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ORIGINAL RESEARCH PAPER

ACCUMULATION OF MERCURY AND LEAD AT SIX KINDS OF FISH IN DURRËS BAY

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SYNOPSIS

This study assessed the concentrations of mercury (Hg) and lead (Pb) in sea water, muscle and liver of *Mugil cephalus*, *Sparus aurata, Merluccius merluccius, Scorpanea porcus, Mullus barbatus* and *Dicentracus labrax.* These samples were collected in five stations in Durres bay. Fish were collected by size (small and large). The samples of water were analyzed using Absorber Spectometry Atomic "SOP ASA-01^{A}" and fish samples were analyzed using AAS -10 varian.

The mean value of lead (Pb) in muscle was 0.18±0.12 mg/kg wet weigh for small fish and 0.437±0.3 mg/kg wet weigh for large fish. The mean value of mercury (Hg) varied from 0.10±0.056 for small fish and 0.307±0.1 mg /kg wet weigh for large fish. Metal levels in muscle were lower than recommended limiting standards.

INTRODUCTION

The accumulation of toxic metals to hazardous levels in aquatic biota has become a problem of increasing concern (Manahann, 1994; Idodo–Umeh, 2002). Fish are widely consumed, firstly because they are part of the local diet, but also because of their high protein, low saturated fat and omega fatty acids content, that are known to contribute to a health (Kenedy et al., 2009). The importance of fish as a source of protein and the interest in understanding the accumulation of heavy metals at the trophic levels of the food chain, extend the focus towards finfish (Obasohan, 2007). The use of fish as bio-indicators of metal pollution of aquatic environments and suitability for human use from toxicological view point has been documented. Fish absorb heavy metals from the surrounding environment (Ginsberg & Toal, 2009) depending on several factors such as the characteristics of the species under consideration, the exposure period, the concentration of the element, as well as abiotic factors such as temperature, salinity, pH and seasonal changes. Hence, harmful substances like heavy metals, released by anthropogenic activities

will be accumulated in marine organisms through the food chain; as a result, human health can be at risk because of consumption of fish contaminated by toxic chemicals. For this reason, fish muscles are commonly analyzed to determine contaminants concentrations. In general, studies on heavy metals can be important in two main aspects. First, from the public health point of view, where the attention has been drawn to the necessity of measuring the accumulation of heavy metals; particularly these metals which causes serious health hazards to humans (e.g. Cd, Pb, Hg). Second, from the aquatic environment point of view, the main problem has been to prevent biological deterioration and to identify the sources which threaten ecological equilibrium (Khaled, 2004). The present study had the purpose to determine the concentration of heavy metals (mercury Hg and lead Pb) in seawater, muscles and in the fish liver of species: *Mugil cephalus, Dicentracus labrax, Sparus aurata ,Scorpanea porcus, Merluccius merluccius and Mullus barbatus* of Durres bay with a view to determining the pollution levels and ascertain the suitability of the fish for human consumption. Lead and mercury are also two dangerous contaminant of water, marines fauna and flora. Data from European Food Safety Authority (EFSA) showed that the exposure to Hg and Pb may effects like neurotoxicity, carcinogenicity, endocrine and reproductive failures in adults. Moderate exposure to Pb and Hg can also significantly reduce human semen quality and is related to many diseases in adults and children (e.g., damage to DNA or impairment of the reproductive function, Herreros et al., 2008). The choice of fish was based on its importance in the fisheries of the area for both food and economic purposes.

The study consist in the presentation of some results obtained on the evaluation of mercury and lead in water and some fish species collected in Porto Romano bay. The contamination of this area from the heavy metals is as a result of historically activity of ex leather factory and other chemical factories in the Porto Romano area before 1990. After 1990 the activities were interrupted, but the negative impact on environment was continuing and the area is in great danger even today. The area around the chemical plant at Porto Romano is considered the most critical, including land, building materials and ground water (UNEP, 2000).

MATERIAL AND METHODS

This study was carried out in the gulf of Durres (Porto Romano Area). The heavy metals evaluated in this study were: Mercury (Hg) and Lead (Pb). For the evaluation of heavy metals presence in sea water, were selected 5 stations for sampling which are:

1. at the delta of hidrovorium, 2.at the Ciklori, 3.at the BishtiPalles, 4.at the Currila; and 5. at the Kallmi The fish samples were collected from this area and they present in the same time the group of the fish more preferred by the

consummators. The fish species included in this study were: *Mullus barbatus, Sparus aurata, Mugil cephalus, Dicentrachus labrax, Scorpaena porcus, Merluccius merluccius*. The samples were collected from fisherman that fishing in this area. Samplings were collected accidentally according the procedure by Guidelines for monitoring chemical contaminants in the sea using marine organisms (UNEP 1993). For every samples were evaluated all the indicators and were labelled and stored in hermetical and freezing conditions, until they were transported at the lab.

The fishes were separated in two groups according to their weight. First was the group of fish with average weight 90 gr, and the second with an average weight of 220 gr. Each group consisted by six fish and in total there were evaluated 72 samples.

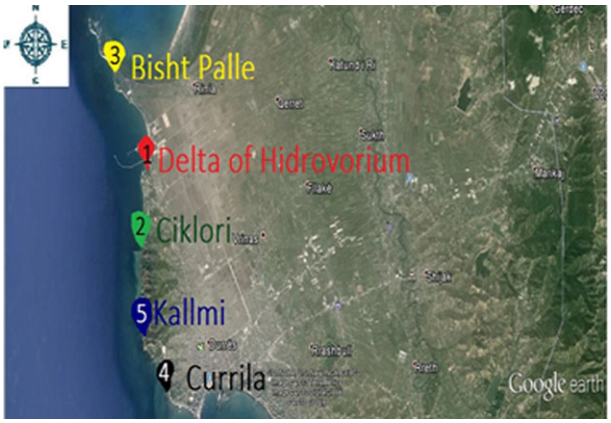

Figure 1:
Map of sample point at Durres bay.

ANALYTICAL PROCEDURES FOR EVALUATION OF SEA WATER SAMPLES

Sea water samples were preserved in sterile plastic bottles, treated before with nitric acid in a concentration of 0.5 ml / 0.5 litter water. Before analytical evaluation, water was filtered from waste in order to avoid the influence of them in the final results (UNEP 1993). Water samples initially were treated with HNO3 (mixing with water in ratio 100 ml water and 1 ml HNO3). The evaluation were conducted with the Atomic Absorber Varian “ASA-01A"

ANALYTICAL PROCEDURES FOR EVALUATION OF BIOTA SAMPLES

The fish were prepared before evaluation. It was treated with distilled water and after that they were weighted. The fish scales and the skin were removed and then they were filleted. The materials were fragmented and homogenized with the aim to obtaining an homogeneous mass (Schmitt and Finger 1987). For the disaggregation of samples were used 5 ml concentrated HNO3. The prepared samples were covered in the Teflon cylinder and then they were put in the furnace of type Berghof Speed TM, with wave S-3 MW + V. 3.0, for 20-30 minutes. After burning, the samples were diluted in water with 2% HNO3 deyonizated and were

mixed well before their evaluation (AOAC, 1990). The analytic evaluation was conducted by AAS variant 10. The statistical evaluation was carried out with the program Microsoft Office Excel 2007.

RESULTS AND DISCUSSION

The results taken by the evaluation of the water samples from the 5 stations in Porto Romano beach are presented in the table 1.

Table 1: The concentration of Mercury and Lead in sea water (mg/l)

Sample	Hg mg/l	Pb mg/l
1*	< 0.0005	< 0.108
2**	< 0.0003	< 0.100
3***	< 0.0005	< 0.108
4****	< 0.0003	< 0.100
5*****	< 0.0003	< 0.100

*1 the delta of hidrovorium; **2 the Ciklori; ***3 the BishtiPalles;
****4 the Currila; *****5 the Kallmi

Analitic evaluation of water samples showed that Hg and Pb were present in all the sampling stations. The higher values were registred in the samples colected from the station 1 (at the delta of hidrovorium) and 3 (at the new Port of deposits in the Bisht Palle).This change is visible and thought to be related with the sampling position and proximity to the coast, where are potential terrestial sources for the contamination. The presence of Pb, shown on table 1 is comparable with the values obtained by the authors Lazo P., et al (2003) in their study in Durres, while comparing the concentrations of Hg and Pb in our study with data obtained from studies in the Mediterranean Sea (0.016-20.5 µg / l) (UNEP 2000; EEA 2005, 2007) have been resultet in lower values.

The presence of Hg and Pb in these areas as well as uneven distribution of them, show that their origin can be from several sources, they can be with terrestrial origin or as a result of the geomorphological structure of Durres Bay area, or as and anthropogenic sources.

EVALUATION OF HEAVY METALS IN MUSCLES

Concentration levels of heavy metals (Pb and Hg) in muscle tissues are given in Table 2.

Table 2: The average concentrations of Hg and Pb in muscle of fish.

Fish species	Heavy metals			
	Pb (ppm /wet weight)		Hg (ppm /wet weight)	
S. aurata	Muscle 90 gr	Muscle 220 gr	Muscle 90 gr	Muscle 220 gr
M. cephalus	0.048±0.02	0.098±0.03	0.11±0.08	0.21±0.05
M. merluccius	0.06±0.04	0.18±0.063	0.05±0.06	0.24±0.08**
S. porcus	0.048±0.03	0.25±0.09*	0.09±0.01	0.13±0.07
M. barbatua	0.192±0.13	0.504±0.36**	0.2±0.03	0.41±0.18**
D. labrax	0.095±0.06	0.28±0.14	0.11±0.06	0.29±0.09
M ±D.s	0.18±0.12	0.437±0.3*	0.10±0.056	0.307±0.1**

*P<0.1, **P<0.01, ***P<0.001

The value of lead (Pb), varies from 0.05 to 0.19ppm wet/weight in a small fishes and 0.098 ppm to 0.504 ppm wet weight at a large fishes. The values of mercury (Hg) varies from 0.05 ppm to 0.2 ppm wet weight in small fishes and 0.13 ppm to 0.41 ppm wet weight large fishes.

The mean concentration of lead in *M. barbatu*s was significantly higher (P≤ 0.01) than all other fish types with average value of 0.504±0.36 ppm, followed by *D. labrax and S. porcus* with averages of 0.28±0.14 ppm wet/ weight and 0.25 ±0.09 ppm wet/ weight.

Marcotrigiano et al.,(2003); Corsi et al., (2002); Henry et al., (2004) at their studies at Adriatic sea, Jon sea and French coast, have reported the lower value for Pb (0.0016 – 0.01 mg/kg). The reporting from Kalay et al., (1999) (for Pb- 0.42–3 mg/kg), Yilmaz (2003) (7.45 mg/kg for Pb), Turkmen et al., (2008), (Pb 0.27- 0.87 mg/kg) for Mediterreanean sea are higher then results in our study.

As are reflected in the table 2, there are significant differences in the values of metal between the different species of fishes. It is well known that it's very difficult to compare the metal concentrations in the same tissue at the different species, because in these species the accumulation of heavy metals is influenced by different factors. These factors include: the aquatic environments, concerning the type and the level of water pollution, feeding habits whether omnivorous or carnivorous etc. Kamaruzzaman, et al.(2010), indicated that there were a relation between metal concentration and several intrinsic factors of fish such as organism size and age of fish. This investigation showed that different fish species contained different concentrations of a certain metal in their muscles. Kalay et al.(1999) have reported that different fish species accumulate metals in their tissue on different values. Moreover, Canli & Atli, (2003) have reported that levels of heavy metals in fish depended by fish species and aquatic environments. On the other hand, Farkas et al., (2000) attributed the differences of concentrations of metals between fishes by feeding habits, the bio-concentration capacity of each fish species and by the

biochemical characteristics of the metal. In addition Romeo et al., (1999) described that the ability of fish to accumulate heavy metals depends on ecological needs, metabolism, degree of pollution in sediment, water and food, as well as salinity and temperature of water.

The authors Storell et al., (2004); Juresa & Blanusa., (2003); Karadede & Unlu., (2007) in their studies have concluded that in the benthic fishes, the accumulation of heavy metals was higher than in pelagic fishes. *Scorpaena porcus*, *Mullus barbatus* and *Dicentrachus labrax* are known as benthic fish, as gluttonous fish and predators (Rakaj, N. 1995). Because of that, the accumulation of pollutants was higher than in other species.

CONCENTRATIONS OF HG AND PB IN MUSCLE AND LIVER

To accomplish this task, there were selected six fish for each species. Average weights of fish were 150-220 gram. The samples were treated according the relevant procedures (AOAC 1990) and the results are presented in table 3.

Table 3. Mean values (± SD) of Hg and Pb in muscle and liver of six fish species.

Fish species	Hg (ppm/ ww)		Pb (ppm/ ww)	
	Muscles	Liver	Muscles	Liver
S. aurata	0.1 ± 0.07	0.32 ± 0.04	0.073 ± 0.06	0.089 ± 0.1
M. ephalus	0.15 ± 0.05	0.26 ± 0.09	0.1 ± 0.1	0.195 ± 0.15
M. merlucius	0.09 ± 0.01**	0.3 ± 0.1	0.1 ± 0.12	0.176 ± 0.1
S. porcus	0.20 ± 0.09**	0.5 ± 0.2	0.2 ± 0.14	0.73 ± 0.5
M. barbatua	0.09 ± 0.01	0.3 ± 0.2	0.106 ± 0.1	0.236 ± 0.2
D. labrax	0.14 ± 0.04**	0.37 ± 0.2	0.29 ± 0.2	0.39 ± 0.3
M ± D.s	0.13 ± 0.05	0.32 ± 0.09	0.161 ± 0.12	0.3 ± 0.23

***P<0.001; **P<0.01; *P<0.05

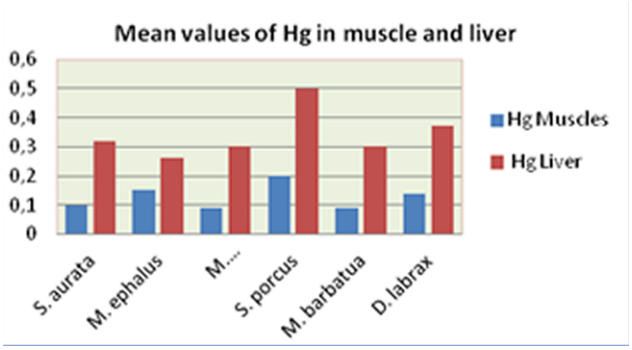

Figure 2:
The average value of Hg concentration at muscle and liver of six kinds of fish.

According to the results presented in the table 3 and figure 2 seems to be clear that the accumulation of heavy metals were higher in liver than in muscle

($P<0.01$, $P<0.001$). In the comparison with values of Pb and Hg in the muscular tissue of fish with values of Pb and Hg in their liver, they are higher at the last one. The fish liver exhibited highest tendency to accumulate both the metals. Dural *et al*. (2007) and Ploetz *et al*., (2007) reported high level of lead in the liver. The higher levels of trace elements such as lead and chromium in liver relative to other tissues may be attributed to the affinity or strong coordination of metallothionein protein with these elements (Ikem *et al*., 2003).

The metal concentration is higher in liver than in muscle because muscles are not primary storage location. The heavy metals are stored in the liver first and then are transferred to the muscle.

The fish and other vertebrate proteins have metal binding, such as the liver metaltionina. These proteins bind metals causing liver to accumulate more metals than other organs (Atlie & Canli, 2003), De Smet, 2001). The liver is highly active in the uptake and storage of heavy metals hence it is consider as a good indicator of water pollutions with heavy metals. Thought, that fish liver may represent a good bio indicator of metal pollution (Dural *et al*., 2007).

According to above references, in our study, in all evaluated samples resulted that the heavy metals level in liver was higher than in muscles. Those conclusions support the results of our study, where all samples evaluated, the concentration of heavy metals were higher in liver than in muscles.

COMPARING OF THE RESULTS WITH EU STANDARTS

The control of food quality in our country is based on the norms of EU directive (2002).

The comparing of the data of Hg concentration levels in muscles tissue of fish species showed lower concentration level than the EU regulation (0.5 ppm, EU, 2002). The Limit allowed for consumption is 0.2 ppm Pb. In *Scorpena porcus* and *Dicentrarchus labrax* species, the values of Pb are (0.212, 0.202 ppm). Those levels are inside the limit. The Implementation of these directives is an important step for food safety structures, because the food contamination by heavy metals above the norm, presented a serious threat for the health of consumers

CONCLUSIONS

Present study provides information on the concentration of lead and mercury in sea water and fish from Durres bay. The concentrations of heavy metals in the muscles of the six studied species were considerably lower than the maximum levels set by EU directive. The fish's liver exhibited highest tendency to accumulate both lead and mercury, while the accumulation of both metals were lower in fish's muscle. Having information on concentration of heavy metals in fish is important for both biodiversity and natural habitats protection and also for the human health.

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