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Mercury and Selenium Content in *Otolithes ruber* and *Psettodes erumei* from Khuzestan Shore, Iran

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Abstract In this paper the level of selenium and mercury is analyzed in edible part and liver of *Psettodes erumei* and *Otolithes ruber* two commercial fish in Persian Gulf. The average concentration of Hg and Se in edible parts of *P. erumei* was 0.077 ± 0.062 and 0.044 ± 0.018 (μg g^{-1}ww), and in liver was 0.127 ± 0.122 and 0.132 ± 0.610 (μg g^{-1}ww) respectively. In *O. ruber*, the average concentration of Hg and Se in edible parts was 0.348–0.27 and 0.06 ± 0.021 (μg g^{-1}ww) and in liver was 0.176 ± 0.174 and 0.093 ± 0.022 (μg g^{-1}ww), respectively. *P. erumei* has higher mean molar ratio Se/Hg (1.98) compared to *O. ruber* (0.88).

Keywords Liver · Mercury · Fish · Selenium

Fish are used as good indicators of heavy metals in aquatic systems. Likewise, fish is the main source of trace elements like mercury and selenium in human diet. Approximately 90% of human health risk related to fish consumption is associated to mercury-contaminated fish (Burger and Gochfeld 2005; Ruelas-Inzunza et al. 2008; Berry and Ralston 2008). According to neurotoxic effect of mercury, it is listed as one of the six, most dangerous chemical substances by International Program of Chemical Safety (IPSC) (Bhattacharyya et al. 2010; Raymond and Ralston 2004). The intake of Se could be a nutritional factor that modifies the toxicity of MeHg and evaluations of health risk posed by Hg exposure requires coincident consideration of the Se and Hg content in particular species (Raymond and Ralston 2004).

Persian Gulf is the main source of fishery in south of Iran. There is no evidence regarding natural resources of mercury in site, while most of mercury pollution is related to oil industry. The aim of this study was to determine the mercury and selenium content of selected fish to investigate the correlation between these two elements and determine the accurate Hg exposure in local population through fish intake and to assess whether or not selenium is adequate to mercury detoxification. Population of this region has fish–based diets and this study is the first report of mercury and selenium concentration simultaneously in Persian Gulf.

Materials and Methods

According to USEPA recommendation to examine a predator species and a bottom species for contamination monitoring study (Mcclain et al. 2006), we chose two species that have more consumption rate in south of Iran, i.e., *Otolithes ruber* as predator and *Psettodes erumei* as the bottom feeder. The details of species characteristics are summarized in Table 1. *O. ruber* (22) and *P. erumei* (40) were caught in shore of Khuzestan province in Iran. Samples were placed on ice and moved to laboratory then weighed, and their standard and total lengths were measured. Liver and edible parts were removed and placed in polyethylene bags, which were then labeled and stored at −20°C.

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Table 1 Feeding habit and biometry of selected species

Species	Diet favorable	Ecology	Mean ave (weight, g)	Mean ave (length, cm)
Psettodes erumei	Nekton (bony fish)	Intertidal	735.5	36.1
Otolithes ruber	Zoobenthos (shrimps/prawns)	Intertidal	1,138.59	48.4

Homogenous mass was obtained and wet weight of each sample was recorded. Samples were freeze-dried (OPER-FDU-7012) for 24 h to get at stable weight then dry weights of samples were measured. Afterwards, specimens were powdered and kept in polyethylene bottles to be analyzed. All containers and laboratory tools were washed with detergent, pure water and put in nitric acid (20%) for 24 h. They were finally rinsed with double distilled water and dried. Nitric acid (65%) was of regent grade (Sharlau). H_2O_2 30% was extra-pure (Merck), and deionized water used for all dilution was (0.05 μm_c).

Total mercury was determined by Atomic Absorption Spectrometry Leco AMA-254. Accuracy of total Hg analysis was checked by running three samples of Standard Reference Materials (SRM) (National Institute of Standards and Technology (NIST)): SRM 1633b, SRM 2709, and SRM 2711. Recovery varied between 94.8% and 105%. The detection limit of the method used was 0.001 mg/kg in dry weight. For AAS measurement, approximately 1.0 g of each homogenized dry sample was digested with 9 mL HNO_3 (65%) and 3 mL H_2O_2 (30%) in closed digestion vessels and digestion procedure was based on EPA3052 update method by using Microwave digester (Milestone START D).

After cooling the vessels, digested content was diluted to 25 mL with ultra-pure water and Se concentration was assayed by using Graphic Furnace Atomic Absorption Spectrophotometer (Perkin Elmer 3030) with background correction and detection limit of 0.20 μg/g wet weights. All specimens were run in batches which included blanks, spiked specimens and standard calibration curve. The average accepted recovery for spike was 96%. Also 20% of samples were analyzed twice. Statistical analysis was carried out by using Excel and SPSS software. After normality test (Kolmogrov-Smirnov), we chose non-parametric correlation due to the obtained results.

Results and Discussion

Table 2 lists the concentration of mercury and selenium in all samples. High concentration of Hg was found in edible part of *O. ruber* (1.41 μg g^{-1}ww) whose diet was completely dependent on zoobenthos. Furthermore, the average size and weight in *O. ruber* were higher than those in *P. erumei* ($p < 0.05$). Then, higher mercury content in *O. ruber* is due to longer time of exposure to mercury in this species. Mercury concentration in edible part of *P. erumei* was significantly lower than that in liver ($p < 0.05$). The difference of mercury content in species can reflect differences in tropic level, habitat condition, and feeding behavior (Chen et al. 2002; Burger et al. 2001). The difference in studied species was certainly caused by habitat condition and size dissimilarity.

According to uniform size of *O. ruber*, significant correlation ($p < 0.05$) was found between mercury concentration and weight and length only in *P. erumei*. Correlation between weight and length with mercury has been discussed in numerous studies (Jewett and Duffy 2007; Chen et al. 2002; Burger et al. 2001). Also, such correlation may not exist when growth of species stops and fish are mature, although mercury accumulation continues (Burger et al. 2001).

Compared to EPA standard (0.2 ppm critical value for human consumption and 0.3 ppm) Hg concentration in edible part of *O. ruber* showed significantly higher mercury content. In *P. erumei*, no significant difference was observed between Hg concentration and standards, and all data were below the standard level.

Selenium is a micronutrient element, but in high concentration causes adverse effects. International standard for selenium range is from 0.3 to 2 ppm (Burger and Gochfeld 2005). Concentration of selenium in this study (both species) is significantly lower than adverse level for species themselves and human consumption. Selenium content in liver of both species was higher than that in edible part. Due to the role of the liver as storage organ for glutathione (Parkman and Hultberg 2002), it is expectable to find more selenium in liver than edible parts, and similar results have been reported by Hamilton (2004).

There are significant differences in levels of selenium in the two species. Higher selenium level in *P. erumei* can refer to habitat condition as a sedimentary fish because sediment accumulated more selenium and benthic organism linked to selenium exposure (Hamilton 2004). Likewise, we did not find significant correlation between selenium level with size and weight in both species.

Significant correlation between selenium and mercury concentration reflect beginning the detoxification process and proceeding of Hg–Se complex, detoxification process is under the influence of species type, tissue properties, chemical form of selenium and mercury, and the exact

Table 2 Mercury and Selenium concentration in *Otolithes ruber* and *Psettodes erumei* (μg g^{-1} ww)

Mean Se (ppm) ± SD	Max Se	Min Se	Mean Hg (ppm) ± SD	Max Hg	Min Hg	Tissue	Species
0.132 ± 0.061	0.341	0.043	0.127 ± 0.122	0.510	0.007	Liver	*Psettodes erumei*
0.44 ± 0.018	0.117	0.006	0.077 ± 0.062	0.248	0.005	Edible part	
0.093 ± 0.022	0.125	0.039	0.176 ± 0.174	0.942	0.003	Liver	*Otolithes ruber*
0.060 ± 0.021	0.118	0.028	0.348 ± 0.27	1.414	0.106	Edible part	

mechanism are not apparent (Lourdes et al. 1991; Chen et al. 2002). Positive correlation was found between the two elements in both species and highest correlation was in edible part of *O. ruber*. But this correlation was not statistically significant in both species.

More than 90% of total Hg concentration in fish is formed as methyl mercury (Ruelas-Inzunza et al. 2008); then we can estimate the monthly consumption rate by using EPA calculation as follows:

$$R\ (\text{meals mo}^{-1}) = [(\text{RFD}) \cdot \text{BW} \cdot (30.44)\ \text{dmol}^{-1}]/[\text{CF (IR)}]$$

RFD stands for reference dose that was set about 0.0001 mg kg^{-1}, BW represents body weight which is expected to be 70 kg in adults and 14.5 kg in children, CF denotes methyl mercury in specimen (mg kg^{-1}) and IR stands for consumption rate which is assumed to be 227 g $week^{-1}$.

Allowable fish consumption rate for adult was achieved to be 2.6 meals for *O. ruber* and 13.4 meals for *P. erumei*. Also, the allowable consumption level for children was calculated to be 2.7 and 0.5 meals respectively, for *P. erumei* and *O. ruber*. Since 2003, several investigations have been performed by Faculty of Natural Resource and Marine Science, Tarbiat Modares University (TMU) in Persian Gulf; the results are summarized in Table 3.

All data are represented as dry weight. We assume dw/ww ratio to be approximately 0.3 for all species and data was converted to wet weight for comparison of Hg concentration with EPA standard (0.2 ppm). All of fish species studied except *P. erumei* had mean concentration above EPA value. Mercury average in edible part of fishes from Persian Gulf is 2.09 ppm with maximum average of 5.61 ppm.

To obtain molar ratio in studied species, all data are converted to wet weight and then calculated as mole concenturion by using the following formula:

$$1000 * \text{ppm ww/atomic weight (atomic weigh of selenium : 78.96 g mol}^{-1}\text{, mercury : 200 g mol}^{-1}\text{)}.$$

The avearege mole concentration of elements and Se/Hg ratio are summerized in Table 4. Se/Hg molar ratio in both species except edible part of *O. ruber* is more than 1.0, but *P. erumei* has higher mean molar ratio (1.98) compared to *O. ruber* (0.88). This is due to a combination of high mercury and low selenium content in edible part of *O. ruber*.

After classification of *P. erumei* into three class sizes based on EPA method reported by Mcclain et al. (2006), mercury and selenium concentrations were set in each class. The results show through smaller size, amont of

Table 3 Total Mercury level in fishes and shrimp from Persian Gulf (2003-2006)

Hg (μg/g ww) edible part	Sampling area	Species
1.34	Khuzestan	*Otolithes ruber*
0.35	Khuzestan	*Psettodes erumei*
1.00	Boosheher	*Carcharhinus dussumieri*
1.5	Boosheher (Dayir)	*Carcharhinus dussumieri*
1.45	Boosheher(Gonaveh)	*Carcharhinus dussumieri*
5.61	Hormozgan	*Euryglossa orientalis*
3.38	Khuzestan (Mahshar)	*Boleophthalmus dussumieri*
0.3	Persian Gulf	*Penaeus semisulcatuse*
0.08	Persian Gulf	*Penaeuse merguiensis*
1.1	Persian Gulf	*Metapenaeus stabbbingi*
0.21	Persian Gulf	*Metapenaeus affinis*
0.08	Persian Gulf	*Parapenaeupsis stylifera*

Table 4 Mol concentration and molar ratio of selected species in Persian Gulf

Species	Mean Hg nmol (g^{-1})		Mean Se nmol (g^{-1})		Se/Hg		Hg/Se	
	Liver	Edible part	Liver	Edible part	Liver	Edible part	Liver	Edible part
Psettodes erumei	0.64	0.38	1.63	0.56	2.5	1.47	0.39	0.67
Otolithes ruber	0.88	1.73	1.18	0.76	1.34	0.43	0.74	2.2

Table 5 Selenium mercury molar ratio in *Pesstodes erumei* for 3 class size

Number	Class size (cm)	Weight	Length (cm)	Mean Hg nmol(g^{-1})	Se/Hg
9	41.6–55.3	1,585.5	47.5	158.5	0.57
15	31–41.6	621.8	35.9	65.6	1.83
13	<31	284.5	27.9	40.9	2.7

Mercury decrease and Selenium concentration increase (Table 5) regarding the hypothesis that species with the lowest mercury content had the highest level of selenium (Campbell et al. 2010; Burger et al. 2001). This investigation suggests that inside the species, smaller species have higher selenium content.

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