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Original Article

Changes in chemical composition and heavy metal levels in mullet (Mugil cephalus) fish during traditional smoking

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ABSTRACT

This study was carried out to assess the changes in chemical composition and heavy metal levels of mullet fish following hot and cold smoking. Mullet fish samples were collected in September 2020 from two fish farms (1 and 2) in Fayoum Governorate, irrigated by El-Batts and El-Wadi drains, respectively. The findings of determining biochemical characteristics (moisture, protein, lipid, and ash) revealed that the moisture content decreased from initial 74.82% to 63.22 and 59.32 in raw, cold and hot smoked products obtained from farm 1, respectably. While these levels were 72.10% decreased to 61.25% and 58.06% in raw, cold and hot smoked products, while protein and lipid contents increased after smoking in both fish farms samples. Also, ash contents have been found to increase from 1.23% and 1.11% in raw samples to 5.14% and 6.52% in cold and hot smoked products from farms (1 and 2). Levels of Lead (Pb), Cadmium (Cd) and Zinc (Zn) have been determined in raw and smoked products. Lead (Pb) levels were 0.013 ppm in raw samples from farm 1, increased from 0.103 ppm in farm 1 raw samples to 0.210 and 0.252 ppm in cold and hot smoked samples, respectively. Sam trend obtained in farm 2 samples. Cadmium (Cd) and Zinc (Zn) levels increased after cold and hot smoking in all mullet fish samples.

Keywords: Mullet fish, smoking fish, chemical composition, Heavy metals.

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1. INTRODUCTION

Fish has been traditionally been the main source of animal protein of the diet in many people. Fih are one of our most delicious and nutritious foods. Fish are an excellent source of high-quality proteins and also provide minerals and vitamins so necessary for good nutrition.

The real importance of fish in human diet is not only in its content of high-quality protein, but also to the two kinds of omega-3 polyunsaturated fatty acids: eicosapentenoic acid (EPA) and docosahexenoic acid (DHA). Omega-3 (n-3) fatty acids are very important for normal growth where they reduce cholesterol levels and the incidence

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of heart disease, stroke, and preterm delivery (Burger and Gochfeld, 2005 and Al bader 2008). To prolong the shelf life of fish, it is preserved by many processes including sun drying, solar drying, canning and smoking among others.

Fish smoking is a method of preserving fish, according to Clucas and Ward (1996) it combines three effects: Preservative value of the smoke (the smoke produced from the burning wood contains a large number of compounds, some of which will kill bacteria e.g., phenols); drying (The fire, which produces the smoke also, generates heat and this will dry the fish); cooking (if the fish are smoked at a high temperature, the flesh will be cooked and this will destroy the enzymes and kill the bacteria). Smoking can inhibit the formation of toxins in products (University of Florida, 2004), reduce the growth of bacteria, due to lower water activity by smoking in combination with salting and drying which creates a physical surface barrier **(**Rørvik, 2000 and Swastawati et al., 2000**).** The spoilage and pathogenic microflora of smoked products are affected by density of smoke, concentration of active components of the smoke in combination with the salt content, and the time and temperature of smoking **(**Kolodziejska et al., 2002**).** Two types of smoking process can be distinguished: Cold and hot smoking. Cold Smoking involves temperatures of 30 - 40°C and the product is not cooked. Cold smoking is used for flavour and the end product is similar in keeping quality for fresh fish. Hot Smoking involves temperatures of more than 800C and the fish is cooked during processing **(**NIOMR, 2012**).**

Contamination of fish tissues by heavy metals is arisen mainly from the contamination of feed; water, air beside the accidental addition which can be associated with soils naturally high in these elements, environmental pollution from local industry, and feeding grain (Essa and Rateb, 2011). The accumulation of heavy metal in tissues of organisms can result in chronic illness and cause potential damage to the population. Human exposures to heavy metals have become a major health risk (Yabe et al., 2011). The mineral content of fish can be affected by processing or cooking methods (Atta et al., 1997) and some studies have reported a considerable reduction of the heavy metals in food after cooking (Ersoy, 2011 and Talab et al., 2014). The reduction in trace metals concentrations as affected by cooking methods may be due to the release of these metals with the loss of drip as free salts, possibly in association with soluble amino acids and un-coagulated proteins bounded with metals (Ersoy et al., 2006).

The purpose of this study was to see how the smoking process affected the chemical composition and heavy metal levels of mullet fish from farms 1 and 2 in Fayoum Governorate

2. MATERIALS AND METHODS

2.1. Materia

***Fish sample*:** Mullet (*Mugil cephalus)* samples were obtained from two farms (1 and 2) irrigated from El-Batts and El-Wadi drains water, respectively during November, 2020.The averages of weight and length were 305±40g and 33±2 cm for raw samples obtained from farm (1), while, 255±50g and 30.5± 2.5 cm for raw samples obtained from farm (2). Fish samples were immediately transported in ice box from farms to Fish Processing and Technology Lab., Shakshouk Fish Research Station, National Institute of Oceanography and Fisheries (NIOF), Egypt.

***Ingredients*:** Sodium chloride (BONO) produced by Egyptian Salts and Minerals Company (EMISAL) was used. It composed of 98.5% sodium chloride, 30-70 ppm potassium iodate and 0.3% humidity. Sawdust as smoke source was purchased from carpentry workshop at Fayoum city.

***Smoking methods**:* The traditional methods of cold and hot smoking were carried out in smokehouse that prepared by Abd El-Mageed (1994) with some modifications at Shakshouk Fish Research Station, (NIOF). The smokehouse had inside dimensions of 2.20×1.0×3.5m with perforated metal sheets placed 75 cm above the smoke source. Mullet fish samples were washed gently with tap Water and immersed in brine solution at a ratio of 1:1 (w/v) containing 10% Nacl for 2 hrs, rinsed with tap water for 1 min to remove the excess salt, drained; semi-dried at 25-28°C in sunny air for 2 hrs and hooked in smokehouse above the smoke source by about 2.5 m for 10-11 hrs. at 35-45°C for cold smoking method, and by about 1.5 m for 5-6 hrs at 40-90°C for hot smoking method using sawdust as smoke source. After smoking the fish samples were cooled under ambient temperature. Both cold and hot smoked mullet fish samples were analyzed immediately after smoking for physiochemical, sources of danger (biogenic amine, heavy metals, microbiological) and sensory properties.

Analytical Methods

Analysis was made on fresh mullet fish meat samples immediately after the preparation and after smoking.

***Proximate analysis*:** Determination of crude protein, moisture, ash and fat contents of the fresh and smoked fish were carried out in triplicate according to AOAC (2012). Moisture content was determined according to AOAC (2012) using an electric oven at 105±2°C until a constant weight is reached. Total nitrogen was determined by using micro kejldahl method according to AOAC (2012) and crude protein content was calculated by multiplying total nitrogen percentage by 6.25 and expressed as percentage weight of sample. The crude fat content was determined by standard Soxhlet extraction method as described at AOAC (2012) using petroleum ether. Sodium chloride was determined as described by Kenkel (1994). 5g of sample homogenized with 50ml distilled water for 2 minutes in mortar and filtrated by filter paper whatman No.1, then 5ml of filtrate were taken in 50ml conical flask which titrated by standard silver nitrate (Ag NO3) solution 0.1N in presence of 1ml 5 % potassium chromate (K2CrO4) solution as indicator, the titration continued until getting of reddish-brownish color. The ash content was determined according to AOAC (2012) using a muffle furnace at 550°Cfor 16 hours or until white ash was obtained. The carbohydrates ware calculated by difference method.

Determination of Heavy metals: Heavy metals analysis according to the method described by Manutsewee *et al.*, (2007), lead (Pb), cadmium (Cd), and zinc (Zn) were determined using Atomic Absorption Spectrophotometer.

***Statistical analysis*:** chemical composition and heavy metals were analyzed statistically using SPSS version 16 software program 2007.

3. RESULTS AND DISCUSSION

3.1. Chemical composition of smoked mullet fish products

The effect of cold and hot smoking on proximate chemical composition of mullet fish *(Mugil cephalus*) obtained from farms 1 and 2 were tabulated in Table (1).

The moisture content of fresh mullet fish was found to be significantly reduced, dropping from 74.82 % in fresh fish to

63.22 and 59.32 % in cold and hot smoked mullet fish from farm 1, respectively. Also, the moisture content of fresh mullet fish from farm 2 sharply decreased from 72.10% in fresh fish to 61.25 and 58.06% in cold and hot smoked, respectively. The loss of moisture content during fish smoking could be attributed to the loss of water during smoking process (Steiner-Asiedu et al., 1991). Also, Said El-din et al., (1996) and Hegazy (1998) reported that the decrease in moisture content after fish smoking might be due to the temperature and reaction between the amino groups and the phenols as well as the reaction between smoke components and sulfhydryl groups of fish proteins and that consequently decreased the chemical groups which are able to bind water. From data it could be noticed that the higher loss of moisture content was observed in hot smoked samples (20.72%) comparison with found in cold smoked samples (14.88%) of smoked mullet fish obtained from farms 1, while the loss of hot smoked samples (19.77%) of smoked mullet fish obtained from farms 2 was higher than that of cold smoked samples (15.05%). The loss in moisture content of hot smoked samples than cold smoked might be due to that the used temperature of hot smoking was higher than that of cold smoking.

While, protein, fat, ash, sodium chloride (NaCl) and carbohydrate contents were increased by the effect of smoking process, they were 19.59, 4.28, 1.23 and 0.08% on wet basis (w.w.) of fresh mullet fish from farm (1) and were increased to 24.75, 6.62, 5.14, 3.17 and 0.27%, respectively of cold smoked samples and increased to 26.84, 7.91, 5.61, (NaCl) 3.70 and 0.32%, respectively of hot smoked samples. Also, protein, lipid, ash, sodium chloride (NaCl) and carbohydrate contents of fresh mullet fish from farm (2) were 19.34% protein, 7.38% lipid, 1.11% ash and 0.07 carbohydrate and were increased by smoking to 25.27, 7.82, 5.61, 5.22, 3.35 (NaCl) and 0.44%, respectively of cold smoked samples and increased to 27.42, 7.50, 6.52, 4.05 sodium chloride and 0.50%, respectively of hot smoked samples. The increase of protein, fat, ash, sodium chloride (carbohydrate NaCl) and carbohydrate contents during fish smoking process could be due to the loss of water during smoking process, consequently dry matters were increased. Moreover, Abd El-Mageed (1994) stated that the high increase in ash content was mainly due to brining treatment of fish fillets before smoking process. The similar results were reported by Abd El-Mageed (1994) on cold and hot smoked silver carp, Mohamed (2018) on cold smoked mullet fish, El-Lahamy et al., (2018) on hot and cold smoked catfish fillets, Abo-Zeid (2020) on cold smoked catfish fillets and El-Sherif et al., (2021) on hot and cold smoked sagan fish**,** they decided that after smoking; moisture content was significantly decreased (*P> 0.05*) from 74.47% of fresh fish to 56.44% and 64.66% in hot and cold smoked fish samples, respectively while, the contents of crude protein, crude lipid, ash, sodium chloride and carbohydrates were significantly (P<0.05) increased; protein content was increased from 21.26% to 28.55% and 26.24%, lipid content was increased from 2.39% to 6.39% and 3.30%, ash content was increased from 1.70% to 8.14% and 5.21%, salt (NaCl) was increased from 0.20% to 3.95% and 3.32% and carbohydrate content was increased from 0.28% to 0.48% and 0.59% in hot and cold smoked sagan fish samples, respectively.

Table (1): Effect of smoking process on chemical composition of mullet fish obtained from farms 1 and 2 (w.w.)

Constituent (%)	Farm 1			Farm 2		
	Fresh fish	Smoked fish			Smoked fish	
		Cold	Hot	Fresh fish	Cold	Hot
Moisture	74.82 ± 0.086	63.22 ± 0.410	59.32 ± 0.290	72.10 ± 0.300	61.25 ± 0.080	58.06 ± 0.210
Crude protein	19.59 ± 0.158	24.75 ± 0.203	26.84 ± 0.215	19.34 ± 0.087	25.27 ± 0.100	27.42 ± 0.091
Lipid	4.28 ± 0.300	6.62 ± 0.100	7.91 ± 0.082	7.38 ± 0.113	7.82 ± 0.210	7.50 ± 0.311
Ash	1.23 ± 0.096	5.14 ± 0.035	5.61 ± 0.150	1.11 ± 0.205	5.22 ± 0.081	6.52 ± 0.181
Salt (NaCl)	-	3.17 ± 0.210	3.70 ± 0.095	-	3.35 ± 0.092	4.05 ± 0.140

Data are calculated as mean ± (SD) Standard deviation; (n=3), Farm 1: Irrigated from El-Batts drain, Farm 2: Irrigated from El-Wadi drain, w.w.: On wet weight basis.

3.2. Heavy metals of smoked mullet fish products

The heavy metal contents (lead, Pb; cadmium, Cd; and zinc, Zn) of raw and smoked mullet fish obtained from Farms (1 and 2) in Fayoum Governorate were shown in Table (2). The results indicate that the concentration of Pb in raw mullet fish from farm (1) was 0.103 (ppm) increased to 0.210 and 0.252 (ppm) after cold and hot smoking respectively, but the concentration in raw mullet fish from farm (2) was 0.052 (ppm) increased to 0.190 and 0.210 (ppm) after cold and hot smoking, respectively. Cd concentration in raw mullet fish from farm (1) was 0.215 (ppm) decreased to 0.109 and 0.170 (ppm) after cold and hot smoking, respectively, but the concentration in raw mullet fish from farm (2) was 0.120 (ppm) decreased to 0.075 and0.090 (ppm) after cold and hot smoking, respectively. Also, the concentration of Zn was 1.120 (ppm) in raw mullet fish from farm (1) increased to 1.760 and 1.980 (ppm) after cold and hot smoking, respectively, while the concentration in raw mullet fish from farm (2) was 0.880 (ppm) increased to 1.055 and 1.750 (ppm) after cold and hot smoking, respectively. These obtained data for investigated heavy metals were lower than the permissible limit (Pb, 2; Cd, 0.5 and Zn, 40 ppm) set by (EOS, 2005 and FAO⁄WHO, 1999). The reduction in trace metals concentrations as affected by cooking methods may be due to the release of these coagulated proteins bounded with metals, while the increase in metals may be related to decrease in the moisture content that occur during processing methods **(**Ersoy et al., 2006). Similar and non-similar results were found by many researchers, Amin et al., (2015) illustrated that heavy metals increased during fish smoking may indicate that some of the smoke constituents might react with the metals in fresh fish during the smoking process, forming water insoluble complexes, they determined many heavy metals in fresh and smoked catfish and tilapia and found that the levels

of Pb of fresh catfish and tilapia were 1.27 and 01.13 increased to 2.23 and 2.03 (ppm), respectively also Cd of fresh catfish and tilapia fish were 0.47 and 0.43 increased to 1.76 and 2.00 (ppm), respectively as affected by hot smoking. Shehata et al., (2018) reported that the value of Cd content in raw grass carp was 0.07 mg/100g sample decreased to 0.023 mg/100g of smoked grass carp treatment by 10% salt and 0.020 of smoked grass carp treatment by 16% salt, and they found that the Zn content was 9.92 mg/100g of raw grass carp increased to 24.38 mg/100g of smoked grass carp treatment by 10% salt and 18.80 mg/100g of smoked grass carp treatment by 16% salt.

Table 2. Effect of smoking process on heavy metals (w.w.) of mullet fish obtained from farms (1 and 2)

Heavy metals (ppm)	MPLs (ppm)	Farm 1			Farm 2		
		Fresh fish	Smoked fish		Fresh fish	Smoked fish	
			Cold	Hot		Cold	Hot
Lead (Pb)	2	0.103 ± 0.011	0.210 ± 0.003	0.252 ± 0.113	0.052 ± 0.021	0.190 ± 0.001	0.210 ± 0.112
Cadmium (Cd)	0.5	0.215 ± 0.020	0.109 ± 0.116	0.170 ± 0.005	0.120 ± 0.021	0.075 ± 0.210	0.090 ± 0.004
Zinc (Zn)	40	1.120 ± 0.009	1.760 ± 0.018	1.982 ± 0.051	0.880 ± 0.110	1.055 ± 0.014	1.750 ± 0.008

Data are calculated as mean ± (SD) Standard deviation; (n=3). Farm 1: Irrigated from El-Batts drain. Farm 2: Irrigated from El-Wadi drain. W.w.: On wet weight basis. MPLs: Maximum permissible limits as reported by EOS, 2005 and FAO/WHO, 1999.

4. CONCLUSION

From the results of present study it could be concluded that although the hot smoked samples of both two farms have a higher contents of crude protein, lipid and ash, but also, have a higher concentrations of heavy metals (Pb, Cd, Zn) than cold smoked products.

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