



Heavy Metal Detection in *Scorpaena Porcus* Linnaeus, 1758 from Sinop Coast of the Black Sea and Potential Risks to Human Health

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Abstract

The current research was performed to detect the heavy metal amounts (Hg, As, Cd, Pb, Cu, Zn) in one of the most common fish species (*Scorpaena porcus* Linnaeus, 1758) captured from the south shores of the Black Sea during the fishing season in 2016. Heavy metals were examined by using ICP-MS (Inductively Coupled Plasma - Mass Spectrophotometer). The amounts of the metals (Hg, Pb and Cd) in some specimen were under the detection limits. The maximum levels of all measured metals are as low the recommended limit by the admitted organizations. It was shown that the measured metal amounts in edible tissue of the *S. porcus* were under the well-being levels for people consumption for the average Estimated Daily Intake (EDI) and Hazard Index (HI<1).



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Introduction

Seafood especially fish species are consumed high in the Black Sea coast since they are sources of energy and protein with high biological value, and contribute to the intake of essential nutrients, and vitamins A and D, with well-being benefits.^{1,2} Marine organisms are exposed to pollutants like toxic chemicals in contaminated coastal ecosystem. These chemicals off the anthropogenic sources and activities are frequently let into coastal areas and

especially non-essential metals are major well-being threat on account of their poisonousness, extended continuity, bioaccumulation, and bio-magnifications in the food-web. Non-essential metals such as Pb, Cd, As and Hg can reason for brain and central nervous system harm.³⁻⁸ They are very crucial to determine and monitor metal amounts in fish, the fact that metal ions can readily pile up in their edible tissues. Coastal ecosystems are contaminated by pollutants, industrial wastes, petroleum products,

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paints, fishing and touristic activities, domesticated and farming drains in the form of pieces, inorganic and organic mixtures. These metal ions gathering in fish become considerable and eventually toxic. Because of fish is one of the major diets to be consumed for in good health, hence, heavy metals in edible tissues of fish threaten people health.

Coastal ecosystems are much sensitive to heavy metal contaminants specifically; little fish get enriched with the taken substances. Thus, it should be used for bio monitoring studies.

Turkey is encircled with four different seas and fishing is one of the largest sources of income for the country⁹ and the Black Sea has a great importance in terms of fishing resources for Turkey. In the last half century, the Black Sea has undergone significant changes triggered by human activities and exposed to a severe pollution. Pollutants such as heavy metals and certain synthetic chemicals are easily absorbed with food, but they are not easily removed, and even low organisms in the food chain can be affected.¹⁰⁻¹² In very recent review it is well documented that heavy metals can be extremely toxic even at low concentrations.¹³ Heavy metals are quickly absorbed in sediment particles suspended in the coastal water, which settlement in the floor.^{14,15} Marine organisms accumulate heavy metals to levels many times higher than those in water or sediment¹⁶⁻¹⁹ and they can reach dangerous levels in fish species. *Scorpaena porcus* Linnaeus, 1758 has a native stock in the Black Sea and located in various habitats containing seagrasses, sandy, muddy and rocky substrates.²⁰ It lives a solitary and sedentary life and feeds on small fishes (gobies, blennies), crustaceans and other invertebrates.²¹ *S. porcus* is an important commercial fishes for the Black Sea and also Sinop which is one

of the most important fishing spots of the Black Sea and this species is susceptible to chronic coastal pollution.²⁰

The current study was aimed to provide information on heavy metal amounts in the dorsal (edible) tissues of commercial demersal Black Scorpionfish existing in Sinop fish markets and to appraise the probable risk related to their consumption. The amounts of mercury (Hg), arsenic (As), cadmium (Cd), lead (Pb), copper (Cu) and zinc (Zn) were determined in the muscles of *S. porcus* from Sinop shores. The estimated daily intakes (EDI) and hazardous quotients (HI) in edible tissues of fish were also calculated to detect the welfare threats owing to the consumption of probable contaminated fish.

Materials and Methods

Samples and sample preparation

The Black Scorpionfish specimens were purchased from haphazard commercial market bound up with the availability of the species for sale. A total of fifty specimens were purchased during the fishing season in 2016 from Sinop shores of the Black Sea (Figure 1). The total lengths (cm) and the body weights (g) of each fish individuals were measured and then were washed with deionized water, sealed in polyethylene bags and kept in a freezer at -21°C until metal analysis (Figure 2). All plastic and glassware used were rinsed and soaked in 10% (v/v) HNO₃ overnight. They were rinsed with deionized water and dried prior using. All acids and oxidants were of high quality from Merck, Germany. The samples digested with Suprapur® HNO₃ using a microwave digestion system (Milestone Systems, Start D 260) for analysis. Fish muscles were analysed by an ICP-MS, Agilent Technologies,

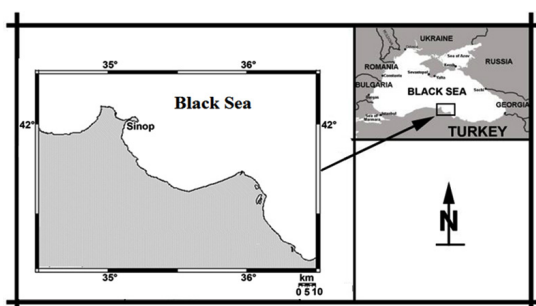


Fig. 1: Sinop coasts of the Black Sea



Fig. 2: *Scorpaena porcus* from Sinop coasts of the Black Sea

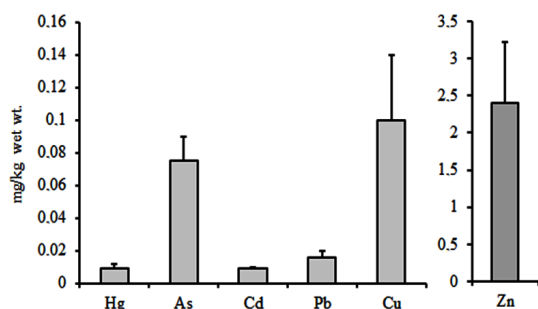


Fig. 3 - Mean levels and standard deviation of Hg, As, Cd, Pb, Cu and Zn found in edible tissues of in Scorpaena porcus from Sinop shores of the Black Sea in 2016.

7700X and analytical quality was controlled with certified reference material NRCC-TORT-2 lobster hepatopancreas.

Assessments hazard index (HI) of heavy metals in fish

Danger from heavy metals intake right ingestion may be characterized using a hazard index (HI) as the rate of the estimated daily intakes (EDIs mg/kg of body wt. per day) and the reference dose (Rf. D. mg/ kg per day). The HI was found by employing the equation:

$$HI = EDI / Rf. D.$$

If $HI > 1.0$, the EDI of a certain metal pass over the Rf. D., so indicating that there exists a possible hazard metal. It counts on both the metal levels and the quantity of consumption of fish. The EDI of chemicals was found employing the following equation:

$$EDI = C_{metal} \times W / b. wt.$$

Where

C_{metal} is the amounts of the metals in edible tissues of fish; W appears for the daily mean intake: it is given as 17 g/day for adults²²; b. wt. is the body weight of 70 kg for adults.

Results

Mean lengths (cm) and weights (g) *S. porcus* specimens were measured as 15.12 ± 2.34 and 69 ± 8 , respectively. The recovery percentages results ranged from 96% to 104%. Mean metal levels in Black Scorpionfish from Sinop coasts are given in Figure 3. The heavy metal amounts found in the dorsal part of Scorpionfish varied for Hg: Nd-0.012, As: 0.06-0.09, Cd: Nd-0.01, Pb: Nd-0.02, Cu: 0.05-0.14 and Zn: 0.9-3.22 mg/kg wet wt. When the maximum values of the metals were taken into consideration, the order of the metal concentrations was found as $Zn > Cu > As > Pb > Hg > Cd$.

In the present study, all studied metals in Scorpion fish were quite low and did not exceed the allowable limit, so there is no hazard to *S. porcus* for consumers. The amounts of the metals in Black Scorpionfish were under the limits set by international and national regulations (Table 1). Non-essential metals like Hg, Cd, As and Pb are heavy and toxic chemical in fish, the existing of these metals in fish may have threat on people health. As is toxic and is found at quite low levels in fish. The United Kingdom previously imposed a limit of 1 mg/kg for As in fish with separate limits feasible to certain seafood categories. This arrangement was revoked in 2002. There is no maximum level set for arsenic in foods at EU level. Cu and Zn are essential metals to all biota and they make health threat when had in large amount exceeded the allowable limits.

Table 1 - The allowable limits of the metals in the edible fish tissues (mg/kg wet weight)

Standards	As	Cd	Pb	Cu	Zn	Hg
MAFF Seafood Safety (Fish Product) ²³	--	<0.2	2	20	50	--
The European Commission Regulation ²⁴	--	0.05	0.2	--	--	0.5
Georgian Food Safety Rules 25	2	0.2	1	10	40	0.5
Turkish Food Codex ²⁶	--	0.1	0.4	20	50	0.5
GAIN Report Russian Federation ²⁷	2	0.2	1	10	40	0.5
The European Commission Regulation ²⁸	--	0.05	0.3	--	--	0.5
Turkish Food Codex ²⁹	--	0.05	0.3	--	--	0.5

Fish may concentrate heavy metals in their edible tissues, becoming extremely toxic in the course. A number of land-based waste products, notably toxic heavy metals, exert a direct effect on commercial fish stocks. Especially non-essential metals such as

Hg, As Cd and Pb turn into a concentrated structure thanks to the food-chains, posing a toxic risk to species in higher trophic levels. These predators may have levels of the heavy metals millions of times greater than the surrounding water. Eventually, people who are living in the coastal areas are the most affected by these pollutants.³⁰

Table 3. Comparison of heavy metal concentrations in muscle tissues in *S. porcus* with the other studies conducted in the Black Sea, Marmara Sea and Aegean Sea (ND: Not Detected)

Location	d.w./w.w.	unit	Metals						References
			Hg	As	Cd	Pb	Cu	Zn	
Black Sea- Sinop	w.w.	mg/kg	ND-0.012	0.06-0.09	ND-0.01	ND-0.02	0.05-0.14	0.9-3.22	This Study
Black Sea- Sinop	w.w.	mg/kg	-	-	0.02-0.023	0.03-0.07	0.88-1.7	7.44-12.3	32
Black Sea- Sinop	w.w.	mg/kg	0.01± 0.00	0.14± 0.09	ND	0.04± 0.03	0.07± 0.009	-	33
Black Sea- Sevastopol	-	mg/kg	0.06± 0.01	0.80± 0.10	0.04± 0.01	0.16± 0.04	0.60± 0.10	5.14± 1.25	34
Marmara Sea- Yalova	w.w.	mg/kg	-	-	0.20± 0.07	0.83± 0.19	5.29± 1.88	26.2± 4.31	9
Aegean Sea	d.w.	µg/g	-	-	0.80± 0.06	0.66± 0.06	0.73± 0.06	95.3± 8.7	35
Aegean Sea-Izmir	w.w.	µg/g	-	-	0.005-0.04	0.01-0.08	0.03-0.09	0.92-2.23	36

Daily intake of metals and hazard index

The daily intakes (EDIs) of the metals were estimated taking into account the mean of metal in the edible tissues of *S. porcus* and the mean taken of that fish per day for adults as reported by United States Environment Protection Agency.³¹ Table 2 shows that (EDI) of toxic metals (Hg, Cd, Pb, As) and essential metals (Cu, Zn) for adults. They are significantly lower than the allowed limits of international and national regulations (Table 1). Estimated hazarded indexes (HIs) of the metals suggest that the metals in fish samples do not pose any apparent danger to the population, where the HIs of all the metals studied were below the value of 1³¹ as given by Table 2.

The comparison of heavy metal concentrations in muscle tissues in *S. porcus* with other studies was given in Table 3. In the Sinop coasts of the Black Sea, the maximum metal concentrations reported for Zn, Cu and Cd by Bat *et al.*³², for As by Turk Çulha *et al.*³³ Maximum Hg concentration was found in this study for Sinop but in the entire Black Sea maximum Hg concentration reported by Rudneva *et al.*³⁴ in Sevastopol. The data obtained from the studies performed in the Sinop coasts were taken into consideration, the maximum metal concentrations in the Black Scorpionfish were under the limits set by international and national regulations. However Uluozlu *et al.*³⁵ reported that the Zinc levels in *S. porcus* were found to be higher than legal limits in the Aegean Sea.

As a result, the concentrations of heavy metals in *S. porcus* in this study were lower than the other studies conducted in the Sinop coasts (except for Hg). Considering public health in adult persons with respect to the investigated heavy metals, the estimated daily intakes (EDIs) did not exceed the tolerable intakes. Therefore, consuming *S. porcus* does not involve any danger to the public health in terms of studied heavy metals.

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