Indian Journal of Geo Marine Sciences
Vol. 48 (01), January 2019, pp. 163-168

Heavy metals health risk appraisal in benthic fish species of the Black Sea

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Received 02 August 2017; revised 17 November 2017

Present study is to provide information on the Hg, Cd, Pb, Cu and Zn levels in the muscle of red mullet *Mullus barbatus barbatus* Linnaeus, 1758 and whiting *Merlangius merlangus* (Linnaeus, 1758) from Sinop Peninsula of the Black Sea in 2015 fishing season from September to December. This study also compare the measured values with national and international standards for food and human health.

[**Keywords:** Black Sea, heavy metal, *Mullus barbatus barbatus, Merlangius merlangus*]

Introduction

As a result of the heavy metals transport from industrial areas into the environment and their chemical persistence, many marine ecosystems like the Black Sea are faced with spatially or temporally alarming high levels of heavy metals[1,2,3]. Some of essential heavy metals are biodegradable and quickly decay into harmless or less harmful forms, while non-essentials are non-biodegradable and remain dangerous for a long time[4,5,6]. Now, there is a growing concern worldwide over the indiscriminate use of such heavy metals, resulting in environmental pollution and toxicity risk to marine organisms[7].

Heavy metals tend to accumulate in advanced organisms through bio-magnification effects in the food chain. Thus they can enter into human body and accumulate in the human tissues to pose chronic toxicity. Chronic assimilation of heavy metals is a known cause of cancer[8,9,10].

The basin of the Black Sea tend to retain these material and here bacteria feed on it and break it down, using up life-giving oxygen as they do so. In the worst situations, very much treatment sewage is discharged into the sea that the bacteria remove the oxygen from the water, killing life here and on the seabed. Any remaining organic material sinks to the bottom of the Black Sea, and it is causing the shortage of oxygen and contains high amounts of hydrogen sulphide[11,12,13]. In this case, most benthic organisms including fish are affected.

Fish is a healthful food in consequence of its nutritional usefulness pertinent to its proteins of high biological quality, creditable lipid composition, valuable mineral compounds and vitamins. The special to compound of its lipid parts, ample in essential ω-3 polyunsaturated fatty acids (PUFA), especially eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), and weak in cholesterol makes it as the important part of human food. Thus, it is very important to determine the heavy metals concentrations in commercial fish in order to evaluate the possible risk of fish consumption for human health[14,15,16,17].

Moreover, the Marine Strategy Framework Directive (MSFD) established a framework for the development of marine strategies designed to achieve Good Ecological Status (GES) in the marine environment, by the year 2020, using 11 qualitative descriptors. The concentration of contaminants including heavy metals in the marine environment and their effects need to be assessed taking into account the impacts and threats to the ecosystem[18]. Contaminants in fish and other seafood for human consumption do not exceed levels established by Community legislation or other relevant standards[19].

Total sea fishing production in Turkish waters was reported as 397.731 tons in 2015, where 1.281 tons red mullet and 13.158 tons whiting[20]. There is a need for more information on contaminant levels in fish of Turkey. Present study provides information on the metal concentrations in the edibletissue of two benthic fish species, consumed commonly in the Black Sea coast of Turkey, and compares the results with national and international permissible concentrations

and with also those reported in earlier studies. The heavy metals investigated include mercury, cadmium, lead,copper and zinc because they are known to accumulate in the environment and in fish, and are known to cause adverse health effects if consumed in sufficient quantities[21,22,23,24].

Materials and Methods

Red mullet and whiting were sampled during the September-December in 2015 from Sinop Peninsula of the southern Black Sea (Fig. 1) and only consumed sizes were used. Fish samples were then labelled, preserved and transported to the Hydrobiology laboratory. All the samples of the edible tissues were dissected and stored at -21^{0}C. Metal analysis in the samples was performed using m-AOAC 999.10- ICP/MS (Inductively Coupled Plasma – Mass Spectrometer) method by validated Laboratory Services. EN 15763 European Standard methods was made. Statistical analyses were performed using SPSS software (ver. 21). Data were analysed by one-way of analysis of variance (ANOVA). Means were compared by Duncan multiple comparison test ($p<0.05$)[25].

The average heavy metal weekly or daily intake was calculated according to the following formula: Heavy metals intake level = average heavy metal content X weekly or daily consumption of fish per person/ body wt.

Target hazard quotient (THQ), which is a ratio of the estimated exposure (EDI) to the oral reference dose (Rf. D), is used to assess the potential non-carcinogenic risk of the consumers of the perceived contaminated food.

$$THQ = \frac{EDI}{RfD}$$

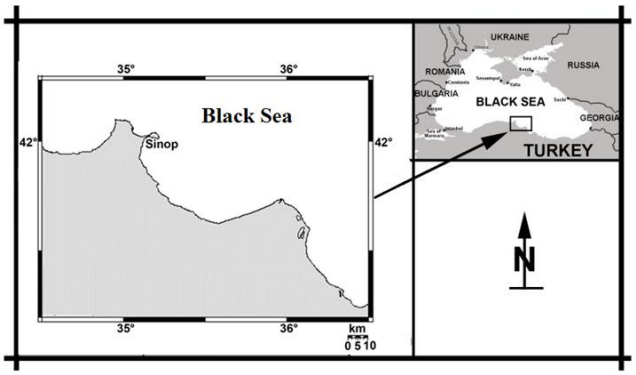

Fig. 1 — Sampling region

According to U.S. Environmental Protection Agency[26]the Rf. D for Hg, Cd, Pb, Cu and Zn are 0.0005, 0.001, 0.0035, 0.04 and 0.3 mg/kg/day, respectively.

Health risk assessment of consumers from the intake of metal-contaminated fish was characterised by using the THQ. THQ < 1 means the exposed population is unlikely to experience some non-carcinogenic adverse effects during the life time. Otherwise, THQ > 1 means that there is a chance of non- carcinogenic effects, with an increasing probability as the value increases.

The annual quantity of fish consumed is 6.2 kg / person in 2015[20], which is approximately to 17 g/day for Turkey. The body weight of adult person is 70 kg.

Results and Discussion

The results obtained for Hg, Cd, Pb, Cu and Zn levels in red mullet and whiting from Sinop Peninsula of the Black Sea during fishing seasons September to December in 2015 is presented in Figures 2-6.

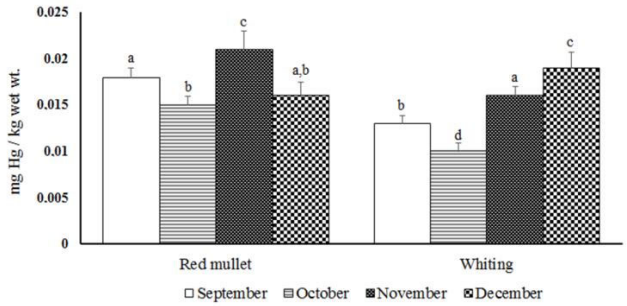

Fig. 2 — The means with standard deviations (vertical line) of Hg concentrations (mg/kg wet wt.) in the dorsal muscle tissues of red mullet and whiting from Sinop coastal waters of the Black Sea during fishing season in 2015. The same letters beside the vertical bars in each graph indicate the values are not significantly different (P>0.05).

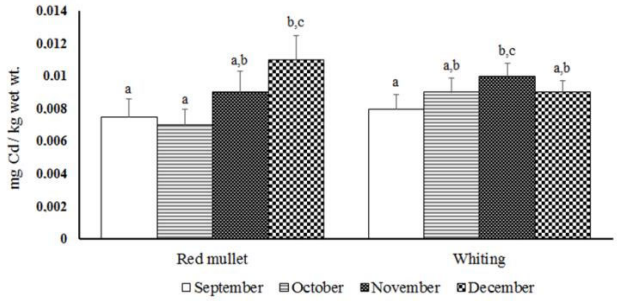

Fig. 3 — The means with standard deviations (vertical line) of Cd concentrations (mg/kg wet wt.) in the dorsal muscle tissues of red mullet and whiting from Sinop coastal waters of the Black Sea during fishing season in 2015. The same letters beside the vertical bars in each graph indicate the values are not significantly different (P>0.05).

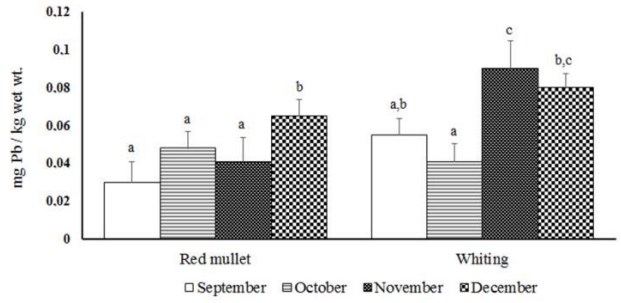

Fig. 4 — The means with standard deviations (vertical line) of Pb concentrations (mg/kg wet wt.) in the dorsal muscle tissues of red mullet and whiting from Sinop coastal waters of the Black Sea during fishing season in 2015. The same letters beside the vertical bars in each graph indicate the values are not significantly different (P>0.05).

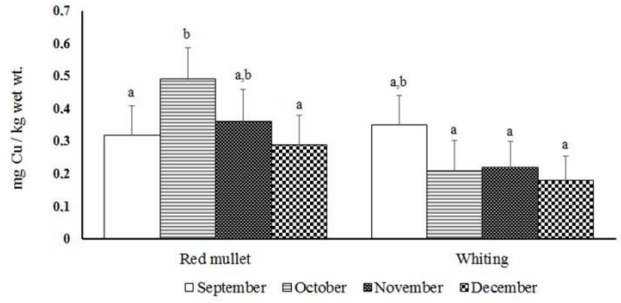

Fig. 5 — The means with standard deviations (vertical line) of Cu concentrations (mg/kg wet wt.) in the dorsal muscle tissues of red mullet and whiting from Sinop coastal waters of the Black Sea during fishing season in 2015. The same letters beside the vertical bars in each graph indicate the values are not significantly different (P>0.05).

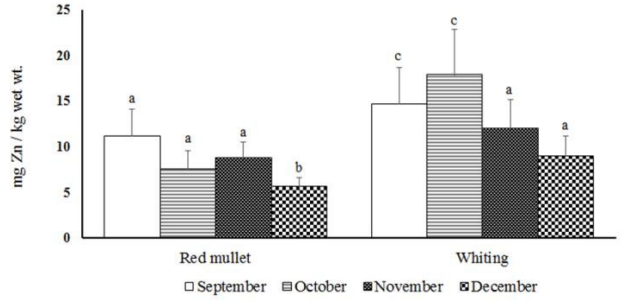

Fig. 6 — The means with standard deviations (vertical line) of Zn concentrations (mg/kg wet wt.) in the dorsal muscle tissues of red mullet and whiting from Sinop coastal waters of the Black Sea during fishing season in 2015. The same letters beside the vertical bars in each graph indicate the values are not significantly different (P>0.05).

The fish samples were found to contain Hg levels ranging from 0.010 to 0.021 mg/kg wet wt. with the highest level recorded in the (*M. b. barbatus*). Highest Cd levels were recorded in the same species and concentrations ranged from 0.007 to 0.011 mg/kg wet wt. Concentrations of between 0.03 and 0.09 mg/kg wet wt. were recorded for Pb with the highest levels found in the *M. merlangus*. Levels of between 0.18 to 0.49 mg/kg wet wt. were detected for Cu with the highest accumulation recorded in the red mullet. Finally, Zn levels ranged from 5.61 to 17.88 mg/kg wet wt. with the highest levels found in the whiting.

European Commission Regulation[27] and Turkish Food Codex[28] clarify that maximum concentrations of Hg, Pb and Cd are 0.5, 0.30 and 0.05 mg/kg wet wt. in the edible tissues of fish, respectively. There are no maximum levels set for Cu and Zn in European Commission Regulation[27]. On the other hand the allowable values for Cu and Zn are 30 and 50 mg/kg wet wt., respectively established by Turkish Legislation[29] and the Ministry of Agriculture, Forestry and Fisheries, U.K.[30].Overall, the findings from this study revealed that Hg, Cd, Pb, Cu and Zn levels in the muscle were lower than the maximum permissible limit as recommended by the international and national authorities[27,28,29,30].

The admissible weekly intake of heavy metals as Provisional Tolerable Weekly Intake (PTWI), are set by the Food and Agriculture Organization/World Health Organization (FAO/WHO) Joint Expert Committee on Food Additives (JECFA) [31, 32]. PTWI is the potential quantity of a contaminant to which an individual can be subjected per week over a vital without an unacceptable risk of health effects. The estimated daily intake (EDI) and estimated weekly intake (EWI) in the current study were estimated and showed in Table 1. Intake estimates were expressed as mg/kg body wt. / weekly and daily.

Estimated THQs of Hg, Cd, Pb, Cu and Zn levels were below the value of 1 (Σ HQn = 0.0231; Fig. 7), therefore the metals in the edible of *M. b.barbatus* and *M. merlangus* do not hazard any apparent threat to the people and these fish species are healthy as food.

A comparative study was also carried out between the available recent data on the metals in edible tissues of these fish species from different regions of the Black Sea with those of the present study, to observe their trend and status in regional contexts. The concentrations of essential heavy metals in the edible parts in both fishes in the present study were higher than those in non-essential metals. These findings are the expected and in agreement with many authors[22, 23, 24.] The essential metals, such as Zn and Cu are in higher concentrations, probably owing to their function as co-factors for the activation of a number

Table 1 — Estimated Weekly Intakes (EWI) and Estimated Daily Intakes (EDI) of heavy metals in edible tissues of *M. b. barbatus* and *M. merlangus* from fish market of Sinop Peninsula of the Black Sea.

Metals	PTWI[a]	PTWI[b]	PTDI[c]	EWI[d] (EDI)[e]	
				M. b. barbatus	*M. merlangus*
Zn	7	490	70	1.33 (0.19)	2.1 (0.30)
Cu	3.5	245	35	0.056 (0.008)	0.042 (0.006)
Pb	0.025	1.75	0.25	0.007 (0.001)	0.0063 (0.0009)
Hg	0.004	0.28	0.04	0.0028 (0.0004)	0.00224 (0.00032)
Cd	0.007	0.49	0.07	0.00133 (0.00019)	0.00119 (0.00017)

[a]PTWI (Provisional Tolerable Weekly Intake) in mg/week/70 kg body wt.
[b]PTWI for 70 kg adult person (mg/week/70 kg body wt.)
[c]PTDI (Permissible Tolerable Daily Intake) (mg/day/70 kg body wt.)
[d]EWI (Estimated Weekly Intake) (mg/week/ kg body wt.)
[e]EDI (Estimated Daily Intake) (mg/day/ kg body wt.)

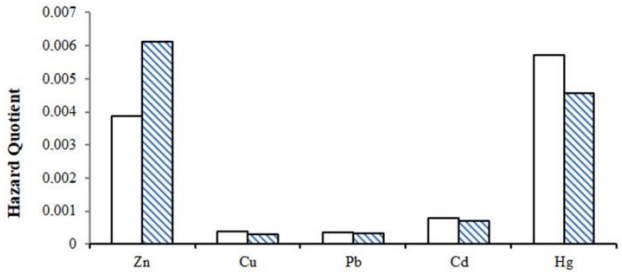

Fig. 7 — Hazard quotients of Hg, Cd, Pb, Cu and Zn via consumption of *M. b.barbatus*(white bars) and *M. merlangus* (hatched bars) from Sinop Peninsula of the Black Sea.

of enzymes and regulated to maintain a certain homeostatic status in fish. Whereas, the non-essential metals such as Hg, Cd and Pb have no biological function or requirement and their concentrations in fish are considerably low.

The concentration of Hg in muscle tissue was slightly higher in red mullet (0.021 mg/kg wet wt.) than those in whiting but the values are not significantly different (P>0.05). Maximum concentration of Cd was observed in *M. b. barbatus* (0.011 mg/kg wet wt.) while the maximum Pb level was found in *M. merlangus* with 0.09 mg/kg wet wt. The Hg concentrations in red mullet and whiting were lower in the present study than those in other studies[33,34,35]. Similarly Cd levels in both species were also lower than other studies[35,36,37,38]. The Pb concentrations in whiting were similar to the other study[39]. However, higher than reported in those studies[34], but lower than other studies[35,37,38]. Likewise Pb levels in red mullet were similar to studies[39, 40], higher than reported by Ergül and Aksan[34] and Alkanet al.[41] and considerably lower than those in studies[35,37,42,43]. Recently two studies with *M. merlangus*[23] and *M. barbatus*[24] from Sinop Peninsula of the Black Sea showed that non-essential heavy metals are below the detection limits and no any hazard to consumers. This present study agrees with those two studies.

Jitar et al.[44] found higher concentrations of Cd and Pb in *M. barbatus* from Romanian coasts of the Black Sea than those in the current study. Harmelin-Vivien et al.[45]also found high Hg levels in red mullets from the Romanian coast compare with the current study.

Conclusions

The results obtained in the present study on concentrations of heavy metals in the edible tissues of *M. b.barbatus* and *M. merlangus* show that the levels of heavy metals were lower than the recommended standards. It is worth noting that consumption of these fish from the studied area as food may not possible health hazards to humans at the time of the study. Furthermore, the results obtained in this study would go a long way in fortifying the scanty baseline data for the assessment of the distribution of heavy metals in red mullet and whiting.

Like the Black Sea coasts of Turkey, different fish species are consumed across Europe, therefore it is impossible to make general conclusions on fish consumption. It is suggested that each country needs to consider its own template of fish consumption, especially commercial fish species and cautiously appraise the peril of exceeding the tolerable weekly intake of heavy metals while acquiring the wellness from fish consumption[17].

Acknowledgement

This work was carried out at the University of Sinop, Fisheries Faculty, Department of Hydrobiology. This study was presented as poster in the 3rd International Symposium on EuroAsian Biodiversity (SEAB-2017),

Belarusian State University, Faculty of Biology, 5-8 July 2017- Minsk, BELARUS..

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