Research Article
Turkish Journal of Maritime and Marine Sciences Volume: 1 Issue: 1 (2015) 10-17

Some Essential Macroelements in the Muscles of *Argyrops spinifer* from Karachi Harbour, Pakistan

Pakistan'ın Karaçi Limanından Toplanan *Argyrops spinifer'in* Kaslarında Bazı Temel Makroelementler

Türk Denizcilik ve Deniz Bilimleri Dergisi Cilt: 1 Sayı: 1 (2015) 10-17

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ABSTRACT

In the current study the concentrations of Mg, Ca, K and Na in the muscles of *Argyrops spinifer* from Karachi Harbour, Pakistan during different seasons of February 2014 to January 2015 were measured. The mean concentrations (±SD) of Mg, Ca, K and Na were 247±59, 403±79; 160±46 and 278±52 µg g^{-1} dry wt., respectively. There were no differences in the concentrations of macroelements between seasons (P>0.05). The levels of macroelements in edible muscle of *A. spinifer* from Karachi Harbour in Pakistan were well below than the maximum levels set by international law and, therefore, the muscle tissues of the samples analysed were fit for human consumption in this region.

Keywords: Macroelements, Mg, Ca, K, Na, *Argyrops spinifer*, Karachi Harbour

Article Info
Received: 31 March 2015
Revised: 7 April 2015
Accepted: 8 April 2015

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ÖZET

Mevcut çalışmada Pakistan'ın Karaçi limanından Şubat 2014 ile Ocak 2015 tarihlerinde farklı sezonlarda toplanan *Argyrops spinifer* etlerindeki Mg Ca, K ve Na konsantrasyonları ölçülmüştür. Mg Ca, K ve Na'un ortalama konsantrasyonları (±SD) sırasıyla 247±59, 403±79; 160±46 ve 278±52 µg g^{-1} kuru ağırlık olarak bulunmuştur. Sezonlar arası makroelement konsantrasyonlarında bir farklılık yoktur ($P>0.05$). Pakistan'ın Karaçi limanından toplanan *A. spinifer*'in yenilebilir kas dokularındaki makroelement düzeyleri uluslararası yönetmeliklerde belirtilen maksimum değerlerin altında bulunmuş ve analizi yapılan kas dokuları örnekleri bu bölgedeki insan tüketimi için uygun bulunmuştur.

Anahtar sözcükler: Makroelementler, Mg, Ca, K, Na, *Argyrops spinifer*, Karaçi limanı

1. Introduction

Fish is consumed readily in most countries because of their high protein supplies, essential amino acids, vitamin, and mineral content (Raja et al., 2009) and is relatively cheap. Fish flesh is easily digestible because it contains long muscle fibres compared to red meat (Pirestani et al., 2009). Fish are exposed to chemicals in polluted coastal waters. Chemicals with a potential to cause harm to human health if consumed with fish are present naturally in marine environment and their levels especially in coastal regions can be increased by anthropogenic inputs. These pollutants, mainly originating from industrial discharges are continually released into marine coastal ecosystems may result in locally much higher levels and actual health effects.

The macroelements magnesium, calcium, potassium and sodium are essential to human health (Walker et al., 1996), but all elements are harmful at excessive levels (O'Neill, 1993). Mg and Ca are the first two members of the alkaline earth group of metals and are major component of the Earth's crust and their chemical reactions are similar. Whilst K and Na are the same group in periodic table and their simple salts have similar solubility (O'Neill, 1993). Accumulation of pollutants in the edible tissues of fish may result in ecological changes and is a good indicator of the pollutant's bioavailability (Phillips, 1977 and 1980) which may pose risks to human health (Underwood, 1977).

Pakistan is largely arid and semi-arid, receiving less than 250 mm annual rainfall and has a coastline of about 990 km and an exclusive economic zone (EEZ) of about 240,000 km^2. It roughly divided into two main sections on the basis of its physiographical characteristics. First, the Sind coast is about 320 km long with continental shelf deep stretches into the ocean, and is located in the south-eastern part of Pakistan. Second, the Baluchistan coast is 670 km long with steep and narrow continental shelf at south-western part of the country (United Nations Environment Programme (UNEP), 1990). The area near Karachi is more vulnerable to coastal erosion and accretion than the other deltaic region, mainly due to human activities together with natural phenomena such as wave action, strong tidal currents and rises in sea level. Pakistan is one of the countries facing water pollution, mainly due to untreated discharge of industrial wastes into rivers and a rapid

increase in the discharge of municipal waste water (Khan et al., 2012). Karachi coast of Pakistan is located on the northern border of the Arabian Sea and its population is over 18 million. Many important industrial zones and marine transport facilities are located along Karachi coasts (Ahmed and Bat, 2015a). Elements are the major component of the waste effluents discharged from Karachi municipality and Karachi is the most important fish harbour in Pakistan coast (Ahmed and Bat, 2015b).

Fish are at the top of marine food chains and vulnerable to poisoning from chemicals contained in their diet. Thus, it is important to determine element levels in fish, because they can easily accumulate in fish. Fish are important diet in Pakistan (Ahmed et al., 2015) and *Argyrops spinifer* is commercial fish and is liked by consumer. The aim of this study was to investigate the concentrations of Mg, Ca, K and Na in the edible tissues of King soldier bream *A. spinifer* locally knows as Sorro Malelak from the Karachi Harbour of Pakistan and to verify whether or not interspecific differences in the levels of these macroelements among seasons are notable. Further, their hazardous levels were compared with available certified safety guidelines proposed by National Academy of Sciences, Food and Agricultural Organization (FAO) and World Health Organization (WHO) for human consumption.

2. Material and Methods

Total of 45 fish samples were collected from Karachi fish harbour (Figure 1) directly from local fishermen during different seasons (Pre-Monsoon, Monsoon and Post Monsoon) from February 2014 to January 2015. The lengths (cm) and weights (g) of fish samples obtained for element analyses are given in Table 1. Muscle tissues extracted from the dorsal part were kept in plastic bags at -21ºC until analysis. Samples were taken from five fish for each season. The muscle tissues of the fish were dissected for analysis according to the method described by the United Nations Environment Programme (UNEP) (1984). Approximately 5 g of each muscle samples were dried to constant weight at 105ºC. The samples were then calcinated at 600ºC for 4 h. The ash was dissolved in 10 ml of 0.1 M HCl (Gutierrez et al., 1978). Then each sample was transferred into 50 ml volumetric flasks with 25 ml distilled water. The working solutions with a concentration of elements were prepared by appropriate dilutions of the stock solution immediately prior to their use. The calibration curve was established by plotting the absorbance readings for a set of standards against the concentration. The precision of analysis was estimated by variations from the mean value reported and in all experiments several blanks were performed with the reagents used in order to check for possible contamination (Lajunen, 1992; Cresser, 1994). Laboratory glassware was kept overnight in a 10% v/v HNO_3 solution and then rinsed with double distilled water. All chemicals used for macroelements determination were of Analytical Grade (Merck, Germany) and all solutions were prepared using deionized water. The concentrations of macroelements were measured with Perkin Elmer Atomic Absorption Spectrophotometer (A Analyst 700) using Hollow cathode lamp. The absorption wavelengths were as follows: 285.2 nm for Mg, 422.7 nm for Ca, 766.5 nm for K and 588.9 nm for Na. The detection limits of Mg, Ca, K and Na were 0.59, 1.14, 0.30 and 0.99 µg L^{-1}, respectively. Macroelement contents were expressed as µg g^{-1} dry weight.

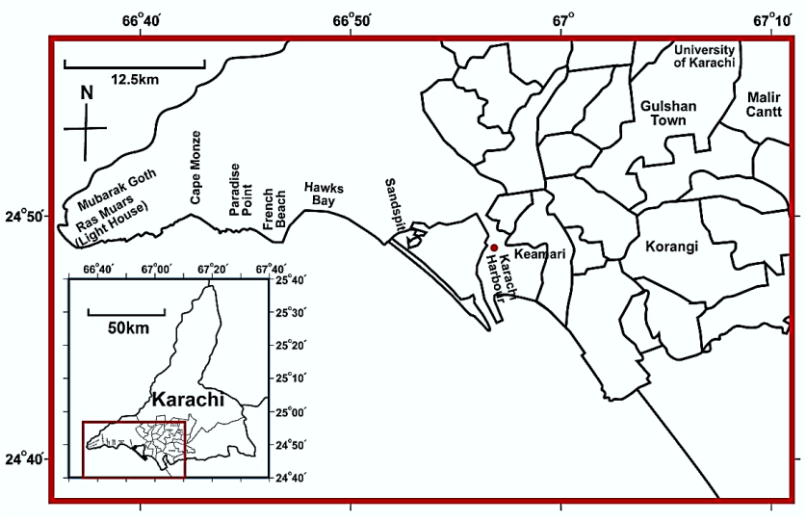

Figure 1. Location of Karachi harbour

Table 1. Mean± SD, minimum and maximum of length (cm) and weight (g) of *Argyrops spinifer* during different seasons of February 2014 to January 2015.

Seasons		Length (cm)	Weight (g)
Pre-M	Mean	31	186
	Std. Deviation	1.1	5.8
	Minimum	29	176
	Maximum	32	192
M-soon	Mean	31	181
	Std. Deviation	1.1	5.7
	Minimum	30	186
	Maximum	34	198
Post-M	Mean	32	189
	Std. Deviation	1.0	5.3
	Minimum	30	182
	Maximum	33	196

Descriptive statistics (mean, standard deviation and ranges) and one-way analysis of variance (ANOVA) were conducted to test significant interspecific differences in the content of the elements studied among seasons (Zar, 1984).

3. Results

The commercially important fish *A. spinifer* was marketed by local fishermen in the most important fishing municipalities in Karachi Fish Harbour, Pakistan to determine macroelements in edible tissues. The mean (±SD) and minimum-maximum concentrations of Mg, Ca, K and Na in the muscle of *A. spinifer* were summarized in Table 2. The mean concentrations (±SD) of Mg, Ca, K and Na were 247±59, 403±79; 160±46 and 278±52, respectively. Maximum Mg

and K levels were found in post-Mon season, whereas Ca and Na levels were determined in Mon-soon. However, there were no clear differences in the contents of these elements in the muscles of *A. spinifer* from different seasons ($p>0.005$).

Table 2. Mean± SD, minimum and maximum levels (µg/g dry wt.) of essential elements in the muscles of *Argyrops spinifer* during different seasons of February 2014 to January 2015.

Seasons	Elements	Mean ± SD	Min. - Max.
Pre-M		222 ± 54	115 - 331
M-soon	Mg	242 ± 55	119 - 327
Post-M		278 ± 57	157 - 356
Pre-M		406 ± 63	322 - 551
M-soon	Ca	433 ± 67	302 - 583
Post-M		368 ± 95	222 - 541
Pre-M		166 ± 45	102 - 236
M-soon	K	158 ± 45	121 - 249
Post-M		157 ± 51	115 - 283
Pre-M		263 ± 44	213 - 349
M-soon	Na	284 ± 61	210 - 430
Post-M		287 ± 51	213 - 383

4. Discussions and Conclusion

Studies have shown that fish are able to accumulate and retain macroelements from their environment and it has been shown that accumulation of elements in edible tissues of fish is dependent upon exposure concentration and duration, as well as other factors such as size and metabolism of organisms. The body weights and lengths of the fish samples were the same (see Table 1) and had no impact on the concentrations of these elements. Mg, Ca, K and Na belong to the group of essential elements and have known function in biochemical processes for both animals and humans. These elements have a high potential for bio-concentration in fish and are accumulated in their tissues. A. spinifer prey on benthic invertebrates, mainly molluscs and are important food fish. Mg is important in small quantities for proper osmotic functions in fish. Mg functions as a cofactor of many enzymes involved in energy metabolism, protein synthesis, RNA and DNA synthesis, and maintenance of the electrical potential of nervous tissues and cell membranes (FAO/WHO, 1998). Average Mg content in edible tissues of fish samples varied from 115 to 356 µg g-1 in the current study. Ca, K and Na are also important for metabolism of organisms. In the case of Ca levels, however, were slightly higher in the fish samples. The results indicated that, Ca values were varied from 222 to 583 µg g-1 in A. spinifer. K like Na is also essential element in fish. They are necessary for human health, but deficiency or increase in these elements intake is a risk for human. K and Na are varying from 102 to 283 µg g-1 and 210 and 430 µg g-1 (dry wt.), respectively.

Of great concern to pollution impact are levels of pollutants in aquatic organisms

including fish which live in coastal areas more directly exposed to land based sources and to higher water levels (Bat et al., 2009). Because of the most important fishery region, it is possible that anthropogenic activities related to industrialization and urbanization has impacted negatively on the quality of Karachi coasts. Recently, Bat (2014) reviewed the heavy metals in fish from the Black Sea coast and suggested that they are considered good biomonitors for metal levels in marine ecosystems because they occupy different trophic levels. Therefore the current study focused on the use of commercial fish that are widely distributed and could be used to make assessment of different seasons. Another aim of this study is to protect human health. The King soldier bream A. spinifer is edible fish of economic importance. The diet of fish has increased in importance because of their high protein supply, low saturated fat and omega fatty acids content that are known to contribute to good health (Kaya et al., 2004; Turan et al., 2006).

Recommended Dietary Allowances (RDA) of Mg for adults of both sexes is accepted to be 4.5 mg/kg, and this value is approximately 280 mg for women and 350 mg for men ages 19 and above (National Academy of Sciences, 1989). The recommended Ca allowance for adults is based on an estimate of 200 to 250 mg/day of obligatory loss and an estimated absorption rate of 30 to 40% and an intake of 1,200 mg is recommended for both sex groups from ages 11 to 24 years (National Academy of Sciences, 1989). A safe minimum intake of Na might be set at 500 mg/day and the minimum requirement of K is approximately 1,600 to 2,000 mg / day (National Academy of Sciences, 1989).

The average daily fish consumption in Pakistan is 5 g per person (Anonymous 2010). Estimated Daily Intake (EDI) for an adult person on basis of the current study results were calculated as 0.575±1.78 µg for Mg, 1.11±2.915 µg for Ca, 0.51±1.415 µg K for and 1.05±2.15 µg for Na, respectively. Macroelement levels in the edible tissues of A. spinifer from Karachi coasts of Arabian Sea were lower than the set values; hence adverse effects of these elements are not expected for human health.

Karachi coasts itself are facing a problem of unmanaged fisheries, of unrestricted intense shipping activities and of the dumping of toxic wastes (Mukhtar and Hannan 2012; Khattak et al. 2012; Jilani and Khan, 2013; Jilani, 2015). Similar findings were found by many researchers (Ahmed and Bat, 2015a,b,c,d; Ahmed et al., 2015); these studies suggested that there was no possible health risk to consumers due to intake of studied fish species under the current consumption rate in the Karachi Harbour of Pakistan. However Ahmed and Bat (2015b) emphasized that metal pollution effects on fish species should be carried out continuously before reaching any exact conclusion.

Based on the results of the current study, it was concluded that Sorro Malelak from Karachi Harbour in Pakistan seems to be appropriate for consumption. However a possible hazardous may occur in the future depending on the agricultural, industrial and fishing development in this region. Therefore the data of this study provides an insight into the potential impact of macroelements in the edible tissues of fish.

5. Acknowledgements

Suggestions from two anonymous reviewers are greatly appreciated.

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