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Distribution of Trace Elements in the Tissues of *Upeneus pori* and *Upeneus molucensis* from the Eastern Cost of Mediterranean, Iskenderun Bay, Turkey

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Abstract: Samples of *Upeneus pori* and *Upeneus molucensis* were collected in the Iskenderun Bay, Northeastern Mediterranean coast of Turkey the contents of Fe, Zn, Al, Cu, Pb, Mn, Ni, Cr, Cd in the liver, skin and muscle tissues were determined by ICP-AES. Statistical comparisons revealed that metal concentrations were significantly different in each tissue from different fish species. Al, Pb, Ni and Cd concentrations detected in the *Upeneus moluccensis* increased in following order; Muscle<Liver<Skin, for Fe, Zn, Cu and Cr Muscle<Skin<Liver. Al, Pb and Fe concentrations detected in the *Upeneus pori* increased in following order; Muscle<Skin<Liver, for Zn, Muscle<Liver<Skin, for Ni skin<muscle and for Cr Skin<Muscle<Liver. Pb and Ni concentrations didn't show any significant differences between the tissues for this species. The concentrations of these metals measured in the muscle of the three species studied generally were lower than the levels issued by FAO and Turkish legislations. Only the Pb levels in two species and Cd levels in *Upeneus molucensis* were higher than the acceptable values for human consumption designated by various health organisations.

Key words: Mullidae, *Upeneus molucensis*, *Upeneus pori*, heavy metals, Mediterranean, Iskenderun Bay

INTRODUCTION

Metallic elements are environmentally ubiquitous, readily dissolved in and transported by water and readily taken up by aquatic organisms. Metals enter the aquatic environment by atmospheric deposition, by erosion of the geological matrix or through anthropogenic sources, such as industrial effluents and mining wastes (Alam *et al*., 2002). Fish are often at the top of the aquatic food chain and many concentrate large amounts of some metals from the water (Mansour and Sidky, 2002). Fish is considered as one of the main protein sources of food for humans. Water pollution leads to fish contaminated with toxic metals, from many sources, e.g., industrial and domestic waste water, natural runoff and contributory rivers (Rashed, 2001). Trace metals can be accumulated by fish through both the food chain and water (Hadson, 1988). Essentially, fish assimilate metals by ingestion of particulate material suspended in water, ingestion of food, ion-exchange of dissolvedmetals across lipophilic membranes, e.g., the gills and adsorption on tissue and membrane surfaces. Metal distribution between the different tissues depends on the mode of exposure, i.e., dietary and/or aqueous exposure and can serve as a pollution indicator (Alam *et al*., 2002). Fish living in polluted waters may accumulate toxic trace metals via their food chains. The bioaccumulation of metals is therefore an index of the pollution status of the relevant water body and is a useful tool studying the biological role of the metals present at elevated levels in aquatic organisms, especially fish (Tariq *et al*., 1993).

Iskenderun Bay, in which there are large quantities of untreated industrial and domestic sewage, has one of the polluted coastal waters of Turkey and also has an economic importance for fishery. In this study, the levels of trace metals in demersal fish samples collected from Iskenderun Bay, Turkey were determined by ICP-AES.

MATERIALS AND METHODS

Sample collection: Fishing was carried out from Iskenderun Bay, eastern coast of Mediterranean. Fish were caught by fishermen's nets and transported daily to the laboratory. The samples were placed in ice, brought to the laboratory, washed, separated by species and then stored frozen at -18°C prior to analysis. Total size and weight of fishes were shown in Table 1.

Reagents: All reagents used were of analytical grade. Working standards of Fe, Zn, Al, Cu, Pb, Mn, Ni, Cr and Cd were prepared by diluting concentrated stock solutions (Merck, Germany) of 1000 mg L^{-1} in ultra-pure water (MilliQ, Milli- pore-USA).

Sample preparetion: The edible portions of the tissues from the samples were removed, homogenized and about

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Table 1: Mean length and weight of fish species

Species	n	Weight (g)	Length (cm)
Upeneus moluccensis	20	31.63±1.48	13.71±0.20
Upeneus pori	20	22.79±0.76	12.68±0.11

Values are expressed as X±Sx

1.0±0.2 g was taken for analysis. Five milliliters of nitric acid were added to the sample, covered and left overnight at room temperature. Then the samples were digested, using a waterbath at 60°C for 3 days. The completely digested samples were allowed to cool to room temperature, filtered (glass wool) and made up to 35 mL (UNEP, 1984).

Chemical analyses: All digested samples were analyzed, in triplicate, using an ICP-AES Varian Liberty Series-2. The standard addition method was used to correct for matrix effects. The following absorption lines were used; Cd 226.5 nm, Zn 213.8 nm, Fe 259.9 nm, Al 396.1 nm, Cu 324.7 nm, Pb 220.3 nm, Mn 257.6 nm, Ni 352.4 nm, Cr 267.7 nm. Standards were prepared from stock standard solution of metals.

Determination of recovery: Instrument was calibrated with standard solutions prepared from commercial materials. Analytical blanks were run in the same way as the samples and determined using standard solutions prepared in the same acid matrix. All chemicals and standard solutions used in the study were obtained from Merck and were of analytical grade. The quality of data was checked by the analysis of standard refenrence material (DORM-2 National Research Council, Canada) Recovery rates ranged from 93-100% for all investigated elements.

RESULTS AND DISCUSSION

The concentrations of some heavy metals (Al, Pb, Zn, Fe, Cd, Ni, Cu, Cr, Mn) in the tissues of *Upeneus moluccensis* and *Upeneus pori* were determined. Mean concentrations and associated standard deviations of these metals in the skin, liver and muscle of these fish collected from Iskenderun Bay are shown in Table 2 and 3. Results of statistical comparisons of tissue metal concentrations among 3 tissues are also shown in Table 2 and 3. Some data weren't presented as the samples were lower than detection limits. Data were analysed statistically by a series of Duncan multiple range test to identify any differences among tissues (a, b and c) (Table 2 and 3).

Data shown in different letters are significant at the 0.05 level. For skin; the highest Pb (5.64 μg g^{-1} dw), Fe (17.27 μg g^{-1} dw), Zn (4.01 μg g^{-1} dw) Cr (1.53 μg g^{-1} dw)

Table 2: The mean concentrations and standard deviation of metals in the different tissues of *U. pori*

	Heavy metal concentrations		
Metals	Skin	Muscle	Liver
Al	14.767±0.787^{b}	6.728±0.179^{a}	30.240±3.554^{c}
Pb	5.640±1.191	4.518±0.877	11.159±11.159
Fe	17.277±1.456^{b}	2.525±0.224^{a}	131.133±18.711^{c}
Zn	4.016±0.449^{a}	0.016±0.016^{b}	1.145±1.145^{c}
Ni	0.026±0.020	0.036±0.036	ND
Cd	ND	ND	ND
Cu	ND	ND	ND
Cr	1.534±0.859^{a}	3.548±1.091^{a}	30.139±18.740^{b}
Mn	ND	ND	ND

Table 3: The mean concentrations and standard deviation of metals in the different tissues of *U. molucensis*

	Heavy metal concentrations		
Metals	Skin	Muscle	Liver
Al	20.737±2.372^{c}	5.902±0.216^{a}	13.258±0.701^{b}
Pb	5.067±0.723^{b}	1.596±0.183^{a}	4.536±0.631^{b}
Fe	8.628±1.106^{a}	3.472±1.338^{a}	211.722±8.058^{b}
Zn	2.451±0.455^{a}	0.161±0.056^{a}	66.334±11.130^{b}
Ni	2.419±0.408^{b}	0.576±0.103^{a}	1.853±0.725^{ab}
Cd	1.063±0.108^{b}	0.297±0.030^{a}	0.747±0.139^{b}
Cu	6.009±0.571^{b}	1.397±0.079^{a}	24.993±4.991^{c}
Cr	0.635±0.241^{ab}	0.122±0.050^{a}	1.103±0.667^{b}
Mn	0.028±0.017^{a}	0.077±0.029^{b}	ND

Data shown in different letters are significant at the 0.05 level

concentration were detected in *U. pori*; the highest Al (20.73 μg g^{-1} dw), Ni (2.41 μg g^{-1} dw) concentration was detected in *U. molucensis* from Iskenderun Bay. For muscle tissue; the highest Al (6.72 μg g^{-1} dw), Pb (4.51 μg g^{-1} dw), Cr (3.54 μg g^{-1} dw), concentration were detected in *U. pori*; the highest Fe (3.47 μg g^{-1} dw), Zn (0.16 μg g^{-1} dw), Ni (0.57 μg g^{-1} dw) concentration was detected in *U. molucensis* from Iskenderun Bay. For liver tissue the highest Al (30.24 μg g^{-1} dw), Pb (11.15 μg g^{-1} dw), Cr (30.13 μg g^{-1} dw) was detected in *U. pori*; Fe (211.72 μg g^{-1} dw), Zn (66.33 μg g^{-1} dw)) concentration was detected in *U. molucensis* from Iskenderun Bay (Table 2 and 3).

As in Table 1 and 2, the general trend of heavy metal concentrations are in the order for *U. pori*: Al>Pb>Cr>Fe>Ni>Zn for muscle tissue and for *U. molucensis*: Al>Fe>Pb>Cu>Ni>Zn>Cr>Mn for muscle tissue. Al, Pb, Ni and Cd concentrations detected in the *Upeneus moluccensis* increased in following order; Muscle<Liver<Skin, for Fe, Zn, Cu and Cr Muscle<Skin<Liver.

Al, Pb and Fe concentrations detected in the *Upeneus pori* increased in following order; Muscle<Skin<Liver, for Zn, Muscle<Liver<Skin, for Ni skin<muscle and for Cr Skin<Muscle<Liver. Pb and Ni concentrations didn't show any significant differences between the tissues for this species. Statistical comparisons revealed that metal concentrations were significantly different in each tissue

from different fish species. This may be related to the differences in ecological needs, swimming behaviors and the metabolic activities among different fish species. The differences in metal concentrations of the tissues might be as a result of their capacity to induce metal-binding proteins such as metallothioneins. The quantity of heavy metals accumulated depends on age, habitat and feeding behaviour of the fish. Both species are carnivorous bottom living organisms, feeding on a wide variety of small animals particularly crustaceans and worms.

The present data showed that metal concentrations in the liver and skin were highest in all the fishes. It is well known that large amount of metallothionein induction occurs in liver tissue of fishes. Waterborne metals affect directly fish body surface. They enter the organism mainly through the gills but certain amount of metals accumulate in the skin, affecting the scales, epidermis or receptors. Measurements of metal concentrations in the skin show much lower values compairing to such organs as gills, liver or kidneys but higher than in the muscles (Heath, 1987; Canli and Furness, 1993; Roesijadi and Robinson, 1994; Jezierska and Witeska, 2001).

Research done by Kalay *et al*. (2004) in the Gulf of Mersin show Cd levels higher in the liver tissues than muscle tissues of *Mullus barbatus* ve *Sparus aurata*. The results show that Cd levels of *Mullus surmuletus* are rather higher in muscle than liver tissue, while it is similar level in *Upeneus molucensis* with previous research.

The heavy metal concentrations in several fish species from the Iskenderun Bay of the Mediterranean Sea were determined by Yilmaz (2003). The range of metal concentrations were as follows: Fe, 41.84-70.28; Ni, 0.94-1.22; Cr, 1.28-1.46; Pb, 1.03-7.45; Zn, 19.55-38.23 (wet wt.). Much higher concentrations of Pb, Fe, Zn, Ni in the liver and skin of *U. molucensis* and Ni concentrations in the liver of *U. pori* were found in the study. Concentrations of some heavy metals in *Mugil* sp. and *Sparus aurata* have been reported for the Iskenderun Bay. The range of metal concentrations were as follows: Fe, 30.7-43.2; Cd, 4.1-7.6; Pb, 14.0-24.6; Zn, 20.8-32.2 for *Sparus aurata;* Fe, 40.4-57.2; Cd, 5.4-10.2; Pb, 19.4-28.5; Zn, 26.6-39.2 for *Mugil* sp. The ranges of all metal concentrations are lower in the study except Fe and Zn for liver tissues. At the same time, the heavy metal concentrations in red mullet collected from Marmara sea are generally lower than the study (Topcuoglu *et al*., 2004).

Some amphipod crustaceans from the Atlantic are known to accumulate atypically high cadmium concentrations in their body (approx. 60 μg Cd g^{-1}, Rainbow, 1989). Other studies also demonstrated relatively high levels of cadmium (approx. 8 μg Cd g^{-1}) in amphipods from the Mediterranean (Fowler, 1986). The hypothesis of metal accumulation through diet should not be neglected regarding high cadmium concentrations found in Upeneus molucensis from the Iskenderun Bay.

When considering the metal content in marine organisms, suitable for human consumption, the most important aspect is their toxicity to humans. The limit value for cadmium in the edible part of fish, proposed by the European Commission (Commission of the European Communities, 2001), is 0.1 μg g^{-1} wet weights. In this context, *Upeneus molucensis* samples analyzed presented concentrations exceeding the proposed limits by the European Directive. Furthermore, they were far below the permissible limits for human consumption. Moreover, comparisons with the Canadian food standards (Cu: 100 μg g^{-1}; Zn: 100 μg g^{-1}), Hungarian standards (Cu: 60 μg g^{-1}; Zn: 80 μg g^{-1}) and Australian accepted limits (Cu: 10 μg g^{-1}; Zn: 150 μg g^{-1}) demonstrate that the content of these metals in the edible part of the examined fish is lower than the guidelines mentioned before.

Turkish legislation establishes maximum levels for four of the metals studied. The limit is not accepted above 0.1 mg kg^{-1} for Cd, 1.0 mg kg^{-1} for Pb, 20.0 mg kg^{-1} for Cu, 50 mg kg^{-1} for Zn for human consumption. Food and Agricultural Organization limits for Cd and Pb is 0.5 and 30 mg kg^{-1} for Cu and Zn. The concentrations of these metals measured in the muscle of the three species studied generally were lower than the levels issued by FAO and Turkish legislations (FAO, 2006; Anonymous, 1996). Only the Pb levels in two species and Cd levels in *Upeneus molucensis* were higher than the acceptable values for human consumption designated by various health organisations.

CONCLUSION

Accumulating of heavy metals in fish muscle may be considered as an important warning signal for fish health and human consumption. The present study shows that precautions need to be taken in order to prevent future heavy metal pollution. Otherwise, these pollutions can be dangerous for fish and human health.

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