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## **CHEMICAL EVALUATION OF SOME FRESH AND FROZEN FISH**

(With 3 Tables)

By

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### **التقييم الكيميائي لبعض أسماك الطازجة والمجمدة**

**عزة السيد على حسان ، الشحات أبو مسلم طوسون فرحات**

أجريت هذه الدراسة بهدف معرفة التأثير الكيميائي من تجميد الأسماك وأيضاً بهدف معرفة مدى تلوث المياه ببعض المعادن الثقيلة السامة مثل الرصاص والكاديميوم والنحاس وانعكاس هذا التلوث على الأسماك فقد تم تجميع ٢٥ سمكة بشكل عشوائي من بحيرة المنزلة بمحافظة الدقهلية وتجميع ٢٥ عينة ماء من نفس البحيرة. وتجميع أيضاً ٢٥ عينة سمك بشكل عشوائي من أسواق مدينة المنصورة. وقد أسفرت النتائج عن وجود زيادة معنوية في الكادميوم في أنسجة الأسماك الطازجة والمجمدة ووجود زيادة معنوية في النحاس في أنسجة الأسماك المجمدة وبالنسبة لعينات الماء فقد أسفرت النتائج عن وجود زيادة معنوية في الرصاص والكاديميوم والنحاس. أما بالنسبة للقواعد النيتروجينية الكلية وحامض الثيوباربيتوريك والهستامين فقد كانت أعلى من المستوى المسموح به في الأسماك المجمدة ولكنها كانت في المستوى المسموح به في الأسماك الطازجة. مما سبق يتضح أن تعرض الأسماك في المياه لبعض المعادن الثقيلة السامة يؤدي إلى ترسيب هذه المعادن في أنسجة الأسماك وأيضاً يتضح أن تجميد الأسماك يؤدي إلى تغيرات كيميائية سلبية تمثلت في ارتفاع القواعد النيتروجينية الكلية وحامض الثيوباربيتوريك والهستامين وهذه التغيرات الكيميائية لها تأثيرها السلبي على الصحة العامة لذا ينصح باستهلاك الأسماك بسرعة وفي حالة التجميد يكون التجميد لفترة قصيرة.

### **SUMMARY**

The aim of this study was to know the chemical effect of the freezing process on the quality of fish and to know the water pollution by some heavy metals and the reflection of this pollution on fish. A total of 50 random samples fresh and frozen fish were collected from Manzala lake in Dakahlia Governorate (25 fresh fish). Also, from the different markets in Mansoura (25 frozen fish) and 25 samples of water were collected randomly from Manzala Lake in Dakahlia Governorate. All samples

were examined chemically. The results showed an increase in Cadmium in tissues of fresh and frozen fish and increase in copper in tissues of frozen fish. Meanwhile the water samples showed increase in lead, cadmium and copper. Concerning total basic nitrogen, thiobarbituric acid and histamine levels they were above the permissible limits in frozen fish, while in fresh fish were within permissible limits. From the above we can conclude that the exposure of fish in water to some heavy metals lead to perception of these heavy metals in tissues of fish as well as freezing of fish lead to negative chemical changes, represented by increase of total volatile basic nitrogen, thiobarbituric acid and histamine, therefore fresh fish should be consumed as soon as possible and surely within 3 days from purchased because of longer storage may result in rapid rise in total volatile basic nitrogen, thiobarbituric acid and histamine, that causes a potential threat to consumers health.

*Key words: Fish, heavy metals, histamine.*

## INTRODUCTION

Fish have been used as a food in most countries over the world. It is high desirable food due to its contribution of high quality animal protein, its richness in calcium, phosphorus and its generous supply vitamins. (Campton, 1981). Meanwhile, availability of these nutrients depends on a large extent on the methods of storage (Ryder *et al.*, 1993). Freezing is a mean of arresting either partially or completely the deteriorative action of enzymes. It is an essential type of partial, gentle dehydration in which the water is removed in the form of ice and the activity of enzymes in general rapidly reduced or redirected as the temperature is reduced below the freezing point of about  $-1\text{C}^{\circ}$ . this means that the deteriorations suffered by frozen fish are qualitatively different and the entail biochemical changes (Connell 1990; Alasalvar *et al.*, 1992). Freezing cannot reverse deteriorations that have already occurred. Fish with a certain degree of prefreezing spoilage will retain it throughout freezing, frozen storage and thawing. Chemical quality and physical damage is an important factor which influences the quality of the end product (Berna and Sukran, 2004; Noguerras *et al.*, 2007).

To that extent controlling the quality of frozen fish includes controlling or selecting the quality of the raw material and controlling the preparation of fish for the freezing process (Johnston *et al.*, 1994; Simeonidou *et al.*, 1997). Sensory quality is influenced not only by microbial activity but also by chemical substance and biochemical

changes in lipid composition during storage causing rancidity (Kaitaranta, 1982). Cadmium poisoning is reported to cause I'tai-I'tai, Byo disease with symptoms largely referable to bone and muscle pain, it also causes growth retardation, testicular damage and is carcinogenic to human and animals. (Gossel and Bricker, 1990). The highest lead and cadmium levels were found in muscles. (Jureasa and Blanusa, 2003). Acute exposure to Cu causes hypotension, haemolytic anemia and cardiovascular collapse, while chronic exposure resulted in jaundice in humans (Gossel and Bricker, 1990). Copper is a powerful hepatotoxin and causes severe hemolysis due to its oxidant effect on the red blood cells (RBCs) and hepatocellular membranes (Christodoulopoulos and Roubies, 2007; Mendel *et al.*, 2007). However, contamination with copper may be due to pesticides containing copper and from water ponds contaminated with copper containing pesticides and algicides. (Mc.Gavin and Zachary, 2007). Fish is inherently perishable products even under refrigerated conditions, deterioration of their quality may due to several factors, physically, chemically, decomposition by endogenous enzyme activity and inferior handling (Potter, 1986; Cobb *et al.*, 1976). Histamine is a pharmacologically important compound associated with the development of specific allergic reactions in the human body. It has been incriminated in several outbreaks and episodes of food poisoning (Priebe, 1984). The significance important of histamine in fish has been discussed by several authors (Baranowski *et al.*, 1990; Awad and khalafalla, 1993; Lopez-Sabater *et al.*, 1994). Scombroid intoxication is caused by ingestion of certain species of fish containing high level of histamine fish involved usually is subjected to time/temperature abuse (Bryan, 1988). Although histamine is the main factor involved in scombroid intoxication, other agents capable of potentiate the physiological activity of histamine playing a role in the etiology of it (Hunger Ford and Arefyev, 1992). This study was decided to determine the level of some toxic heavy metals as lead (Pb), cadmium (Cd) and copper (Cu) in the tissues of fish and in water from Manzala Lake, also to determine the total volatile basic nitrogen (TVB-N), thiobarbituric acid. (TBA) and histamine

## **MATERIALS and METHODS**

A total 50 random samples of fresh fish and frozen fish (25 of each) were collected from Manzala Lake in Dakahlia Governorate, different markets in Mansoura City and 25 samples of water were

randomly collected from Manzala Lake. All samples were transported in an ice box to the laboratory without delay. The samples were subjected to the chemical examinations according to AOAC (1990).

- Determination of lead, cadmium and copper in fish tissues was done according to the methods described by Heckman (1970); Greig *et al.* (1982) where tissue samples were measured by using Atomic Absorption Spectrophotometer according to Capar (1977).
- Determination of lead, cadmium, copper in surface water was carried according to the method prepared by Polpraset (1982); Sprenger *et al.* (1987).
- Determination of total volatile basic nitrogen (TNBN) mg/100gm: It was done according to FAO (1980).
- Determination of thiobarbituric acid number (TBA) mg MD/Kg: It was done according to Pikul *et al.* (1983).
- Determination of histamine content was done by using thin layer chromatography method (TLC), (Infosamak, 1989).
- Statistical analysis of variance (ANOVA) and t-test was carried out following the method described by Kirkwood (1989).

## RESULTS

**Table 1:** Some heavy metals concentrations (ppm) in tissues of the examined fish samples

Fish samples / Heavy metal	Fresh fish	Frozen fish
Lead	0.257±0.065	0.125±0.023
Cadmium	0.096±0.008	0.075±0.006
Copper	0.420±0.03	0.542±0.04

Permissible limit of heavy metal in fish tissue according to WHO, (1992), cadmium 0.05 ppm, lead 0.5 ppm and copper 0.5 ppm.

**Table 2:** Heavy metals concentrations (ppm) in water samples collected from different locations from Manzala Lake.

Heavy metals	Lead	Cadmium	Copper
water samples from Manzala Lake	0.53±0.14	0.068±0.005	0.98±0.017

**Table 3:** Some chemical analysis of the examined fish samples. (n=25 of each).

Fish samples	Parameters	Fresh fish	Frozen fish
	TVBN	12.3±0.4	22.1±1.3
	TBA	0.293±0.04	0.822±0.05
	Histamine	7.2±0.65	20.6±1.1

## DISCUSSION

Lead level in fish tissues has been affected by seasonal variation as it increased in winter and also affected by age due to bioaccumulation of the metal in fish muscle (Gossel and Bricker, 1990). Table 1 revealed that the mean values of lead in fresh fish and frozen fish were (0.257±0.065 and 0.125±0.023)ppm respectively and these were in agreement with Jureasa and Blanusa, (2003) but others recorded higher results (Okoye, 1994; Abo-Salem *et al.*, 1992). Table 1 showed that the mean values of cadmium in fresh fish and frozen fish were (0.096±0.008 and 0.075±0.006) ppm respectively.

Nearly similar results were recorded Jureasa and Blanusa (2003); Allen *et al.* (2003), while higher levels were reported by El-Sofy (1996) and lower levels were recorded by El-Kelish (1995). The obtained results in Table 1 indicated that the mean copper concentrations were (0.420±0.03 and 0.542±0.04) for fresh and frozen fish respectively. Nearly similar results recorded by (Sallam, 1997; Jaffar *et al.*, 1988). Meanwhile higher levels were reported by (Szefer *et al.*, 2003; El-Nabawi *et al.*, 1987). The obtained results in Table 2 showed that lead, cadmium and copper concentration in water samples collected from Manzala Lake were with mean values of (0.53±0.14 - 0.068±0.005 and 0.98±0.017) ppm respectively. These values were lower than Sabery *et al.* (2007) but exceed the permissible limit of lead and cadmium in water according to WHO (1992).

Table 3 showed TVBN mean values for fresh and frozen fish were (12.3±0.4 and 22.1±1.3) mg/100gm respectively, these results were in agreement with Acuff *et al.* (1984). The increasing of TVBN during freezing storage indicated possible spoilage of fish, such increase may be attributed to the production of volatile basic compound such as ammonia, as reported by Putro *et al.* (1985); Galli *et al.* (1993). Determination of TVBN was considered the most objective method for determining fish freshness (Fontes *et al.*, 2007). Increasing of TVBN

values of the market samples reflected their poor quality and unhygienic market conditions (Sharma and Goswami, 2010). Also Table 3 revealed that the mean thiobarbituric acid (TBA) values of the examined fresh and frozen fish samples were ( $0.293\pm 0.04$  and  $0.822\pm 0.05$ ) mg MD/kg respectively and these were in agreement with Undeland and Lingnert (1999). However these results were lower than Sohad *et al.* (2008) who recorded an increase in thiobarbituric acid value (TBA) with freezing storage times.

During freezing storage of an underutilized medium fat content fish species was studied as an index for lipid oxidation by Santiago *et al.* (2002).

Table 3 showed that histamine concentration in fresh and frozen fish were with the means ( $7.2\pm 0.65$  and  $20.6\pm 1.1$ ) respectively and these were nearly in agreement with Ahmed and Yassien, (2000). Higher results were obtained by Park *et al.* (1980); Awad and Khalafalla (1993). Scombroid poisoning is known as histamine poisoning as it is believed to be caused by ingestion of mishandled fish contains a hazardous level of histamine especially when freezing (Taylor *et al.*, 1989).

Histamine amounts depend on production date and increase by closing to expiration date of samples, Hosseini *et al.* (2009). Proteinase and decarboxylase enzymes can be work under refrigerated or freezing temperature, the seriousness of the problem dicated the complete corporations between medical, public health and veterinary authorities. Food hygienists are the better advisor in that respect as many physicians are not familiar with scombroid fish poisoning Ahmed and Yassien (2000). Fresh fish should be consumed as soon as possible and surely within 3 days from purchased as recorded by Ahmed and Yassien (2000) because of longer storage may result in rapid rise in histamine content, volatile nitrogen basic compound and thiobarbituric acid that cause a potential threat to consumers health.

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