriculture Organization and the World Health Organization.

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### INTRODUCTION

With more than 30,000 known animal species, fish form the biggest group in the animal kingdom that is used for the production of animal-based foods. Only about 1000 of these species are commercially fished and used for food production. Fish is consumed as fresh fish or as frozen, salted, dried, smoked, or canned products (1). It constitute an important source of protein for many people throughout the world (2).

Also fish has long been a favorite meal of people living around the Arabian Gulf and has been a major source of food for people living in this region (3).

Beside good health benefits of fish, there were many reports about fish contamination by chemical in the environment (4), Fish may concentrate large amounts of metals from water and they might be toxic for human consumption (5). Heavy metals may enter fish bodies in three possible ways, through the body surface, gill and the digestive tract (6). Fish may be contaminated by toxic elements during fish growth, transportation, and storage. Contamination may also occur during production handling and canning process (7).

The aim of this study is to assess the concentrations of trace elements in fish muscles that resulted from natural and industrial pollution and study their accumulation to assess the risks, to ensure consumer safety and draw attention to their public health effects.

## **MATERIALS AND METHODS**

fresh fish (*Otolithes ruber*, *Saurida tumbil*, *Pseudorhombus malayanus*, *Acanthopagrus latus*, *Hypophthalmichthys molitrix* and *Tenuialosa ilisha*), frozen fish (*Megalaspis cordyla*, *Ctenopharyngodon idella*, *Labeo rohita* and *Acanthopagrus latus*) and canned fish species (sardines, mackerel and tuna) were used. They were collected from local and super markets in Basra city. Fresh and frozen fish species were classified as stated in (8), (9) and (10).

After collecting fresh and frozen fish, each group were kept separately in containers filled with crushed ice until it reaches the laboratory. Fish were washed with tap water and then distilled water. After that, heads, skins, peels and bones were removed by using cleaned and sterilized knives and tools, then meat chopped by chopping machine. The canned fish, oil and water solution was discharged and meat was mashed as described in fresh and frozen fish. Samples were freeze-dried and kept in freezer at  $(-18 \pm 2)^{\circ}\text{C}$  after putting in clean and sterilized glass bottles.

### **Analysis of trace elements**

Trace elements concentrations were determined according to (11). Freeze dried samples were digested on heater with a mixture of concentrated nitric and perchloric acids with ratio (1:1) until get clear solution, this solution was diluted with deionized water, then absorbance of trace elements was measured by flame atomic absorption

spectrophotometer and concentrations were calculated according to the standard curve for each element.

### **Statistical analysis**

Statistical analysis used for transactions, has been done by using statistical program mentioned in (12)

## **RESULTS**

Results in tables (1), (2) and (3) showed concentrations of trace elements (dry weight) in muscles of fresh, frozen and canned fish species. They showed that most of fish muscles contained trace elements and the concentrations of some metals exceeded the permitted limits set by FAO and WHO.

Table (1) shows that the highest concentration mean of copper and zinc was recorded in *Acanthopagrus latus* muscles, 11.93 and 25.80 mg/kg respectively, while highest concentration mean of lead was found in muscles of *Saurida tumbil* 3.19 mg/kg, and nickel recorded high concentration mean in *Pseudorhombus malayanus* and *Acanthopagrus latus* muscles 0.31 mg/kg.

It is noted in table (1) that higher concentration mean of cobalt and manganese was found in muscles of *Tenualosa ilisha* and *Hypophthalmichthys molitrix*, 0.35 and 1.86 mg/kg respectively.

Results of statistical analysis showed a significant differences ( $P < 0.05$ ) in the concentration of manganese among *Hypophthalmichthys molitrix*, *Tenualosa ilisha*, *Saurida tumib*, *Pseudorhombus malayanus* and *Acanthopagrus latus*. While there were no significant differences in the content of *Otolithes ruber*, *Hypophthalmichthys molitrix*, *Tenualosa ilish*, *Saurida tumibl*, *Pseudorhombus malayanu* and *Acanthopagrus latus* of this element. No significant differences were observed ( $P > 0.05$ ) in fish content of copper, zinc, lead, nickel, cobalt and cadmium.

**Table (1) concentrations of trace elements (mg/kg) dry weight in the fresh fish muscles**

<b>Trace elements</b> <b>Fish Species</b>	<b>Cu</b>	<b>Zn</b>	<b>Pb</b>	<b>Ni</b>	<b>Co</b>	<b>Cd</b>	<b>Mn</b>
<i>Otolithes ruber</i>	5.11 <sup>a</sup>	21.68 <sup>a</sup>	0.81 <sup>a</sup>	0.21 <sup>a</sup>	0.10 <sup>a</sup>	0.23 <sup>a</sup>	0.90 <sup>ab</sup>
<i>Saurida tumbil</i>	8.52 <sup>a</sup>	8.75 <sup>a</sup>	3.19 <sup>a</sup>	0.18 <sup>a</sup>	0.16 <sup>a</sup>	2.86 <sup>a</sup>	0.30 <sup>b</sup>
<i>Pseudorhombus malayanus</i>	6.39 <sup>a</sup>	11.55 <sup>a</sup>	0.67 <sup>a</sup>	0.31 <sup>a</sup>	0.31 <sup>a</sup>	2.10 <sup>a</sup>	0.16 <sup>b</sup>
<i>Acanthopagrus latus</i>	11.93 <sup>a</sup>	25.80 <sup>a</sup>	0.24 <sup>a</sup>	0.31 <sup>a</sup>	0.22 <sup>a</sup>	3.00 <sup>a</sup>	0.11 <sup>b</sup>
<i>Hypophthalmichthys molitrix</i>	2.55 <sup>a</sup>	16.90 <sup>a</sup>	0.83 <sup>a</sup>	0.26 <sup>a</sup>	0.28 <sup>a</sup>	1.50 <sup>a</sup>	1.86 <sup>a</sup>
<i>Tenualosa ilish</i>	1.73 <sup>a</sup>	21.69 <sup>a</sup>	ND	0.11 <sup>a</sup>	0.35 <sup>a</sup>	0.66 <sup>a</sup>	0.56 <sup>b</sup>

ND means not detected, and different letters mean there is significant differences ( $P < 0.05$ ).

L.S.D. (Cu=10.84 , Zn=17.62 , Pb=3.522 , Ni=0.3238 , Co=0.2820, Cd=3.038, Mn=1.209)

Table (2) showed highest concentration mean of copper was found in the muscles of *Megalaspis cordyla* 53.74 mg/kg, and the highest concentration mean of zinc and lead recorded in *Acanthopagrus latus* muscles. Also the table showed a highest concentrations mean of nickel, cobalt and manganese were recorded in the muscles of *Labeo rohita*, and the highest mean concentration of cadmium in the muscles of *Acanthopagrus latus*, 3.53 mg/kg.

**Table (2) concentrations of trace elements (mg/kg) dry weight in frozen fish muscles**

Trace elements Fish Species	Cu	Zn	Pb	Ni	Co	Cd	Mn
<i>Megalaspis cordyla</i>	53.74 <sup>a</sup>	32.12 <sup>a</sup>	1.33 <sup>a</sup>	0.43 <sup>a</sup>	0.20 <sup>a</sup>	2.73 <sup>a</sup>	0.14 <sup>b</sup>
<i>Ctenopharyngodon idella</i>	13.21 <sup>c</sup>	6.61 <sup>c</sup>	0.35 <sup>a</sup>	0.37 <sup>a</sup>	0.28 <sup>a</sup>	1.50 <sup>a</sup>	2.26 <sup>ab</sup>
<i>Labeo rohita</i>	39.23 <sup>a</sup>	18.09 <sup>bc</sup>	1.44 <sup>a</sup>	2.3 <sup>a</sup>	0.54 <sup>a</sup>	3.30 <sup>a</sup>	4.50 <sup>a</sup>
<i>Acanthopagrus latus</i>	14.49 <sup>bc</sup>	43.93 <sup>a</sup>	2.10 <sup>a</sup>	0.51 <sup>a</sup>	0.30 <sup>a</sup>	3.53 <sup>a</sup>	0.13 <sup>b</sup>

Different letters mean there is significant differences (P <0.05).

L.S.D.: ( Cu=17.33 , Zn=14.00 , Pb=2.125 , Ni=2.236 , Co=0.4269, Cd=3.317 and Mn=4.156)

The results of statistical analysis showed significant differences (P<0.05) in the content of frozen fish in copper, zinc and manganese, while there were no significant differences (P> 0.05) in the content of the fish of lead, nickel, cobalt and cadmium.

Table (3) showed a concentrations of trace elements in canned fish species: sardines, mackerel and tuna. Another phrase copper and zinc recorded higher concentration mean in mackerel and sardines 56.30 and 82.84 mg/kg respectively, also it is noted from the results that highest concentrations mean of lead and nickel were found in sardines 1.51 and 1.96 mg/kg respectively.

**Table (3) concentrations of trace elements (mg/kg) dry weight in the muscles of canned fish**

Trace elements Fish Species	Cu	Zn	Pb	Ni	Co	Cd	Mn
Sardines	26.01 <sup>b</sup>	82.84 <sup>a</sup>	1.51 <sup>a</sup>	1.96 <sup>a</sup>	0.35 <sup>a</sup>	0.86 <sup>a</sup>	0.16 <sup>a</sup>
Mackerel	56.30 <sup>a</sup>	5.21 <sup>b</sup>	0.25 <sup>a</sup>	1.39 <sup>a</sup>	0.20 <sup>a</sup>	2.22 <sup>a</sup>	0.13 <sup>a</sup>
Tuna	21.75 <sup>b</sup>	32.39 <sup>b</sup>	0.25 <sup>a</sup>	0.33 <sup>a</sup>	0.47 <sup>a</sup>	0.51 <sup>a</sup>	0.81 <sup>a</sup>

Different letters mean there is significant differences (P <0.05).

L.S.D.: (Cu=28.36 , Zn=29.58 , Pb=1.866 , Ni=3.505 , Co=0.4509 ,Cd=3.363 ,Mn=1.198)

The highest concentration mean of cobalt and manganese were found in tuna slices 0.47 and 0.81 mg/kg respectively, while mackerel contained a highest concentration mean of cadmium 2.22 mg/kg.

The results of statistical analysis showed a significant differences ( $P < 0.05$ ) in the content of copper and zinc in canned fish, while no significant differences recorded ( $P > 0.05$ ) in the content of trace elements (lead, nickel, cobalt, cadmium and manganese) in these fish samples.

## **DISCUSSION**

In fresh samples, copper and zinc did not exceed permitted limit for Food and Agriculture Organization, 30 mg/kg for the two mentioned metals (13). Copper is an essential element and it enhance the enzymatic activity of the body. However, it poses health hazard when ingested in large amount (14). Also concentration mean of lead exceeded the allowable limit by the World Health Organization, 2 mg/kg (15). Lead is a contaminant and non essential element, usually detected at low concentrations in crustaceans.<sup>16</sup> Lead can be accumulated in fish directly from seawater and sediments<sup>17</sup>. The result of nickel level was coincided with 17 after estimating nickel in *Platycephalus indicus* muscles. Nickel is an oil related metal showing a nutrient type behavior and can become toxic at higher levels (18). World Health Organization recommends take up (100-300)  $\mu\text{g}$  of nickel per day <sup>19</sup>.

Concentration of cadmium in *Acanthopagrus latus* muscles exceeded recommended limit of 13. Cadmium shows no indication of being an essential element in biological processes, instead it is toxic. It causes slight anemia due to competition between Fe and Cd in the body resulting to iron deficiency (14).

For frozen fish samples, it was obvious that the concentrations of copper, zinc and lead have exceeded the allowable limit set by WHO and FAO, 30 mg/kg <sup>13</sup>. The result agreed with study of (20) when she determined the lead level in the muscles of *Epinephelus areolatus* that frozen for six months. Concentrations of nickel, cobalt and manganese in the muscles of *Labeo rohita*, and concentration mean of cadmium in the muscles of *Acanthopagrus latus*, have exceeded the maximum allowable limits recommended by FAO/WHO <sup>21</sup>, and FAO which was 0.5 mg/kg (13) This result disagreed with the study of (20) which stated that no cadmium was detected in marine hammour frozen for six months.

The effects of freezing on cells, storage temperatures, fish stress and rigor mortis in relation to cellular metabolism during perimortem and postmortem are speculated for higher metals contents in frozen samples. Freezing method is important in determining the size of ice crystals that can rupture cell walls which allow movement of cytoplasmic fluid that contain metals when thawed. Quick freezing method reduces the formation of large ice crystals which aims to yield good quality products in terms of textures, colouration, freshness and tenderness of meat. Contrastingly, slow freezing method causes the fluid in fish tissues to form large ice crystals that damages the delicate tissue cells (22).

For canned fish samples, Copper and zinc concentrations mean in mackerel and sardines, exceeded the recommended limits set by the FAO, 30 mg/kg for the two mentioned metals (13).

Soldering is a source of lead contamination in the canning process. Therefore, the monitoring of lead concentration in canned fish is important for human health (23) and (24). Concentration of cadmium recommended by (21) , and (13) of 0.5 mg/kg, agreed with the concentration mean of cadmium in tuna slices, it is reported that cooking reduces the amount of some metals 25.

We conclude from this study that some of fish samples contained high concentrations of copper and zinc. Other elements concentrations were varying and exceeded toxic levels. Therefore it is recommended to monitor the fishery products of all fish species, fresh, frozen and canned to control concentrations of toxic compounds in order to ensure the health of the consumer.

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تقدير بعض العناصر النزرة السامة في عضلات أنواع من الاسماك الطازجة والمجمدة والمعلبة

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### الخلاصة

قدرت العناصر المعدنية النزرة في عضلات أنواع من الاسماك الطازجة ( النوبيي *Otolithes ruber*, أبو الهيل *Saurida tumbil*, المزلك *Pseudorhombus malayanus*, الشانك *Tenualosa*, الكارب الفضي *Hypophthalmichthys molitrix* والصبور *Acanthopagrus latus* و*ilisha*) والأسماك المستوردة بنوعيتها: المجمدة (الماكريل *Megalaspis cordyla*, الكارب العشبي *Ctenopharyngodon idella*, الكارب الهندي *Labeo rohita* والشانك *Acanthopagrus latus* والمعلبة (السردين, الماكريل والتونة). وقد تراوحت متوسطات التراكيز الكلية لكل من النحاس والزنك والرصاص والنيكل والكوبلت والكاديوم والمنغنيز بين (1.73- 11.93) و(8.75-25.80) و(ND-3.19) و(0.11-0.31) و(0.10-0.35) و(0.23-3.00) و(0.11-1.86) ملغم/كغم وزن جاف على التوالي في عضلات الاسماك الطازجة. وبين (13.21-53.74) و(6.61-43.93) و(0.35-2.10) و(0.37-2.30) و(0.20-0.54) و(1.50-3.53) و(0.13-4.50) ملغم/كغم وزن جاف على التوالي في عضلات الأسماك المجمدة. وتراوحت بين(21.75-56.30) و(5.21-82.84) و(0.25-1.51) و(0.33-1.96) و(0.20-0.47) و(0.51-2.22) و(0.13-0.81) ملغم/كغم وزن جاف على التوالي في عينات الأسماك المعلبة. وقد تجاوزت تراكيز بعض العناصر المعدنية النزرة المستويات المقبولة التي حددتها المنظمات العالمية, كمنظمة الغذاء والزراعة FAO ومنظمة الصحة العالمية WHO.

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