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Heavy Metal Levels of Some Marine Organisms Collected in Samsun and Sinop Coasts of Black Sea, in Turkey

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Abstract: The aim of this study, is to evaluate the heavy metal concentrations of marine organisms in Samsun and Sinop coasts of Black Sea. As test materials, 3 sample groups of red mullet, whiting and mussel, 2 sample groups of turbot, 1 sample group of veined rapa whelk and halibut were collected in Samsun and Sinop cities of Turkey. Heavy metal analyses were carried out by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Lead concentrations of veined rapa whelk, mussel and red mullet sample groups were found to be 0.1435; 0.26-1.87 and 0.0515-0.0815 mg kg^{-1}, respectively. The concentrations of other sample groups were below the maximum permission limits. Cadmium concentrations of veined rapa whelk, mussel and halibut were found as 4.63; 0.41-0.49 and 0.88 mg kg^{-1}, respectively. The cadmium concentrations of the other sample groups didn't exceed the maximum permission limits. Mercury concentrations only in turbot sample groups exceeded the maximum permission limits. Arsenic was detected in all sample groups. Its concentrations of red mullet, whiting, mussel, turbot, halibut and veined rapa whelk were found to be as follows: 1.33-2.375; 0.58-1.085; 1.35-1.91; 0.59-1.56; 4.75 and 6.55 mg kg^{-1}, respectively.

Key words: Heavy metals, marine organisms, mercury, concentrations, mussel, Black Sea

INTRODUCTION

The variability in metal concentrations of marine organisms depends on many factors as, like the position of the fish in the food chain, size, age and characteristics kinetics for elements and their biological half time. Pollutants accumulated in marine organisms are transferred to man through the food chain (Cogun *et al*., 2006; Farkas *et al*., 2000; Naqvi *et al*., 2003; Uluozlu *et al*., 2007).

Marine organisms have been recognized as a useful tool for the monitoring of the environment. Organisms like mussel feeds through to filter organic material and phytoplankton in water. They can filter the toxic materials simultaneously. Besides, their potential employment as biomonitors, several species of crustaceans are included in the diet of coastal inhabitants and the concentrations of heavy metals considered safe for human consumption in such seafood are regulated by legislation (Blasco *et al*., 2002; Kayhan *et al*., 2006; Orescanin *et al*., 2006).

The Black Sea coast length is >4000 km, of which 1400 km belongs to Turkey. The country's fish production from the Black Sea is about 454-500 thousand tones annually. The production of sea snails and mussels is about 20,000 tones annually. The physical, chemical and biologic properties of The Black Sea differ from The Mediterranean Sea. Some pollutants are carried from the Mediterranean and the Marmara Sea to the Black Sea by the lower layer flow of the Marmara Sea. In addition to this, significant quantities of pollutants are carried into the Black Sea by the rivers as follows; Sakarya River, Kizilirmak River, Yesilirmak River and many small rivers (like Filyos River) of Turkey; Chorokhi River of Georgia; Dniester River and Dnieper River of Ukraine; Don River of Russia; Danube River of Romania (Topcuoglu, 2000; Unsal *et al*., 1998).

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MATERIALS AND METHODS

As test materials, 3 sample groups of red mullet (*Mullus barbatus* Linnaeus, 1758), whiting (*Gadus merlangus euxinus* Svetovidov, 1935) and mussel (*Mytilus gallaprovincialis* Lamarck, 1819); 2 sample groups of turbot (*Scopthalmus maeoticus* Palas, 1811); 1 sample group of veined rapa whelk (*Rapana venosa* Valenciennes, 1846) and halibut (*Platichthys flesus* Pallas, 1811) were collected from Samsun and Sinop cities of Turkey. Each sample group was consisted of 10 sub-samples.

Agillent 7500 A Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used for analysis of the concentrations of the selected heavy metals in samples. CEM MARS-5 closed vessel microwave digestion was used for sample preparation prior to analysis.

AOAC Official Methods 999.10 (modified for ICP-MSD) was utilized for sample analysis (Jorhem and Engman, 2000). According to the method, samples were weighed in cells of the microwave about 0.5 g by 2 parallels. Approximately, 10 mL HNO_3 (65%) was added on the samples. After the caps of the cells were closed, microwave of which temperature and pressure control had been made was started up. Temperature of the microwave was 175°C and the time of the process was 20 min. After completing the process, the cells were cooled. The solutions in the cells were passed into glass balloon. The final volume was completed to 25 mL with ultra pour distilled water. The calibration coefficients were prepared by using certificated standard solutions of four metals of 1-20 ppb intervals. Pb, Cd, Hg and As concentrations were analyzed by ICP-MS.

RESULTS AND DISCUSSION

Heavy metal concentrations in the marine samples collected from Samsun and Sinop coast of Black Sea are shown in Table 1.

In Turkey the Maximum Permissible Limits (MPLs) in edible tissues for mollusks are 0.05 mg kg^{-1} for mercury, 1 mg kg^{-1} for cadmium and 1.5 mg kg^{-1} for lead. The MPLs for muscle meat of fish species are 0.05 mg kg^{-1} for cadmium, 0.30 mg kg^{-1} for lead and 0.50 mg kg^{-1} (1 mg kg^{-1} for *Mullus* sp.) for mercury (Turk Gida Kodeksi Teblig, 2008). In European Commission, the MPLs for bivalve mollusks are 0.5 mg kg^{-1} for mercury, 1 mg kg^{-1} cadmium and 1.5 mg kg^{-1} for lead. The MPLs for muscle meat of fish species 0.30 mg kg^{-1} for lead, 0.05 mg kg^{-1} for cadmium and 0.50 mg kg^{-1} for mercury. However, the MPL of mercury for *Mullus* sp. is 1.0 mg kg^{-1} (EC, 2006).

In this study, lead concentration found in veined rapa whelk (0.1435 mg kg^{-1}) was below the MPLs of Turkish Food Codex and European Commission Regulations. However, it was found above for 2 sample groups of mussels (1.085-1.87 mg kg^{-1}). Lead concentrations found for all fish species were below the MPLs. Cadmium concentrations found in veined rapa whelk (4.63) was above the MPLs. It was found below the MPLs for mussels and fish species (except halibut sample, 0.88 mg kg^{-1}). Mercury concentrations found in only 2 turbot sample groups (0.065 mg kg^{-1}) were above the MPLs. The other sample groups were found below the MPLs.

In Turkey, it was investigated 5 heavy metal concentrations in liver and muscle tissues of *Mugil auratus*. Cr and Ni concentrations in all tissues were found below detection limits of 0.05 and 0.1 μg g^{-1} dry weight, respectively. Cu, Pb and Cd were detected as mg/kg dry weight within the limits 0.49-1.30, 0.60-1.21 and 0.15-0.50 in liver tissues and 0.30-1.00, 0.57-1.12 and 0.10-0.40 in muscle tissues respectively (Filazi *et al*., 2003).

In a recent study, arsenic levels in mussels (*Mytilus galloprovincialis*) are studied in Turkey and the levels of arsenic found in analyzed mussels were between 0.019-0.098 mg kg^{-1} (Kayhan *et al*., 2006). The arsenic concentrations found for mussel sample groups in our study were higher than the results of that study.

Table 1: The concentrations of heavy metals in the marine samples

	Pb		Cd		Hg		As	
Sample groups	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Sinop coast								
Red mullet	0.0525	0.0025	<0.02	-	<0.050	-	2.375	0.015
Whiting	<0.0500	-	<0.02	-	<0.050	-	0.580	0.01
Veined rapa whelk	0.1435	0.0055	4.63	0.14	<0.050	-	6.550	0.06
Mussel	0.2600	0.0300	0.47	0.01	<0.050	-	1.910	0.03
Red mullet	0.0515	0.0005	<0.02	-	<0.050	-	1.760	0.02
Whiting	<0.0500	-	<0.02	-	<0.050	-	1.085	0.035
Turbot	<0.0500	-	<0.02	-	0.065	0.001	1.560	0.02
Turbot	<0.0500	-	<0.02	-	0.065	0.004	0.590	0.02
Halibut	<0.0500	-	0.88	0.01	<0.050	-	4.750	0.25
Samsun coast								
Mussel	1.0850	0.0650	0.41	-	<0.050	-	1.350	0.02
Mussel	1.8700	0.0100	0.49	-	<0.050		1.435	0.045
Red mullet	0.0815	0.0025	<0.02	-	<0.050	-	1.330	0.02
Whiting	<0.0500		<0.02	-	<0.050	-	0.630	0.04

In another study from Turkey, the average concentrations of the heavy metal levels in mussels (*Unio stevenianus*) were found to be as follows; 1.43 mg kg^{-1} for lead, 0.09 mg kg^{-1} for cadmium, 5.83 mg kg^{-1} for copper, 15.93 mg kg^{-1} for zinc and 0.06 mg kg^{-1} for arsenic (Yarsan *et al*., 2000). The lead levels of mussels in our study were similar to the result of that study. But the cadmium and arsenic concentrations found for mussel sample groups in our study were below the results of aforementioned study.

In a previous study, carried out in Turkey, the cadmium levels in liver and muscle tissues of *Sparus aurata* and *Mullus barbatus* were determined. The mean cadmium levels of muscle and liver tissues were estimated as (mg kg^{-1}, dry weight) 3.35 and 5.22 in *S. aurata*; 4.78 and 5.27 in *M.barbatus*, respectively (Kalay *et al*., 2004). The cadmium levels of red mullet sample groups in our study were determined lower than the results of this study.

In a study, evaluating the mercury concentrations in the muscle tissues of different kinds of fish species in Italy had shown that the highest mean concentration in *Lophius piscatorius.* was 1.26 mg kg^{-1} (wet weigh). The other mean concentrations were 0.68 mg kg^{-1} in *Lophius budegassa*, 0.39 mg kg^{-1} *Lepidorhombus boscii*, 0.31 mg kg^{-1} in *Mullus barbatus*, 0.19 mg kg^{-1} in *Solea vulgaris*) (Storelli and Marcotrigiano, 2000). The mercury concentrations of red mullets sample groups in our study were found to be lower than the results of that study.

In China Liang *et al*. (2004) have reported the 6 heavy metals levels investigated in veined rapa whelk. It was found (wet weight): 0.05-0.39 mg kg^{-1} for Co, 0.09-0.66 mg kg^{-1} for Ni, 0.15-30.61 mg kg^{-1} for Cd, 0.09-0.75 mg kg^{-1} for Pb, 5.52-172.25 mg kg^{-1} for Cu and 8.65-705 mg kg^{-1} for Zn. The cadmium level of veined rapa whelk in our study were found to be higher than the results of this study. On the contrary, the lead concentrations of veined rapa whelk in our study were determined higher than the results of this study.

On the east coast of the Middle Adriatic, it was investigated heavy metal and arsenic concentrations in soft tissue of *Mytilus galloprovincialis.* Measured concentrations were found to be 2-7 mg kg^{-1} for Pb; 4-30 mg kg^{-1} for As; 1-2.9 mg kg^{-1} for Cr; 2-13 mg kg^{-1} for Mn; 53.4-719 mg kg^{-1} for Fe; 0.8–5 mg kg^{-1} for Ni; 3.7-11.1 mg kg^{-1} for Cu and 59.1-273 mg kg^{-1} for Zn (Orescanin *et al*., 2006). The lead and arsenic concentrations of mussel sample groups in our study were found lower than the result of this study.

Heavy metal concentrations of marine organisms depend on age, environment and feeding behavior. Heavy metal concentrations are higher in internal seas than open seas (Filazi *et al*., 2003; Kayhan *et al*., 2006). Black Sea, as an internal sea, has low salt concentrations (18%). However, the salt concentration is higher (23%) by going down. Also, there is mud flat below 200 m deep. Due to the mud flat contain hydrogen sulfur; there is scarcely no life below this depth (Gozenc, 2007).

CONCLUSION

In this study, mercury, lead and cadmium concentrations were generally found low; eventhough arsenic concentrations were usually found high. The results of our study showed that the marine organisms collected Sinop and Samsun coast of Black Sea were harmless in terms of mercury, lead and cadmium for public health and environment, but it may be harmful to people consumed these organisms and environment in terms of arsenic levels. It is important to control periodically the concentrations of heavy metals in seafood consumed by people for public health. Further studies, including more samples and more species need to be carried out to obtain proper results.

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