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EXAMINATION OF MACRO AND MICRO ELEMENTS IN *PSETTA MAKSIMA* AND *SOLEA VULGARIS* FROM THE BLACK AND NORTH EASTERN MEDITERRANEAN SEAS

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ABSTRACT. The objective of this study was to determine the levels of essential (Ca, K, Na, Mg, Co, Cu, Cr, Fe, Mn) and non-essential (Al, As, Ba, Cd, Ni, Pb, Sr, Li, B) elements in the muscle, liver and skin of *P. maxima* and *S. vulgaris.* Analysis of variance was performed to determine significant differences among tissues. There were no significant differences in the metal concentrations among the tissues of both species with the exception of Fe and Li. The levels of essential metals such as Na, K, Ca and Mg were higher than 10 mg/kg; Fe and Cu were lower than 10 mg/kg. The results showed that the *P. maksima* and S*. vulgaris* are a good dietary source of essential nutrients. However, the concentrations of some non-essential metals in tissues of *P. maksima* and *S. vulgaris* exceeded the acceptable values for human consumption.

Keywords: *Psetta maksima, Solea vulgaris, elements, minerals, heavy metals.*

INTRODUCTION

Due to the increased interest in defining the biological roles of nutrients and their function in the ethology of chronic diseases, knowledge of dietary nutrient intake is needed to optimize human health [1].

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Fish flesh is an important source of minerals. The contents of K, Na, Mg and Ca are up to 10 mg/kg, whereas those of Fe and Cu are less than 10 mg/kg [2-4]. Many elements, which are present in seafood, are essential for human life at low concentrations and, however, they can be toxic at high concentrations. Therefore, many consumers regard any presence of these elements in fish as a hazard to health [5].

For the normal metabolism of fish, the essential metals must be taken up from waters, food or sediment. However, similar to the route of essential metals, non-essential ones are also taken by fish and accumulate in their tissues. Ecological need, sex, size and molt of marine animals were also found to affect metal accumulation in their tissues [6].

Many studies have been conducted on the elements in tissues of fish species in different parts of the world [7-14]. A few studies were done for metals in tissues of the *S. vulgaris* in literature, but it was not reported in Turkey. Moreover, there is no data for the *P. maxima* in literature.

The objective of this study was to determine the levels of both the various essential (Ca, K, Na, Mg, Co, Cu, Cr, Fe, Mn) and non-essential (Al, As, Ba, Cd, Ni, Pb, Sr, Li, B) elements in the muscle, liver and skin of two commercially valuable fish species *P. maxima* from the Black Sea and *S. vulgaris* from Iskenderun Bay, North Eastern Mediterranean Sea.

RESULTS AND DISCUSSION

The concentrations of the macro-microelements analysed in the muscle, liver and skin of *P. maksima* and *S. vulgaris* with means ± standard deviation are given in Table 1 and Table 2.

Analysis of variance was performed to determined significant differences among tissues. Results from this analysis showed that there were no significant differences between the metal concentrations in the tissues of both species with the exception of Fe and Li.

The content (mg/kg) of muscle was 2931.27±234.48 mg Na, 443.03±112.25 mg K, 414.73±132.82 mg Ca, 1744.38±309.36 mg Mg. The levels of macro elements Na, K, Ca and Mg in a given muscle were always higher in *P. maksima* than in *S. vulgaris*. In *P. maksima*, the concentrations of Na, K, Ca, Mg were highest in muscle. However, the highest concentrations in tissues of *S. vulgaris* were found in the liver and skin.

The Ca and K values in muscle of fish samples are lower and the Na, Mg values are higher than that reported in *M. potassou, M. merluccius, S. vulgaris* from Mediterranean (Spain) and similar results reported from Baltic Herring [15-16].

Table 1. Levels (mg metal/kg, wt) of metals in the muscle, liver and skin of *P. maksima.*

Element	Muscle	Liver	Skin
Na	2931.27±234.48*	2716.87±589.09	2787.44±249.51
K	443.03±112.25	132.93±42.79	318.20±160.12
Ca	414.73±132.82	283.25±50.01	289.73±50.01
Mg	1744.38±309.36	1191.78±104.03	1729.56±361.22
Fe	3.26±1.58[a]	64.67±31.53[b]	4.48±1.82[a]
Cu	15.49±8.12	3.85±1.51	12.79±6.38
Mn	0.83±0.15	10.50±4.89	6.82±0.50
Ba	3.05±1.09	5.92±0.43	3.96±1.25
Li	4.35±1.71[a]	8.59±2.32[b]	8.59±0.55[b]
Ni	7.08±1.35	27.83±4.58	8.28±5.66
As	2.42±0.36[b]	4.78±1.29	2.16±0.13
Al	3.68±0.29[a]	2.58±0.68	3.56±2.06
B	ND	ND	ND
Cd	0.13±0.09[b]	0.15±0.10	0.14±0.09
Co	0.71±0.06 [a]	0.35±0.11	0.37±0.05
Cr	0.61±0.05[a]	0.32±0.16	0.78±0.31
Pb	1.11±0.05[a]	0.54±0.33	2.24±1.70
Sr	0.31±0.14	0.53±0.14	1.28±0.86

ND: Not determined [below the limits of detection].

*Standard deviation is given with ±, n=3 within the column values with different letters are significantly different ($P<0.05$), values without letters are not significantly different ($P>0.05$).

The Na, K, Ca, and Mg concentrations in liver of *P. maksima* and *S. vulgaris* were 2716.87-3147.34 mg/kg, 132.93-394.98 mg/kg, 283.25-382.82 mg/kg, 1191.78-2030.87 mg/kg, respectively. The Na, Ca, Mg values in muscle and liver of fish samples are higher than those obtained by Ersoy in ten fish species from different region of North Eastern Mediterranean Sea (Turkey) [17]. The K value was found lower than reported [17].

The Na, K, Ca, and Mg levels in skin of *P. maksima* and *S. vulgaris* ranged between 2787.44-3074.19 mg/kg, 318.20-714.49 mg/kg, 289.73-284.20 mg/kg, 1729.56-1160.62 mg/kg, respectively. Although skin is a consumed part of the fish, it has not been investigated in previous studies.

Fe concentrations in muscle, liver and skin ranged between 3.26-64.67 mg/kg for *P. maksima* and ranged 3.42-112.90 mg/kg for *S. vulgaris*. The Fe concentrations in liver of two fish species-as opposed to the skin

and muscle increased significantly ($P<0.05$). The organs, such as the liver, gonads, kidney and gills are metabolically active tissues and accumulate metals of higher levels [18-19].

Table 2. Levels (mg metal/kg, wt) of metals in the muscle, liver and skin of *S. vulgaris.*

Element	Muscle	Liver	Skin
Na	2064.85±365.02*	3147.34±332.06	3074.19±1087.69
K	330.78±62.60	394.98±342.45	714.49±10.03
Ca	232.41±16.39	382.82±193.62	284.20±117.08
Mg	1726.19±155.42	2030.87±1500.60	1160.62±107.23
Fe	3.42±0.45[a]	112.90±45.60[b]	32.06±08.95[a]
Cu	11.90±4.62	58.17±48.20	4.54±1.63
Mn	8.04±3.92	9.01±6.41	1.72±0.40
Ba	4.35±1.44	2.09±1.38	8.29±6.40
Li	9.41±3.52	24.50±21.91	4.18±1.45
Ni	16.13±9.71	12.13±7.61	6.84±0.86
As	12.07±0.19[b]	2.98±1.18	1.57±0.48
Al	3.06±1.17	2.47±0.72	4.49±2.63
B	ND	ND	ND
Cd	0.39±0.04[b]	0.20±0.14	0.17±0.01[a]
Co	0.34±0.05[b]	0.20± 0.19	0.44±0.05
Cr	0.02±0.01[b]	0.37±0.06[a]	13.33±0.21 [a]
Pb	0.71±0.60	1.41± 1.20	1.65±0.16
Sr	1.00±0.14	1.39±0.56	4.24±2.90

ND: Not determined [below the limits of detection].

*Standard deviation is given in parenthesize, n=3 within the column values with different letters are significantly different ($P<0.05$), values without letters are not significantly different ($P>0.05$).

The Fe level in muscle of fish samples was similar to those reported by numerous studies in fish species from different areas [13, 20-22]. The Fe values in liver are similar to reported by Ersoy and Yilmaz in different fish species [13, 17].

The Fe levels (4.48-32.06 mg/kg) in skin of both species are lower than that reported by Yilmaz in *M. cephalus* and *T. mediterraneus* from Iskenderun Bay [23].

The Mn values in tissues of fish samples ranged from 0.83 to10.50 mg/kg for *P. maksima* and ranged from 1.72 to 9.01 mg/kg for *S. vulgaris*. The Mn levels in muscle of *P. maksima* and *S. vulgaris* was similar to those reported by numerous studies in fish species from different areas [9,17,20,21]. The Mn values in liver were higher than that reported by Ersoy [17]. There is no data concerning Mn level in skin of fish.

The Cu concentrations in muscle, liver and skin ranged from 3.85 to 15.49 mg/kg for *P. maksima* and ranged from 4.54 to 58.17 mg/kg for *S. vulgaris*. The Cu results in muscle of *S. vulgaris* reported by other researcher were much lower than our values [8,9,15]. However, the values in liver of this species are similar to our values determined in liver. On the other hand, the values in muscle of *P. maksima* and *S. vulgaris* are similar to those reported [24]. The Cu level in skin of fish samples is similar to those obtained by Yilmaz [13, 23].

According to the regulations which made by commission of European Union and Turkey, permissible limit for Cu in muscle of fish is 20 mg/kg wet weight [25]. The Cu levels in muscle of both species were not exceed given consumption levels. The Pb values in muscle, liver and skin of fish samples were 0.71-1.11 mg/kg, 0.54-1.41 mg/kg, 1.65-2.24 mg/kg, respectively. The Pb concentrations in muscle of two fish species are similar to those reported by Yilmaz [23]. However, some researcher reported that the Pb concentrations in muscle and liver of different fish species from other areas were much lower than in Pb values determined in our study [20,26]. The Pb values in skin of fish samples were lower than obtained by Yilmaz [23].

The Cd concentrations in muscle, liver and skin ranged between 0.13, 0.15 and 0.14 mg/kg for *P. maksima* and between 0.39, 0.20 and 0.17 mg/kg for *S. vulgaris*, respectively. The results of Cd levels in muscle and liver of *S. vulgaris* are similar to those reported for the *S. vulgaris* from other areas [8-9]. The Cd results in muscle of *P. maksima* and *S. vulgaris* in agreement with those reported in numerous studies [6,21,28]. There is no data concerning the Cd values in skin of fish. The Cd value in muscle of *P. maksima* and *S. vulgaris* exceed acceptable value for Cd in muscle of fish is 0.1 mg/kg wet weight for human consumption designated by the regulations [25]. From the fish health point of view, the Cd value in muscle of fish samples may also be considered as an important warning signal.

As concentrations in muscle, liver and skin for *P. maksima* were 2.42, 4.78 and 2.16 mg/kg, respectively. These values for *S. vulgaris* were 12.07, 2.98 and 1.57 mg/kg, respectively. The As values in muscle and liver of *S. vulgaris* were much higher in the same species [9,21]. Mormede & Davies found lower levels of As in different fish from the Rockall Trough [26]. The As

levels in muscle of fish is 1 mg/kg wet weight due to the regulations in Turkey [25]. The As value in muscle of fish samples exceed acceptable values. Especially, The As values in muscle of *S. vulgaris* were significantly high.

The Cr and Ni concentrations in muscle for fish species obtained were 0.02-0.61 mg/kg and 7.08-16.13 mg/kg, respectively. The Cr values muscle of fish samples are similar to those obtained by numerous studies in fish from different areas [7,9,20]. However, some researchers found much higher levels of Cr in muscle of North Eastern Mediterranean fish [6,29].

The Cr and Ni concentrations in liver of fish samples were found 0.32-0.37, 12.13-27.83 mg/kg, respectively. The Cr contents in liver of *P. maksima* and *S. vulgaris* was lower than reported in Mediterranean Fish [6,29]. However, lower values of Cr found in *S. vulgaris* from other areas [9]. Ni concentrations in muscle and liver for *S. vulgaris* and *P. maksima* were higher than reported [6,29]. The Cr and Ni values in skin of *P maksima* were 0.78 mg/kg and 8.28 mg/kg. However, the values of *S. vulgaris* in skin were 13.33 mg/kg Cr and 6.84 mg/kg Ni. The Cr values in skin of fish samples are similar for *M. cephalus* and *T. mediterraneus* [23]. Whereas the Ni content is skin was higher than reported by the same researcher [23].

The Co concentrations in muscle, liver and skin of *P. maksima* were 0.71, 0.35 and 0.37 mg/kg, respectively. This values for *S. vulgaris* were 0.34, 0.20, 0.44 mg/kg, respectively. The results of Co in muscle of *P. maksima* and *S. vulgaris* are similar to those reported for fish from Black Sea Coast in Turkey [20]. These results in muscle were lower than reported [28]. The concentrations in liver and skin of fish have not been studied in previous works.

The Al concentration in muscle of *S. vulgaris* and *P. maksima* was 3.06 and 3.68 mg/kg, respectively. The Al concentrations in liver and skin of fish ranged from 2.7 to 4.48 mg/kg. There is no data concerning the Al values in tissues.

The Ba, Li, Sr and B were also obtained in different tissues of *P. maksima* and *S. vulgaris*. The Ba concentrations in tissues of both species ranged from 2.09 to 8.29 mg/kg. The Li concentration in tissues of fish samples ranged between 4.18-24.50 mg/kg. The Li values in muscle of *P.maksima* reduced significantly ($P<0.05$) according to liver and skin of the same species. The Sr concentrations in muscle, liver and skin of two fish species were between 0.31-1, 0.53-1.39, 1.28-4.24 mg/kg, respectively. The B concentrations in muscle, liver and skin of fish samples were not detectable (below limits of detection). Unfortunately, there are no data concerning the Ba, Li, Sr and B concentrations in muscle, liver and skin of the marine fish.

CONCLUSIONS

The elements in tissues of *P. maksima* have not been investigated in previous studies. Data concerning mineral content of *S. vulgaris* was not reported in Turkey. Hence, the present study might be accepted as representative data for *P. maksima* and *S. vulgaris* that the species are studied firstly at this region.

The obtained results provided evidence that the studied *P. maksima* and S*. vulgaris* are a good dietary source of essential macro-micronutrients and the levels of some metals were even higher than acceptable values for human consumption.

These results can also be used to test the chemical quality of the marine food, in order to evaluate the possible risk associated with their consumption by human.

Further studies are needed to determine these minerals might have on the health of the consumer.

EXPERIMENTAL SECTION

Materials and Methods

Samples Preparation

The *P. maksima* samples were obtained from Şile in the Black Sea Coast and *S. vulgaris* samples were obtained from Iskenderun Bay in North eastern Mediterranean Sea.

Periodically taken fishes samples were kept in cold iced boxes and transported into Mustafa Kemal University, Science, Research and Application Center (MKUFAM), Tayfur Sökmen Campus, Antakya, as soon as probable under standard conditions. MKUFAM Lab was completed digestion and elements analyses.

Digestion Procedures

For analyses, approximately 0.5 g sample was digested with 10 mL high purity nitric acid (Merck) in CEM® Mars5 (Version 045012) microwave. The conditions of the digestion are 10 min. for ramp time, 10 min hold time at 210°C and 200 Psi. After digestion the samples filtered through Whatman®quantitative (No: 42, 110mm*) filter papers. Laboratory grade hydrochloric acid is added into the initial digested and the sample is refluxed. This digested samples are filtered and the filter paper and residues are rinsed with hot hydrochloric acid and then hot reagent water. Filter paper and residue are returned to the digestion flask, refluxed with extra hydrochloric

and then filtered again. The digested portion is then diluted to a final volume of 20 ml [30]. A blank digest was carried out in the same way. All metals were determined against aqueous standards.

At least three replicates for each sample was prepared in order to increase sensitivity in readings.

Analytic Procedures

Determination of all metal concentrations was carried out by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Varian model-Liberty Series II). For the calibration of the ICP-AES a High Purity® Multi Standards was used. The following emission lines were used; As 189.041, Ca 393.366, Cd 228.802, Co 228.616, Cr 367.716, Cu 324.754, Fe 259.940, K 766.490, Mg 279.553, Mn 257.610, Na 588.995, Ni 221.647, Pb 220.353, Al 396.152, Ba 455.403, Sr 407.771, Li 670.784, B 249.773. Metal concentrations were calculated mg/kg wet weight.

Statistical Analysis

Analysis of variance was used to evaluate the analysis data, and significant differences among means were determined by One-way analysis of variance (ANOVA) and Duncan's Multiple Range Test (P=0.05) (SPSS 12 for windows).

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