Residual Analysis Of Some Heavy Metals In Salted Fish (Feseakh) In Sharkia Governorate

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ABSTRACT

Sixty salted fish (feseakh) samples were collected from several markets in Zagazig and Menia El-Kamh cities, Sharkia Governorate, Egypt for the determination of lead, mercury, cadmium, copper and zinc residues by using Atomic Absorption Spectrophotometer

The mean values of lead, mercury, cadmium, copper and zinc residues in the examined salted fish muscle samples were 5.951, 0.143, 0.376, 13.689 and 35.845 ppm respectively. All the examined salted fish muscle samples showed lead residues above the permissible limits, meanwhile, only 2 (3.33%) out of 60 samples showed mercury residues above the permissible limits. On the contrary, cadmium residues exceeded the permissible limits in 58 (96.66%) out of 60 examined salted fish samples. The copper levels were within the permissible limits in all the examined samples, while 3 (5%) out of 60 samples showed zinc residues above the permissible limits. The statistical analysis of the obtained data showed no significant correlation between metal residues in the examined samples. These results indicate that the salting process is probably the source of the pollution rather than the exposure of the fish during life because the metal pollution during life is associated with a sort of interaction among such metals.

It could be concluded that the use of fish from unpolluted water, controlling the sources of metal pollutions, using of hygienic salts in salting process of the fish and continuous monitoring of metal residues in salted fish were highly recommended to produce salted fish (feseakh) fit for human consumption.

INTRODUCTION

Feseakh has been the most favorable salted fish in Egypt since many thousand years ago. It is produced by salting the mullet fish for a relatively long period. As this process consumes a large amount of salt, there is a great probability that a polluted, unfit salt that contains some heavy metals may be used in feseakh processing to reduce the cost. Moreover, mullet fish may be exposed to different heavy metals during its life before catching and processing.

The heavy metals are recognized as toxic substances due to its serious effects on the main target organs and the low rate of elimination from the consumer body. The lead inhibits the biosynthesis of heme *(1)*, thus chronic lead poisoning is characterized by anemia, muscular pain and neuropathy of both the central and peripheral nervous systems *(2)*. Moreover, chronic lead exposure leads to chromosomal aberration *(3)*. Mercury is an extremely toxic metal due to the high affinity of tissue to it *(4)*. Consumption of fish polluted with mercury leads to neurotic damage, loss of vision, paralysis and death of people as occurred in Minimata, Japan, 1953. Furthermore, it passes through the placenta causing teratogenic effect *(5)*. The chronic cadmium toxicity plays a significant role in the incidence of renal dysfunction *(6)*, human hypertension *(7)*, osteomalacia and pathological fractures *(8)*. Moreover, cadmium was classified as class one human carcinogen *(9)*. Thus, in a previous study, rats suffered from nasal and paranasal carcinoma as a result of feeding salted fish *(10)*. Copper and zinc are essential for animals and humans, however, they can exhibit toxic effects on the consumer health if exceeded the permissible limits. The chronic exposure to copper caused vomiting, epigastric pain, diarrhea and jaundice *(11)*. Although, zinc toxicity from excessive ingestion is uncommon, gastrointestinal distress and diarrhea have been reported following the ingestion of polluted food by zinc *(12)*.

In spite of many reports which gave an alarm from the serious effects of using unfit polluted salts in food processing, the studies about heavy metal residues in the salted fish in

Egypt are relatively few. So, the objective of the present investigation was to determine the lead, mercury, cadmium, copper and zinc residues in the examined mullet salted fish (feseakh) muscles from Sharkia Governorate markets and compare the levels of such metals with the recommended permissible limits.

MATERIALS AND METHODS

Sixty salted fish samples (feseakh) were collected from different markets in Zagazig and Menia El Kamh cities, Sharkia Governorate, Egypt. The samples were placed in polyethylene bags, identified and kept frozen at -20°C till the analysis was conducted.

Preparation of samples:

Each salted fish (feseakh) sample was represented by one gram of flesh dissected from the axial muscles after removal of the scales at this region. The salted fish muscle samples were prepared according to the method previously cited *(13)*. Each sample was transferred to a clean screw capped glass bottle and digested with 10 ml. of digestive solution (nitric/ perchloric acid, 4 :1). Initial digestion was carried out for 4 hours at room temperature , followed by heating at 40- 45°C for one hour in water bath , then the temperature was raised to 75°C until the end of digestion . After cooling to room temperature, the digest was diluted to 20 ml. with deionized water and filtered through 0.45 µm Whatman filter paper. The clean filtrate of each sample was kept in refrigerator to avoid evaporation

Preparation of blank solution:

Ten ml. of digestion solution (nitric/ perchloric acid 4:1) in screw capped glass bottle was subjected to digestion, dilution, and filtration as the examined samples to detect any traces of the studied metals in acids or deionized water.

Quantitative determination of metals in the examined samples:

The quantitative determination of lead, cadmium, copper, and zinc residues was conducted by using UNICAM 969 Atomic Absorption Spectrophotometer, while the mercury was determined by using Perkin-Elmer mod. 2830, USA, Spectrophotometer. The concentrations of metals were calculated according to the following equation: ppm metal in samples = A×B÷W where, A= ppm metal in prepared samples from the digital scale reading of A.A.S., B= final volume of prepared samples in ml. and w = weight of samples in gm.

Statistical analysis:

The statistical analysis of data was conducted by using "Statistic for animal and veterinary science" *(14)*.

RESULTS

The heavy metal residues, in the salted fish (feseakh) muscle samples are showed in table (1). On the other hand, the comparison between the estimated heavy metal residues, in the examined samples, and the recommended permissible levels is outlined in table (2). Meanwhile, table (3) shows the correlation coefficient of the heavy metal residues in the examined salted fish samples.

Table (1) : Heavy metal concentrations (ppm, wet weight) in the examined salted fish (feseakh) muscle samples (n = 60).

Heavy metals	Minimum	Maximum	Mean ±S.E.
Lead	1.45	48.59	5.951±1.1051
Mercury	0.01	0.56	0.143±0.0179
Cadmium	0.03	0.56	0.376±0.0154
Copper	9.50	19.52	13.689±0.2968
Zinc	20.68	125.92	35.845±2.6007

Table (2): Comparison between the estimated heavy metal residues in the examined salted fish (feseakh) muscle samples and the recommended permissible limits (n = 60).

Heavy Metals	Permissible Limits	Within the permissible limits		Over the permissible limits	
		No	%	No	%
Lead	0.5 ppm*(15)*	0.0	0.0	60	100
	0.1mg/kg *(16)*	0.0	0.0	60	100
Mercury	0.5ppm*(15)(16)*	58	96.66	2	3.33
Cadmium	0.05 ppm*(15)*	2	3.33	58	96.66
	0.1 mg/kg*(16)*	2	3.33	58	96.66
Copper	20 µg/gm*(17)*	60	100	0.0	0.0
Zinc	50 ppm *(18)*	57	95	3	5

N.B : ppm = mg/kg = µg/gm

Table (3): Correlation coefficient of the heavy metal residues in the examined salted fish muscle samples.

Metals	Lead	Mercury	Cadmium	Copper	Zinc
Lead		− 0.085	− 0.005	0.002	− 0.179
Mercury			− 0.096	− 0.248	− 0.007
Cadmium				0.192	0.035
Copper					0.068
Zinc					

N.B. : No significant positive or negative correlation between heavy metal residues in the examined salted fish muscles.

DISCUSSION

The present study aimed to estimate the levels of some heavy metals (lead, mercury, cadmium, copper and zinc) residues in the muscles of salted fish (feseakh) collected from Sharkia Governorate markets.

Lead concentrations in the examined samples ranged from 1.45 to 48.59 ppm with a mean value of 5.951 ±1.1051 ppm (table 1). These levels were higher than those previously reported in the salted fish in Egypt (***19, 20*** and ***13***). Moreover, lower lead concentrations than our findings were recorded (***21***, ***22*** and ***23***). Moreover, lower lead levels (4 – 177 ppb) were detected in Finland ***(24)***.

Our estimation showed that the mercury levels in the salted fish (feseakh) muscle samples varied from 0.01 to 0.56 ppm with a mean of 0.143 ±0.0179 ppm. Nearly similar findings of mercury residues were reported in salted fish in Egypt (0.14 ppm) ***(19)*** and (0.104 ppm) ***(13)***. On the contrary, higher mercury levels than those in the present study were found in marine fish (***25***, ***26*** and ***22)***.

Concerning the cadmium residues, it could be detected in the salted fish muscle samples with values which varied from 0.03 to 0.56 ppm and a mean of 0.376 ±0.0154 ppm. These findings agree with those recorded in salted fish ***(13)***, canned fish ***(27)*** and marine fish ***(22)***. On the other aspect, higher cadmium levels than those obtained in the current study were reported in the salted fish ***(19)***. Meanwhile, lower cadmium residues than our

figures were recorded in the salted fish *(24)* and marine fish *(21)*.

The mean value of copper in salted fish muscle samples was 13.689 ±0.2968 ppm with a minimum of 9.50 ppm and maximum of 19.52 ppm. Nearly similar findings were obtained in the salted fish (13.9 ppm) *(13)*. Meanwhile, lower copper concentrations than those in this investigation were detected in the salted fish *(19)*, canned fish *(27)*, and fresh fish *(28)*.

The zinc levels in the examined salted fish muscle samples ranged from 20.68 to 125.92 ppm with a mean of 35.845 ±2.6007 ppm. These levels were lower in comparison with those in the salted fish of previous studies in Egypt *(13, 19)*. On the other side, lower zinc levels than our figures were recorded in the canned fish *(27)* and fresh fish *(28)* in Egypt.

Regarding the comparison between the heavy metal levels in this study and the maximum recommended permissible limits, the obtained results (table 2) showed that all the examined salted fish muscle samples contained lead residues above the recommended permissible limits *(15,16)*. while, only 2 (3.33%) out of 60 salted fish muscle samples showed mercury residues with levels higher than the permissible limits *(15,16)*. On the contrary, the cadmium residues exceeded the permissible limits *(15,16)* in 58 (96.66%) out of 60 examined salted fish samples. On the other aspect, the copper levels were below the permissible limit *(17)* in all the examined salted fish muscle samples, while 3 (5%) out of 60 samples showed zinc residues above the permissible limit *(18)*.

The statistical analysis of the obtained results (table 3) revealed absence of significant positive or negative correlation between the metal residues in the examined salted fish muscles. This result indicates that the salting process is the probable source of the metal pollutions rather than the contamination during the life cycle of the fish before fishing, because there are clear relations between metal residues in the animal tissues during its life cycle. There is an obvious biological antagonism between cadmium and both zinc and copper *(29,30,31)* which gives a significant negative correlation between cadmium and the other two mentioned metals. On the other hand, a significant negative correlation must be expected between the lead levels and both cadmium and copper residues if the pollution occurred during the life cycle of fish as a result of the biological antagonism between the lead and both cadmium and copper *(32,33)*. Thus, the addition of the polluted salts to the mullet fish (feseakh) during the processing, explained the absence of any significant correlation within the obtained metal residues.

Generally, it could be concluded that the majority of the examined salted fish (feseakh) muscle samples suffered from considerable high concentrations of lead and cadmium residues; while, the mercury, copper, and zinc residues were at a relatively low safety levels in most of the examined samples. These pollutions could be probably attributed to the use of contaminated salts in the salting process as previously indicated. The sources of lead and cadmium pollutions in the environment are the industrial effluents, the previous using of leaded gasoline (leaded gasoline has been prohibited in Egypt since few years), phosphate fertilizers, sewage sludge and some herbicides *(34)*.

The using of fish from uncontaminated water, controlling the industrial and agriculture effluents into lakes and surface water; and the using a hygienic salts in the salting process of fish are the preventive measures to produce a hygienic salted fish for human consumption. Moreover, continuous monitoring of the heavy metal residues in the marketed fish is highly recommended to avoid one of the most hazardous sources of metal pollutions in food.

REFERENCES

1- ***Forstner N and Wittmann GTW (1983)***: Metal pollution in the aquatic environment. Springer – Verlag Berlin.

2- ***Goldfrank LR, Flomenbaum NE, Lewin NA,Weisman RS and Howland MA (1990):*** Goldfrank`s Toxicology Emergencies.4th Ed.- Hall International Inc, New Jersey, USA.

3- ***Johnson FM(1998):*** Veterinary Pathology, 5th ed Lea and Febiger. Philadelphia (USA).

4- ***Timbrell JA (1982):***"Principles of Biochemical Toxicology". Taylor and Francis, Ltd., London.

5- ***Sorensen, EMB (1991):*** Metal Poisoning in fish .Oxford and I.B.H. Publishing Co. Bombay.

6- ***Elinder CG and Jarup L (1996):*** Cadmium exposure and health risks: Recent findings. Ambio 25, 370- 373.

7- ***Nishiyama S,Nakamura K and Konish Y (1986):*** Blood pressure and urinary sodium and potassium excretion ion in a cadmium-treated male rats. Enviro. Res, 40: 357:364.

8- ***Friberg L and Elinder CG (1988):*** Cadmium toxicology in human Essential and toxic trace elements in human health and disease, edited by A.S. Prasad (New York: A.R. Liss) pp. 559-587.

9- ***International Agency for Research on Cancer "IARC" (1993):*** Beryllium, Cadmium, Mercury and Exposure in the glass manufacturing Industry IARC Monographs on the Evaluation of carcinogenic Risks to humans. Vol.58 (Lyon: World Health Organization).

10- ***Huang DP, HOJH, Saw D and Toeh TB (1978):*** Carcinoma of the nasal and paranasal region in rats fed Cantonese salted marine fish IARC Sci. Publ, (20): 315- 28.

11- ***Gossel TA and Bricker JD (1990):*** Principals of Clinical Toxicology 2nd ed. Raven press Ltd. New York.

12- ***Goyer RA (1996):*** Toxic effects of metals In: Casarett and Doll's Toxicology: The basic science of poisons. 5th ed., edited by Klaasen, C.D.; Amdor,M.O. and Doull J., pp.691- 736.

13- ***Zaki MSA(1998):*** Heavy metals in fresh and salted marine fish. 4th Vet. Md. Zag. Congress (26- 28 August, 1998).

14- ***Petric A and Watson P(1999):*** Statistics for Veterinary and Animal science. 1st Ed., pp. 90- 99. The Blackwell science Ltd, United Kingdom.

15- ***FAO/WHO (1992):*** Codex Alimentarius Commission, standard program codex committee on food additives and contaminants 24th Session, Hague, 23- 28 March.

16- ***EOSQC "Egyptian Organization for Standardization and Quality Control" (1993):*** Maximum residue limits for heavy metals in food, Ministry of Industry No. 2360/ 1993 pp5, Cairo, Egypt.

17- ***Boletin Oficial Del Estado (1991):*** Separate del Boletin Oficial del Estado Espaniol No.195. Gaceta de Madrid. (cited after Daoud et al 1999).

18- ***Food Stuffes Cosmetics and Disinfectants (1972):*** Act. No. 54 of 1972 Regulation No. R 2064. Marine Food Government Gazette. Government Printer, Pretria.

19- ***Nassar A, El-Syaed Abd Allah and Amal A Mohamed (1996):*** Heavy metals contents of Egyptian salted fish. 7th Sci. Cong. 17- 19 Nov. Fac of Vet. Med. Assiut, Egupt.

20- ***Sallam Kh. And Elgazzar MMM (1997):*** Heavy metal residues in salted and smoked fish marketed at Zagazig city. Alex. J. Vet. Sci., Vol.13, No.5, October.

21- ***Carvalho ML, Santiago S and Nunes ML (2005):*** Assessment of essential element and heavy metal content of edible fish muscle. Anal. Bioanal. Chem. Apr.14.

22- ***Andreji J, Stranai I Massaniji P and Valent M (2005):*** Concentration of selected metals in muscle of various fish species. J. Environ. Sci. Health A. Tox. Hazard subst. Environ. Eng., 40 (4): 899-912.

23- ***Boyen S, Koroleva E, Lee HK and Obbard JP (2005):*** Persistent organic pollutants and heavy metals in typical seafoods consumed in Singapore. J. Toxicol. Environ. Health A. Feb. 13; 68 (3) 151- 166.

24- ***Tahvonen R and Kumpulainen J (1996):*** Contents of lead and cadmium in selected fish species consumed in Finland in 1993-1994. Food Addit. Contam. Aug. Sep. 13 (6) 647- 654.

25- ***Debeka R., Mc Kenzie AD, Forsyth DS, Conacher HB(2004):*** Survey of total mercury in some edible fish and shellfish

species collected in Canada in 2002. Food Addit. Contam. May 21(5): 434- 40.

26- ***Storelli MM, Giacominelli Stuffler R Storelli A and Marcotrigiano Go (2003):*** Total mercury and methylmercury content in edible fish from the Mediterranean sea. J. Food Prot. Feb; 66 (2): 300- 3.

27- ***Daoud JR, Fatma E Gaber and Abdel Fattah ShA(2002):*** Chemical evaluation of some heavy metal residues in some meat and fish products. J. Egypt Vet. Med. Ass. 62, No.3: 107- 117.

28- ***Daoud JR, Aida M. Amin and Menha M Abdel Khalek (1999):*** Residual analysis of some heavy metals in water and oreochromis niloticus fish from polluted areas. Vet. Med. J., Giza. Vol.47, No.3: 351- 365.

29- ***Underwood EJ (1977):*** Trace elements in human and animal nutrition. Academic Press. New York, San Francisco, London. A subsidiary of Harcourt braces Jovanovich. Publisher.

30- ***Ahmed EEK, Haleem HH and Ali AA (1999):*** Effects of copper and ascorbic acid in restriction of cadmium toxicity. J. Egypt Vet. Med. Ass.59 (5): 1549- 1572.

31- ***Salah El Dien WM (2002):*** Studies of heavy metals pollution in poultry farms in relation to production performance. Ph.D. Thesis. Animal, Poultry and Environ. Hygiene. Fac. Of Vet. Med. Zag. Univ.

32- ***Hegazy NIE (2000):*** Effect of "pb" lead and selenium "Se" on hepatotoxic and renalotoxic effects of cadmium "cd" in male wister rats. Ph. D. Thesis, Forensic Med. And Toxicol. Fac. Of Vet. Med. Zag. Univ.

33- ***Venugopal V and Lucky TD (1978):*** Metal toxicity in mammals- 2 (p.409) New York : Plenum Press.

34- ***Goel PK (1997):*** Water pollution (cause, effects and control). Published by H.S. Poplai for new age international (P) limited, New Delhi, India.

الملخص العربي

تقدير متبقيات بعض المعادن الثقيلة في الفسيخ بمحافظة الشرقية

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يعد الفسيخ من الوجبات الشعبية المحببة للشعب المصري منذ عصر الفراعنة قبل آلاف السنين وحتى الآن والفسيخ هو سمك البوري المملح بطريقة تساعد علي حفظه وإعطائه المذاق المميز، ونظرا لانتشار ملح الطعام الغير مطابق للمواصفات والذي يحتوي علي معادن ثقيلة بكميات ضارة فإن هناك احتمالات قوية لاستخدام مثل هذه الأنواع الرديئة من ملح الطعام في بعض الصناعات الغذائية ومن أهمها صناعة الفسيخ الذي يحتاج لكميات كبيرة من ملح الطعام في تصنيعه ، لذلك فقد تم إجراء هذه الدراسة لقياس متبقيات بعض المعادن الثقيلة في عينات من عضلات الفسيخ بمحافظة الشرقية .

تم تجميع ٦٠ عينة فسيخ من أسواق مدينتي الزقازيق و منيا القمح وتم هضم العينات وقياس عناصر الرصاص ، الزئبق ، الكادميوم ، النحاس والزنك بجهاز الامتصاص الذري وقد أسفرت الدراسة عن النتائج التالية ، وجد أن متوسط تركيزات المعادن سالفة الذكر كانت ٥,٩٥١، ٠,١٤٣، ٠,٣٧٦ ، ١٣,٦٨٩ ، ٣٥,٨٤٥ جزء في المليون علي التوالي وقد وجد أن جميع العينات المختبرة كانت تحتوي علي رصاص بتركيزات أعلي من الحدود المسموح بها ، في حين أن عينتين (٣,٣٣%) كانت تحتوي علي زئبق بتركيزات أعلي من الحدود المسموح بها ، خلافا لذلك فقد كانت مستويات الكادميوم أعلي من الحدود المسموح بها في ٥٨ عينة (٩٦,٦٦%) ، أما متبقيات النحاس فقد كانت أقل من الحدود المسموح بها في جميع العينات ، من ناحية أخري فقد احتوت ٣ عينات (٥%) فقط علي زنك أعلي من الحدود المسموح بها.

أوضح التحليل الإحصائي للنتائج عن عدم وجود أي علاقات معنوية سالبة أو موجبة بين متبقيات المعادن الثقيلة بعضها البعض ، وهذه النتائج تدل علي أن الجانب الأعظم من عملية التلوث نتجت أثناء عملية التمليح أكثر منها خلال حياه الأسماك وذلك لوجود علاقات معنوية سالبة بين متبقيات المعادن الثقيلة بعضها البعض في حالة حدوث تلوث أثناء حياه الأسماك ومثال علي ذلك العلاقة العكسية بين مستويات الكادميوم وكلا من الزنك والنحاس وكذلك العلاقة العكسية بين الرصاص وكلا من الكادميوم والنحاس.

من هذه الدراسة نستخلص أن الحد من تلوث الفسيخ بالمعادن الثقيلة يستوجب تشديد الرقابة علي تداول ملح الطعام الملوث واستخدامه في صناعة الأسماك المملحة وكذلك إحكام السيطرة علي المصادر التقليدية لتلوث البيئة بالمعادن الثقيلة مثل الأسمدة العضوية والفوسفاتية والوقود الملوث وكذلك بعض المبيدات ونواتج بعض الصناعات ، كما يوصي بمتابعة قياس متبقيات المعادن الثقيلة في الأسماك المملحة بشكل دوري للوقوف علي حالتها من حيث تلوثها بتلك المعادن.