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## Effects of smoking processes on the nutritional value and fatty acid composition of Zander fish (*Sander lucioperca*)

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**2020SUMMARY:** This study aimed to estimate the nutritional quality of *Sander lucioperca* fillets and alterations in lipid quality following hot and cold smoking processes. Our results revealed that the total fat content of zander fil-lets was 1.86 g/100g. Polyunsaturated fatty acids (PUFAs) were higher than saturated and monounsaturated fatty acids in fresh tissue samples. Arachidonic, docosahexaenoic and eicosapentaenoic acids were the most abundant PUFAs. Differences in the fatty acid compositions of the smoked and fresh fillet were significant, with a decrease in (PUFAs) in the proportion of total fatty acids. The fatty acid profile of the neutral lipids was unchanged after the cold smoking process, whereas PUFAs decreased significantly during both smoking processes, especially the hot smoking process. Our findings showed a partial alteration of polar lipids. Both smoking treatments produced lipoperoxidation and lipid oxidation in the fillets. Other investigational smoking conditions should be tested to reduce such oxidation and hydrolysis in fillets, which could be susceptible to off-flavors and off-odors.

**KEYWORDS:** Fatty acids; Lipoperoxidation; Smoking treatments; Zander fillets

**RESUMEN:** Efectos de los procesos de ahumado sobre el valor nutricional y la composición de ácidos grasos de la *lucioperca* (*Sander lucioperca*). Este estudio tuvo como objetivo estimar la calidad nutricional de los filetes de *lucioperca* y las alteraciones en la calidad de los lípidos tras el proceso de ahumado en caliente y en frío. Nuestros resultados revelaron que el contenido total de grasa de los filetes de *lucioperca* fue de 1.86 g/100 g. Los ácidos grasos poliinsaturados (PUFA) fueron más altos que los ácidos grasos saturados y monoinsaturados en muestras de tejido fresco. Los ácidos grasos araquidónico, docosahexaenoico y eicosapentaenoico fueron los PUFA más abundantes. Las diferencias en la composición de ácidos grasos del filete ahumado y fresco fueron significativas, con una disminución de la proporción (PUFA) en los ácidos grasos totales. El perfil de ácidos grasos de los lípidos neutros se mantuvo sin cambios en el proceso de ahumado en frío, mientras que los PUFA disminuyeron significativamente durante ambos procesos de ahumado, especialmente en el proceso de ahumado en caliente. Nuestros resultados mostraron una alteración parcial de los lípidos polares. Ambos tratamientos de ahumado indicaron lipo-peroxidación y oxidación de lípidos en los filetes. Otras condiciones de ahumado se deben probar en investigación para reducir dicha oxidación e hidrólisis en los filetes, que podrían ser responsables de sabores y olores desagradables.

**PALABRAS CLAVE:** Ácidos grasos; Filetes de *lucioperca*; Lipoperoxidación; Tratamientos de ahumado

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## 1. INTRODUCTION

The *Sander lucioperca* (*S. lucioperca*) is an important freshwater fish species in Tunisian farming. It was introduced for the first time in Tunisia by the ONP (National Office of Fishing) in 1968 (CTA, 2009) in the dam of Nebhana using 30, 000 eggs which were incubated in floating boxes. Following its introduction, the recruitment of *S. lucioperca* in dams was made naturally and the stock recovered on its own. Currently, this species is present in most Tunisian dams (CTA, 2009). The production of *S. lucioperca* in Tunisian dams had a first phase which was characterized by an exponential increase of up to 192.4 tons in 2006. By 2010, the total capture of this species was estimated at 188.7 tons, representing 16.9% of the national production of freshwater fish in Tunisia. Most *S. lucioperca* production comes from the reservoir of Sidi Salem with an average of 84.28 tons/year, followed by the dams of Sidi Barrak with an average of 36.83 tons per year (DGPA, 2010).

The Tunisian fishery market is dominated by the marine species and the demand for freshwater fish is limited, despite their high nutritional value. The price of *S. lucioperca* is low and not adapted to the zander fishery costs. In order to develop the prospects for these markets, the image of fresh fish must be revitalized and its high nutritional qualities must be better shown. Like marine fish, *S. lucioperca* is a valuable source of nutrients and moisture (Guler *et al.*, 2007). In Tunisia, this specie is sold as a fresh product. The application of a smoking process is important to encourage the consumption of freshwater fish and to conserve the highest value of tissues with good acceptance. Smoking, such as hot, cold, liquid and electrostatic treatments, is considered the most traditional conservation method in marine products with lower value to ameliorate its taste and adopt its sensory proprieties such as taste, color... etc. (Ünlüsayin *et al.*, 2001). In addition, this traditional procedure has become a means of producing diversified products with high added value, since it offers an additional marketing preference for some aquatic species, such as freshwater fish, which are not so appreciated by consumers. In this context, the consumption of smoked freshwater fish has increased considerably in recent years because it preserves almost all the freshness of tissues (Rorvik, 2000).

Regardless of the diverse reports on the characteristics of *S. lucioperca* flesh, no information on lipid alteration or biochemical analysis of these freshwater fish is available following the smoking process. The aim of the current study was to assess the nutritional value of *S. lucioperca* fillets and the alterations in their lipid quality following hot and cold smoking treatments.

## 2. MATERIALS AND METHODS

### 2.1. Sample collection and preparation

*S. lucioperca* samples were caught in February 2016 during 13 fishing operations from the dam of Sidi El Barrak (Governorate of Beja, Northwest Tunisia, 37°01'N, 09°39'E). Sampling surveys were conducted during the daytime with the fishermen operating in the dams.

The fish samples were preserved in ice and transferred to the laboratory where they were weighed, measured de-headed and cleaned. The average weight and length of sampled fish were  $281 \pm 20.00$  g and  $47.00 \pm 3.56$  cm, respectively. The fillets were separated into three groups: (i) the first group consisted of the raw fillets stored at  $-40$  °C until analysis; (ii) the second group consisted of cold smoked fillets partially dried for 2 hours in the smoking chamber (Machado 1984) with temperature fluctuating from 30 to 35 °C, and kept at  $-40$  °C until analysis; (iii) the third group consisted of a hot smoked treatment using an industrial smoking chamber with a peripheral smoke generator (Gonçalves and Prentice-Hernández 1998a). This process of thermal treatment of fillets was conducted according to the following sequence: pre-drying of fish surface at 50–60 °C for 150 min, then hot smoking at 65–70 °C for 30 min and finally, steaming to obtain a temperature of 68–72 °C. Oak wood was used for both smoking processes. Finally, the fillets were chilled by cold air at 10 °C. Smoked fish fillets were then vacuum-packed in polyethylene bags, and kept at  $-40$  °C until analysis for a frozen period of 3 days.

### 2.2. Biochemical analysis

#### 2.2.1. Moisture

The moisture of *S. lucioperca* fillets was estimated according to the AOAC (1990) method by drying in an oven at 105 °C. The results were given as the percentage of wet weight ( $n = 6$ ).

#### 2.2.2. Ash

The Ash content of the fillets was evaluated by burning each sample for 12 h in an oven at 525 °C according to the AOAC (1995) method. The results were expressed as a percentage of the wet weight ( $n = 6$ ).

#### 2.2.3. Protein

The total protein content in *S. lucioperca* fillets was determined according to the method of Kjeldahl (AOAC, 1990). Our results were expressed as a percentage of the wet weight ( $n = 3$ ). Total protein content in the smoked and fresh fillets was

determined using the method of Kjeldahl (AOAC, 1990). The results were expressed as a percentage of the wet weight (n = 3).

#### 2.2.4. Lipid extraction and separation

The lipids were determined according to the Folch *et al.*, (1957) protocol. Ten grams of fresh or smoked fillet sample (n=6 for each fillet) were homogenized with a chloroform:methanol (1:2) mixture for 8–10 min at 4 °C using a Polytron homogenizer (Malaysia). The homogenate was added to 5 ml NaCl saturated solution and 20 ml chloroform with Butylated hydroxytoluene (BHT;50 ppm), and then homogenized for 7 min and 5 min, respectively. Then, 20 ml of distilled water were added and homogenized again for 1 min. The obtained mixture was incubated in and ultrasound bath for 10 min, and vacuum cleaner with Buchner funnel and chloroform. The organic fraction was extracted with a separating funnel, dried with sodium sulphate and evaporated to dryness in the rotary evaporator (Stuart™, UK). When evaluating, the obtained oil was solubilized in a known volume of chloroform with BHT (50 ppm) and stored at -20 °C (n = 6 for each sample). Neutral and polar lipids were isolated by liquid chromatography in a silica column (Isolute SPE column, UK) with the recovered elution of 60 ml hexane-diethyl ether (1:2) and 20 ml methanol, respectively.

#### 2.3. Fatty acid analysis

Fatty acid methyl esters (FAMES) were estimated according to the Lepage and Roy, (1986) protocol. The analysis was performed in a Varian Agilent 6890N gas chromatograph, equipped with an auto-sampler and fitted with a split/splitless injector and a flame ionization detector (FID). The separation was carried out in an Innowax 30x0.25 capillary column (25 m × 0.25 mm i.d., film thickness). The temperature was programmed from 180 to 200 °C at 4 °C/min, held for 10 min at 200 °C and heated to 210 °C at 4 °C/min, held at 210 °C for 14.5 min with injector and FID at 250 °C. The fatty acid compositions of the polar and neutral fractions were expressed as the percentage of total fatty acids (n = 6). The fatty acid contents in the total lipids of the fillets were calculated by using C21:0 as the internal standard (10 mg/ml) based on the peak area ratio (n = 6).

#### 2.4. Peroxide value (PV)

The peroxide value of the fillet samples was determined by the ferric thiocyanate method with slight modifications (Chapman and McKay, 1949) based on the ability of lipid peroxides to oxidize ferrous ions at a low pH. The resulting ferric ions reacted with thiocyanate and the concentration of

the complex formed was determined by spectrophotometry (Jenway 6315, UK) at 500 nm. The standard sample was determined by the reaction of a series of aliquots of 10 µg/ml iron (III) chloride standard solution, 10 mM ammonium thiocyanate, and a sufficient amount of chloroform/methanol mixture (7:3). The results were expressed in mequivalent of oxygen per kg of oil (meq O<sub>2</sub>/kg) (n = 3).

#### 2.5. Thiobarbituric acid reactive substances (TBARS)

The TBARS were assessed based on the AOAC (1998) method. An oil sample was solubilized in 1-butanol, mixed with 0.2% TBA in 1-butanol, incubated in a water bath for 2 hours at 95 °C and then cooled under tap water. The absorbance was determined using a spectrophotometer at 532 nm. The standard curve was established by the TBARS reaction of a series of aliquots of 0.2 mM TMP (1, 1, 3, 3-tetramethoxypropane) prepared in 1-butanol. The results were expressed as mg malonaldehyde/kg of oil (n = 3).

#### 2.6. Free fatty acids

Free fatty acids were evaluated according to the method described by Bernardez *et al.*, (2005). 50 mg of each sample were homogenized with cyclohexane and cupric acetate-pyridine reagent and stirred by vortex for 2 min and then centrifuged for 20 min at 9,000 rpm. The activity was detected at 710 nm. The analysis was developed with oleic acid, which used as a standard (n = 3).

#### 2.7. Statistical analysis

All calculations were performed using SAS software (Ver. 09.00). The paired student's test was used to compare the results.

### 3. RESULTS

#### 3.1. Proximate chemical composition

The changes in proximate composition of fresh and smoked *S. lucioperca* fillets are given in Table 1. The Total lipid and protein contents of fresh fillets amounted to 1.86 and 17.66%, respectively and ash content was recorded as 1.12%. Significant differences (P < 0.05) were noted for the moisture, ash, protein, and lipid contents of *S. lucioperca* edible fillets after the smoking process compared to fresh fillets. Also, significant differences in the proximate composition (P < 0.05) were found between the cold and hot processes. The results showed that lipid content increased considerably after the cold treatment (8.98%), and especially after hot smoking (13.24%). The moisture content in hot smoked fillets was

significantly ( $P < 0.05$ ) lower than the cold smoked one. The percentages of crude, protein and fat in smoked fillets were significantly ( $P < 0.05$ ) higher than the fresh ones. The highest value for protein ( $52.66 \pm 4.12\%$ ) and fat ( $13.24 \pm 1.72\%$ ) contents were recorded for the hot smoked fish.

### 3.2. Total fatty acids

The fatty acid composition of *S. lucioperca* fillets treated by hot and cold smoking processes is presented in Table 2. PUFAs (50.18%) represented the majority of total fatty acids in fresh fillets, followed by SFAs (25.1%) and MUFAs (16.9%). The amounts

of n-3 and n-6 PUFA were 29.47% and 24.12%, respectively, where arachidonic (AA, C20:4n-6) and docosahexaenoic acid (DHA, C22:6 n-3) were the most dominant ones.

Significant differences ( $P < 0.05$ ) were observed in the PUFA levels of fresh and smoking fillets. The level of SFAs increased with heat treatment, especially after the cold smoking treatment.

### 3.3. Fatty acids of neutral and polar lipids

The fatty acid compositions of the neutral and polar lipids of *S. lucioperca* fillets following the smoking process are given in Tables 3 and 4, respectively.

TABLE 1. Chemical composition (% on a wet weight basis) of *Sander lucioperca* fillets before (FZ) or after hot (HSZ) and cold (CSZ) smoking processes

	FZ	HSZ	CSZ	ANOVA
Moisture (%)	78.41 $\pm$ 1.32 a	27.65 $\pm$ 0.48 b	32.48 $\pm$ 0.28 c	***
Proteins (%)	17.36 $\pm$ 1.13 a	52.66 $\pm$ 4.12 b	46.22 $\pm$ 5.42 c	***
Lipids (%)	1.86 $\pm$ 0.12 a	13.24 $\pm$ 1.72 b	8.98 $\pm$ 1.81 b	***
Ash (%)	1.12 $\pm$ 0.01 a	4.66 $\pm$ 0.29 b	3.13 $\pm$ 0.21 c	***

Means (n=6) within rows with the same letter are not significantly different ( $P < 0.05$ ). ANOVA: Analysis of variance (One-way ANOVA, Tukey); \* Significance at 0.05; \*\* Significance at 0.01; \*\*\* Significance at 0.001. FZ: fresh zander; HSZ: hot smoked zander; CSZ: cold smoked zander.

TABLE 2. Fatty acid profile (% total fatty acids) of total lipids in *Sander lucioperca* fillets before (FZ) or after hot (HSZ) and cold (CSZ) smoking processes

Fatty acids	FZ	HSZ	CSZ	ANOVA
C14:0	3.71 $\pm$ 0.19 a	6.92 $\pm$ 0.01 b	5.01 $\pm$ 0.02 b	***
C16:0	11.23 $\pm$ 0.89 a	16.55 $\pm$ 0.06 b	14.41 $\pm$ 0.07 c	***
C18:0	5.48 $\pm$ 0.66 a	8.74 $\pm$ 0.02 b	6.31 $\pm$ 0.02 b	***
Other SFAs	4.81	6.42	5.22	-
Total SFAs	25.11 $\pm$ 0.08 a	38.52 $\pm$ 0.06 b	30.95 $\pm$ 0.07 c	***
C16:1 n-7	3.41 $\pm$ 1.51 a	2.45 $\pm$ 0.01 c	3.12 $\pm$ 0.02 c	***
C18:1 n-9	8.53 $\pm$ 2.40 a	6.16 $\pm$ 0.02 b	7.47 $\pm$ 0.02 c	***
C18:1 n-7	1.66 $\pm$ 0.51 a	0.98 $\pm$ 0.01 b	1.31 $\pm$ 0.01 b	**
Other MUFAs	3.42	2.07	3.12	-
Total MUFAs	16.91 $\pm$ 0.05 a	11.63 $\pm$ 0.08 b	15.02 $\pm$ 0.07 c	***
C18:2 n-6	4.82 $\pm$ 0.47 a	3.69 $\pm$ 0.01 b	4.48 $\pm$ 0.01 b	**
C20:4 n-6	11.84 $\pm$ 1.29 a	10.63 $\pm$ 0.01 b	11.07 $\pm$ 0.01 b	**
C20:5 n-3	7.37 $\pm$ 0.46 a	6.32 $\pm$ 0.01 b	6.25 $\pm$ 0.03 b	**
C22:5 n-3	2.30 $\pm$ 0.24 a	1.09 $\pm$ 0.00 b	2.07 $\pm$ 0.01 b	**
C22:6 n-3	19.81 $\pm$ 3.42 a	16.54 $\pm$ 0.02 b	17.14 $\pm$ 0.02 c	***
Other PUFAs	4.11	3.27	4.32	-
Total PUFAs	50.18 $\pm$ 0.13 a	41.54 $\pm$ 0.12 b	45.33 $\pm$ 0.16 c	***

Means (n=6) with the same letter within rows are not significantly different ( $P < 0.05$ ). (One-way ANOVA, Tukey): Analysis of variance; \* Significance at 0.05; \*\* Significance at 0.01; \*\*\* Significance at 0.001. FZ: fresh zander; HSZ: hot smoked zander; CSZ: cold smoked zander. Other SFAs: C15:0. C17:0; Other MUFAs: C20:1n-9; Other PUFAs: C16:2n-4. C16:3n-4. C18:3n-3. C20:2n-9. C20:3n-6. C20:4n-3.

TABLE 3. Fatty acid compositions (% of total fatty acids) of neutral lipids in *Sander lucioperca* fillets before (FZ) or after hot (HSZ) and cold (CSZ) smoking processes

	Neutral Lipids			ANOVA
	FZ	HSZ	CSZ	
C14:0	2.98 ±0.21a	3.06 ±0.17a	3.18 ±0.29a	NS
C16:0	21.51 ±1.04a	23.25 ±0.94a	21.54 ±0.74a	NS
C18:0	3.24 ±0.17a	5.63 ±0.23b	5.72 ±0.19b	**
Other SFAs	1.63	1.69	1.48	
Total SFAs	29.36 ±0.34a	33.63 ±0.32b	31.92 ±0.61a	*
C16:1 n-7	10.99 ±0.32a	8.78 ±0.19a	9.87 ±0.32a	NS
C18:1 n-9	11.56 ±0.34a	13.11 ±0.28a	11.74 ±0.48a	NS
C18:1 n-7	0.83 ±0.15a	0.92 ±0.11a	0.94 ±0.13a	NS
Other MUFAs	0.11	0.34	1.07	
Total MUFAs	23.49 ±0.27a	23.15 ±0.19a	23.62 ±0.29a	NS
C18:2 n-6	7.69 ±0.32a	10.72 ±0.31a	10.55 ±0.32a	NS
C20:4 n-6	12.36 ±0.11a	14.11 ±0.05a	13.28 ±0.09a	NS
C20:5 n-3	3.73 ±0.13a	3.21 ±0.08a	2.67 ±0.11b	**
C22:5 n-3	1.15 ±0.08a	0.89 ±0.04b	1.17 ±0.16a	*
C22:6 n-3	9.73 ±0.17 b	8.08 ±0.13 a	8.68 ±0.21a	*
Other PUFAs	2.13	1.91	2.15	
Total PUFAs	36.79 ±0.21 b	38.92 ±0.17 a	38.45 ±0.24a	*

Means (n = 6) with the same letter within rows are not significantly different (P < 0.05). (One-way ANOVA, Tukey): Analysis of variance; \* Significance at 0.05; \*\* Significance at 0.01; \*\*\* Significance at 0.001. FZ: fresh zander; HSZ: hot smoked zander; CSZ: cold smoked zander. Other SFAs: C15:0. C17:0; Other MUFAs: C20:1n-9; Other PUFAs: C16:2n-4. C16:3n-4. C18:3n-3. C20:2n-9. C20:3n-6. C20:4n-3.

TABLE 4. Fatty acid compositions (% of total fatty acids) of polar lipids of *Sander lucioperca* fillets before (FZ) or after hot (HSZ) and cold (CSZ) smoking processes

	Polar Lipids			ANOVA
	FZ	HSZ	CSZ	
C14:0	3.04 ±0.11a	3.28 ±0.08a	3.22 ±0.13a	NS
C16:0	24.16 ±1.36a	22.02 ±1.18a	20.50 ±1.21a	NS
C18:0	5.05 ±0.12a	8.00 ±0.27b	7.23 ±0.25a	*
SFAs	34.25 ±0.27b	33.3 ±0.36b	30.95 ±0.37a	**
C16:1 n-7	5.45 ±0.26a	5.92 ±0.31a	5.64 ±0.38a	NS
C18:1 n-9	19.38 ±0.56a	19.73 ±1.02a	18.49 ±0.21a	NS
C18:1 n-7	2.30 ±0.21a	2.93 ±0.21b	2.78 ±0.08b	*
Other MUFAs	0.38	0.37	0.42	
Total MUFAs	27.51 ±0.36a	28.95 ±0.45b	28.33 ±0.24b	***
C18:2 n-6	7.72 ±0.08b	7.67 ±0.07c	7.66 ±0.09c	*
C20:4 n-6	22.19 ±0.09a	18.39 ±0.11b	16.94 ±0.13b	**
C20:5 n-3	3.70 ±0.26a	2.94 ±0.21b	3.13 ±0.23ab	*
C22:5 n-3	0.97 ±0.12a	0.66 ±0.06b	0.88 ±0.07a	**
C22:6 n-3	12.00 ±0.29a	10.88 ±0.16b	11.11 ±0.28c	***
Other PUFAs	4.02	4.15	4.07	
Total PUFAs	40.6 ±0.24b	34.69 ±0.11c	33.79 ±0.21c	***

Means (n = 6) with the same letter within rows are not significantly different (P < 0.05). (One-way ANOVA, Tukey): Analysis of variance; \* Significance at 0.05; \*\* Significance at 0.01; \*\*\* Significance at 0.001. FZ: fresh zander; HSZ: hot smoked zander; CSZ: cold smoked zander. Other MUFAs: C20:1n-9; Other PUFAs: C16:2n-4. C16:3n-4. C18:3n-3. C20:2n-9. C20:3n-6. C20:4n-3.



### 3.3.1. Neutral lipids

PUFAs constitute the majority of the fatty acids of neutral lipids, followed by SFAs and MUFAs. Within each of these groups, the major fatty acids were palmitic acid (C16:0), oleic acid (C18:1n-9), and arachidonic acid (C20:4n-6), respectively. The amounts of saturated, monounsaturated and polyunsaturated fatty acid remained stable after the cold smoking process. Saturated and polyunsaturated fatty acids exhibited significant ( $P < 0.05$ ) modifications after the hot smoking process.

### 3.3.2. Polar lipids

The polar lipids showed a profile similar to neutral lipids. PUFAs were also the major group, with total amounts ranging from 33.8 to 40.6% of total fatty acids. Within this group, the main fatty acid was arachidonic acid (C20:4n-6). Based on Duncan's test, PUFAs were reduced significantly ( $p < 0.05$ ) during both smoking processes to reach 34.7 and 33.8% in hot and cold smoked samples, respectively.

### 3.4. Lipid peroxidation

Changes in the peroxide value (PV), thiobarbituric acid reactive substances (TBARS) and free fatty acids (FFAs) of *S. lucioperca* fillets following hot and cold smoking processes are given in Table 5. The results showed that the smoking process had a significant effect ( $p < 0.05$ ) on the development of primary oxidation products in the fillets which was indicated by a higher PV level measured in hot smoked fillets.

In fresh fillets, the TBARS value was given as 0.49 mg MA/kg oil. However, a slight elevation in TBARS between smoking treatments was noted in the hot (1.31 mg MA/kg) and cold (0.78 mg MA/kg) smoked fillets.

The percentage of FFAs in fresh *S. lucioperca* is presented as 1.25% of total lipids. FFA increased significantly ( $P < 0.05$ ) after the smoking process compared to fresh fish to reach 2.27% and 4.29% in cold and hot smoked fillets, respectively.

## 4. DISCUSSION

The total lipid and protein contents of fresh fillets were similar to those found in other species from freshwater, such as *Clarias gariepinus* (Kumolu-Johnson and Ndimele, 2001). Generally, the lipid content of the fillets varied among species (1.46 to 5.77 g/100g) and was affected by the fishing season (1.20 to 18.4 g/100g) (Osman *et al.*, 2001). The ash levels of fresh fillets were similar to those found in other freshwater species such as *Ctenopharyngodon idella* and *Cyprinus carpio* (Afkhami *et al.*, 2011). The apparent increases in lipid as well as some proximate component contents after both cold and hot smoking were mainly due to water loss by evaporation during the process. These increases were more pronounced after the hot smoking process than the cold one. In the current experiment, the difference between cold and hot smoking treatments could be attributed to the fillet composition, thickness, and weight, as well as to the smoking temperature and time. These findings are in agreement with those described by De Souza Franco *et al.*, (2010) for Matrinxa fillets, in that the final moisture content was about 25% after hot and cold smoking processes.

The fatty acid profile reflects the highest nutritional quality of zander, which was similar to a previous study (Guler *et al.*, 2007). Several reports have evidently shown the importance of fish lipids especially long-chain n-3 PUFAs for human health and nutrition (Sidhu, 2003). Significant differences ( $p < 0.05$ ) were found in SFAs and PUFAs of the edible fillets after the smoking process as well as between the cold and hot processes. The apparent increases in the SFA amount, especially after hot smoking was mainly due to water loss by evaporation during this process.

The major fatty acids for the group of neutral lipids were palmitic acid (C16:0), oleic acid (C18:1n-9), and arachidonic acid (C20:4n-6). The high levels of C18:1 and C16:0 were in harmony with other reports (Osman *et al.*, 2001; Passi *et al.*, 2002), where the major SFAs and MUFAs identified in the fish lipids typically enclosed 16 and 18 carbon atoms,

TABLE 5. Peroxide value (PV), TBARS and free fatty acids (FFA) of in total lipids of *Sander lucioperca* fillets before (FZ) or after hot (HSZ) and cold (CSZ) smoking processes

	FZ	HSZ	CSZ	ANOVA	Acceptable limit
PV (meq active O <sub>2</sub> /kg lipids)	0.74 ± 0.05 a	3.46 ± 0.13 b	2.63 ± 0.13 c	***	10–20 meq/Kg (Connell 1975)
TBARS (mg MDA/kg lipids)	0.49 ± 0.05 a	1.31 ± 0.09 b	0.78 ± 0.08 c	***	8 mg MDA/kg (Ozden and Erkan, 2006)
FFA (g /100g lipids)	1.25 ± 0.16 a	4.29 ± 0.12 b	2.27 ± 0.18 c	***	7 g/100g (IFOMA, 1981)

PV: Peroxide Value. TBARS: Thiobarbituric Acid Reactive Substances. MDA: malondialdehyde. FFA: free fatty acids.

Means (n = 3) with the same letter within rows are not significantly different ( $P < 0.05$ ).

(One-way ANOVA, Tukey): Analysis of variance; \* Significance at 0.05; \*\* Significance at 0.01; \*\*\* Significance at 0.001.

FT: fresh zander; HSZ: hot smoked zander; CSZ: cold smoked zander.

respectively. The noticeable reduction in PUFAs may indicate the degradation of these unsaturated fatty acids throughout smoking treatments. Such results were confirmed by the higher increases in PV and TBARS levels from the hot process than the cold one.

Polar lipids were similar to the neutral ones after both cold and hot smoking processes. In fact, PUFAs showed a significant variation after the hot smoking process. Such declines were in line with Azad Shah *et al.*, (2009), who reported significant decreases in PUFAs in herring filets during the smoking process. Because of its great amount of unsaturation, DHA declined by 26.5% after the hot smoking process. PUFAs are particularly susceptible to oxidation and degradation processes through enzymatic and chemical oxidation, which produces a large amount of volatile compounds (Kolakowska, 2002). The oxidative phenomena of membrane lipids might be one of the factors involved in the development of the distinguishing taste and flavor of the analyzed filets during the smoking process. Triqui and Reineccius (1995) showed that lipid oxidation was associated with the decline in n-3 PUFAs, which was probably related to the change in the flavor in anchovy flesh during ripening.

The levels of peroxide value, malonaldehyde (thiobarbituric acid reactive substances) and free fatty acids of *S. lucioperca* filets following hot and cold smoking processes were lower than the values reported for *Euthynnus lineatus* (Chaijan *et al.*, 2006). Higher PV levels were possibly due to the hot temperature of smoking and the high content of polyunsaturated fatty acids known to be very sensitive to oxidative reactions. Previous reports by Hawrysh (1990) showed that lipid oxidation occurs when oxygen molecules react with unsaturated fatty acids to produce lipoperoxides, which are influenced by various elements such as temperature, water activity, pH, and chemical environment (Ashie *et al.*, 1996). According to Connell (1995), the acceptable limit for human consumption of PV of oils is 20 meq O<sub>2</sub>/kg oil. In our present study, none of the analyzed fillet oil samples reached such a value after the hot smoking process. Furthermore, hydroperoxides are decomposed into a wide range of carbonyl compounds, such as aldehydes, ketones, and other compounds which contribute to off flavors in foods as well as color and texture deteriorations (Kolakowska, 2002). Consequently, the increase in secondary oxidation products was determined through the thiobarbituric acid reactive substances.

The initial value for TBARS was 0.49 mg MDA/kg oil, signifying that lipid oxidation did not take place during the post-mortem treatment. Our experimental analysis showed that TBARS levels increased in both smoked filets to reach a value of 1.31 and 0.78 mg MA/kg oil after hot and cold smoking, respectively, which was below the

permissible limit reported by (Ozden and Erkan, 2006). Goulas and Kontominas (2005) revealed that the initial TBA value of chub mackerel (*Scomber japonicus*) amounted to 0.23 mg MDA/kg oil, with this value reaching 0.54 and 0.47 mg MDA/kg after the application of hot and cold smoking processes. The higher TBA value noted with the smoking procedure could be attributed to the dehydration of fish filets and to the augmented oxidation of unsaturated fatty acids as a consequence of smoking at moderately high temperatures (up to 70 °C). Our results were in line with others given by Goktepe and Moody (1998), who detected a two-fold elevation in the TBA value of catfish filets after smoking at a temperature up to 82 °C.

Free fatty acids (FFAs) were determined as a marker of lipolysis in the smoked filets of *S. lucioperca*. The hydrolysis of acylglycerol esters (mainly triacylglycerols) is one of the imperative changes occurring in fish muscle lipids during post-mortem with the discharge of FFAs. In general, the development of FFAs in fish oil during storage is known to be related to some features such as the initial lipid content, the lipolytic activity and the temperature. The percentage of FFAs in fresh *S. lucioperca* represented 1.25% of total lipids. Such a level was lower than those found in herring oil by Aidos *et al.*, (2001). Usually, the FFA content in crude fish ranges from 1 to 7% (Bimbo, 1998). The FFA level increased significantly ( $p < 0.05$ ) after the smoking process compared to fresh fish to reach 2.27% and 4.29% of total fatty acids in cold and hot smoked filets, respectively. Increases were significantly different between both treatments as well. Our obtained results indicated that both treatments were under the acceptable limit (IFOMA, 1981). Such a rise suggested that *S. lucioperca* lipid hydrolysis was produced by lipases or phospholipases, particularly in the hot smoking process. Azad Shah *et al.*, (2009) reported that free fatty acid contents increased from 4.6 to 5.1% within 4 days of natural drying and then progressively increased up to 6.86% after 10 days.

## 5. CONCLUSIONS

The results showed that hot and cold smoking processes have significant effects on lipid quality. PV, TBARS and FFA levels increased more after the hot smoking process than the cold one, indicating a partial degradation of lipids. Our results suggest that *S. lucioperca* is a good source of lipids for the human diet. It is recommended to use the cold smoking process since it better conserves the chemical composition of tissues. Additional investigation on smoking conditions should be carried out to minimize such oxidation and hydrolysis in filets, which could be associated to off-flavors and off-odors.

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