



ACCUMULATION OF CADMIUM AND CHROMIUM IN WATER AND BIOTA IN DURRES BAY (ALBANIA)

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SYNOPSIS

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heavy metals,
fish,
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The present paper evaluates the presence of cadmium and chromium in Durres bay. The object of this study have been sea water, muscles and livers of *Mugil cephalus*, *Sparus aurata*, *Merluccius merluccius*, *Scorpanea porcus*, *Mullus barbatus* and *Decentracus labrax*. The samples of water were analyzed for heavy metals, by using Atomic Absorber Spectrometry "height ASA-01A" and the fish samples were analyzed by using AAS-10 variant. The results showed that in muscles has more concentrated heavy metals than in water, while the liver accumulated more of these metals then in muscles.

INTRODUCTION

The metals are non-biodegradable and are considered as major pollutants causing Environmental cytotoxic, mutagenic and carcinogenic effects in animals and aquatic organisms (More et al., 2003). Aquatic organisms have the ability to accumulate heavy metals from various sources including sediments, soil erosion, runoff, air depositions of dust and aerosol and discharges of waste (Labonne et al., 2001; Goodwin et al., 2003). The pollutions can be transmitted to the fish through some ways as are through food, branchiate, drinking water and through the mouth and skin. Then the pollutants pass in the blood stream and then store in different organs especially in the liver. The present study had the purpose to determine the concentration of heavy metals in seawater, muscles and in the fish liver. The study consist in the presentation of some results obtained on the Evaluation of chromium and cadmium 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. There is a high level of contamination with lindane and Chromium (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: Cadmium (Cd) and Chromium (Cr). For the Evaluation of water level of contamination with those metals were selected 5 stations for sampling:

1. at the delta of hidrovorium, 2. at the Ciklori, 3. at the new port of the deposits in the Bishti Palles, 4. at the Kallmi and 5. at the Currila. 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 of UNEP (1993). For every samples were evaluated all the indicators and were labeled and stored in hermetical and freezing conditions, until they were transported at the lab.

The fishes were separated in tow groups according to their weight. The group of fish with average weight 90 gram, and the other with an average weight of 220 gr. Each group consisted in six fish and in total there were evaluated 72 samples.



Figure 1: Map of sample points, 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 liter 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. The preparation consisted in: treatments with distilled water cleared of debris, weighing and measurement. 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 & 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 deionized and were mixed well before their evaluation (Helrich, 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 cadmium and chromium as the two key elements of the series of heavy metals in highest quantities cause a significant damage to aquatic fauna (EMAD , E. ABOU EL-NAGA et al 2005). In the following table, there are presented the values of cadmium and chromium in water according to sampling stations.

Nr.	Cd mg/l	Cr mg/l
1	< 0.001	< 0.002
2	< 0.001	< 0.001
3	< 0.002	< 0.002
4	< 0.001	< 0.001
5	< 0.001	< 0.001

Table 1: The concentration of heavy metals in sea water (µg / l).

* 1-5 sampling sites

The presence of these metals is evident in all samples and stations. The chromium appears to be increased in value at the third station that is at the hidrovorium delta and at the new port of deposits in Bishti Palles. The chromium values in the station 2, 4 and 5, seem to be in the same levels. The highest level of

cadmium was in the third station, while other stations seem to be in the same level. In Durres, the presence of (Cr) was in high level. It seems to be related with the stocks from the former waste processing leather factory in Porto Romano, transported in the sea water.

THE CONCENTRATION OF HEAVY METALS IN BIOTA

The concentration of heavy metals in different fish species varied in different values. The data of Table No. 2, give us an overview of the distribution of these metals in muscular tissue of fish. The presence of heavy metals was evident in most of the samples estimated. The Cd values, varies from 0.002 ppm to 0.003 ppm in the small fishes and from 0.038 to 0.058 ppm at the large fishes. The Cr values varied from 0.087-0.298 ppm for small fishes, at 0.38 - 0.95 ppm at the larger fishes. Authors, MARCOTRIGIANO & STORELLI (2003) in their studies have reported the higher values that in our study for the Cd (0.05 mg / kg), and similar results for Cr. In the meantime the results reported by KALAY et al. (1999) (Cd, 0.09-0.5 mg / kg), Turkmen et al. (2008) (Cd 0.05 to 12.07) mg / kg, for the Mediterranean Sea were higher than in our study.

TURKMEN et al. (2008) have reported the lower values for the presence of chromium (from 0.09 to 0.36 ppm), compared with results of YILMAZ (2003) (1.46, ppm wet.weight), they were several time highest. The evaluation of chromium in the aquatic environment and also compared with the results of different authors for the Porto Romano area, showed that Cr was in high levels in the aquatic environment and sediments CELO et al. (1999), CULLAJ et al. (2000), LAZO et al. (2003), and for that the highest content of Cr in the fishes tissues were expected.

Table 2: the Values of Cd and Cr in the muscle of fish.

Fish species	Heavy metals in the muscular tissues			
	Cd		Cr	
	V	M	V	M
<i>S. aurata</i>	0.002± 0.001	0.043±0.002	0.12±0.078	0.45±0.1***
<i>M. cephalus</i>	0.028±0.002	0.038±0.001	0.23±0.09	0.38±0.15
<i>M. merluccius</i>	0.027±0.001	0.047±0.001**	0.135±0.05	0.64±0.2***
<i>S. porcus</i>	0.03±0.001	0.058±0.02 ***	0.205±0.1	0.95±0.3 ***
<i>M. barbatua</i>	0.03±0.001	0.049±0.01	0.087±0.06	0.65±0.2
<i>D. labrax</i>	0.027±0.001	0.053±0.01***	0.298±0.1	0.82±0.4***
M ±D.s	0.028±0.001	0.048±0.007	0.179±0.08	0.65±0.22

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

As are reflected in the table, there are significant differences in the values of metal between the different species of fishes. The variations in value between the different species and into the same group of fish are as a result of different way of feeding, the time of exposition in the contaminated environment as well as their size. In fishes which live in the bottom of the sea or otherwise named benthic fish, the concentrations of heavy metals were higher than at other types. KILGOUR (1991), in his study showed that the connection of metal in sediment can raise their percentage in water. There is also showed that benthic animals and predators which live and eat in the bottom of the sea had the higher concentrations of metals in their tissues and organs, then other animals. The authors STORELLI et al. (2004), JURESA & BLANUSA (2003), COGUN et al. (2006), KARADEDE – AKIN. & 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* known as benthic fish, (fish that living in the bottom of the sea), as gluttonous fish and predators (Rakaj, 1995). Therefore is considered that the accumulation of pollutants was higher than in other species.

Table 3: The concentration of heavy metals in muscle and liver.

Fish species	Cd (ppm dw)		Cr (ppm dw)	
	Muscles	Liver	Muscles	Liver
<i>S. aurata</i>	0.032 ± 0.007	0.25 ± 0.2	0.2 ± 0.08	0.161±0.02
<i>M. ephalus</i>	0.04 ± 0.02	0.14 ± 0.1	0.32 ±0.2	1.23±0.04***
<i>M. merluccius</i>	0.018 ± 0.001	0.1 ± 0.1	0.39±0.1	1.065±0.05
<i>S. porcus</i>	0.024 ± 0.003	0.09 ± 0.08	0.47±0.2	0.852±0.01
<i>M. barbatus</i>	0.033 ± 0.01	0.18 ± 0.1**	0.145±0.06	0.192±0.06
<i>D. labrax</i>	0.028 ± 0.01	0.53 ± 0.4	0.362±0.1	0.947±0.09**
M ± D.s	0.029 ± 0.008	0.20 ± 0.16	0.315±0.12	0.741± 0.45

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

	Cd	Cr
Muscle	0.03	0.315
Liver	0.20	0.74

Table 4: The mean concentration of heavy metals in muscle and liver (ppm /wet weight).

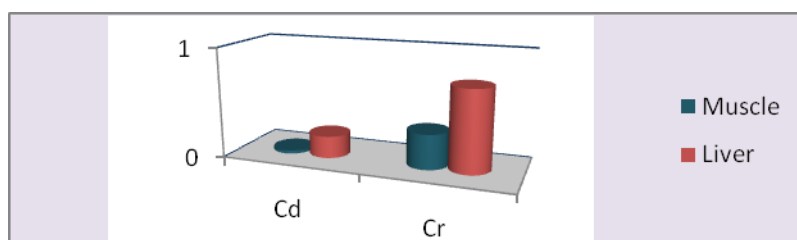


Figure 2: The graphical presentation of Cd and Cr value in muscle and liver.

To accomplish this task, there were selected six fishes for each species, in two respective areas. Average weights of fishes were (150-220 gram). The samples were treated according to the relevant procedures and the results are presented in Table no. 3.

According to the results presented in the tables 3, 4 and diagrams 1 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 Cd and Cr in the muscular tissue of fish with values of Cd and Cr in their liver, they are higher at the last one.

Fish and other vertebrate proteins have metal binding, such as the liver metalionina. These proteins bind metals causing liver to accumulate more metals than other organs (Hamilton & Mehrle, 1986; Roesijadi, 1992; Atli & Canli, 2003; De Smet et al., 2001). Those conclusions support the results of our study, where all samples evaluated, the concentration of heavy metals were higher in liver than in muscles. Ability of metalionine to connect with heavy metals was not at the same levels for all metals, for ex. cadmium, copper and zinc have the highest ability to bind with other metals that metalionina. The studies of this nature are carried out by many authors (Stanec et al., 2005; Lacerda et al., 2007; Schon – Has et al., 2008; Hilal & Ismail, 2008). These studies have evaluated the degree of accumulation of metals in several organs of fish exposed by pollutants in natural conditions. Those studies have been conducted in fishes exposed for a specific period of time in different concentrations of metals. The conclusions of these studies indicate that exposure to metals, both in natural and artificial way, accompanied by their accumulation in various organs the largest accumulation is in the liver, bronchial kidney, bone, brain, etc.

INFLUENCE OF BODY SIZE IN THE CONCENTRATION OF METALS IN AQUATIC ORGANISM

It has been proved that body size can influence in the concentration of metals in aquatic organisms (Bebianno et al., 2003; Saavedra et al., 2004), however, the dependence between body size and concentration of metals is a complex issue that is discussed constantly. Many studies show for a positive correlation between body size and concentration of metals. The authors ADAMS (2004), STANEC et al. (2005), SOLIMAN (2006), DAVIES et al. (2006) and LACERDA et al. (2007), in their works reported that the accumulation of metals had a positive correlation with body size of biota. This can be attributed to the feeding way, the long time of the stay in the polluted environment and metabolic activity of adult's organisms. Other studies showed that relationship between weight/metal has a negative correlation, the metal concentrations were higher in the younger individuals than older one (Duquesne et al., 2004). This correlation can be attributed to the fact that in the small bodies, the protein binding activity metal (metalionina) is higher (Oliver et al., 2002) and mechanisms of detoxification with low efficiency at the small organisms (Catsiki et al., 1994; Raspor et al., 2004). In the relationship between weight / metal, have

influence also the various factors and the concentration of metal in the environment (Cravo & Bebianno, 2005), the possibility of providing food (Saavedra et al., 2004). Exposure to tidal influence (Labarta et al., 1997), the diversity between the populations (Cubanda et al., 2001). The concentration of metals in Biota is also a complex issue as well as aquatic ecosystems themselves. The biology of feeding in water organisms is different and also the reaction to the polluted environment is different. Also, the nature of aquatic ecosystems, water currents and underwater, geomorphologic structure are the other factors that play an important role in the contamination and its spread in sea environment. For this reason and the results reported by different authors for water ecosystems various and in some case they are not in accordance.

Table 4: Average values of heavy metals in two groups of fish.

	Cd	Cr
Fish 90 gr	0.028	0.18
Fish 220 gr	0.048	0.65
Mean	0.038	0.41

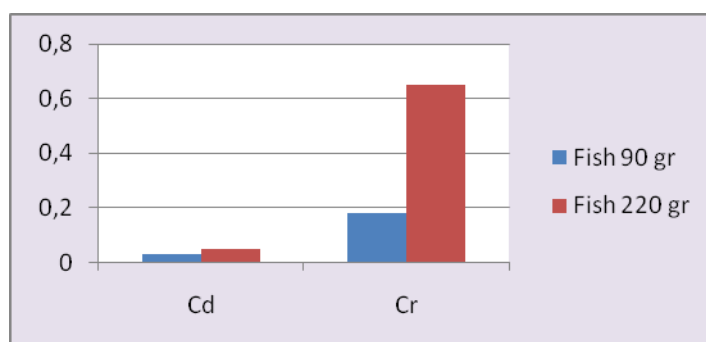


Figure 3: The values of heavy metals in two groups of fish.

According to our results (Tab. 4, Fig. 3) there is evident that the accumulations of heavy metals generally increase with increasing the size of biota, but not in all the cases this correlation is significant. The groups of fishes with average weight 90 grams had a lower concentration of metals then the groups of fish with average weight 220 gr.

COMPARING THE VALUES OF HEAVY METALS BETWEEN WATER AND BIOTA

In the numerous studies is reported that the concentration of heavy metals in Biota is many times higher than in the living environment. Aquatic organisms can accumulate these environmental pollutants many times more than the aquatic

environment themselves. However efficiency making metals from contaminated water may vary with environmental requirements biota, their metabolism and by the level of the contamination of water, food and sediment. An important role is played by other factors such as salt, temperature, interactive agents, etc. (Tandjir & Djebbar, 2007).

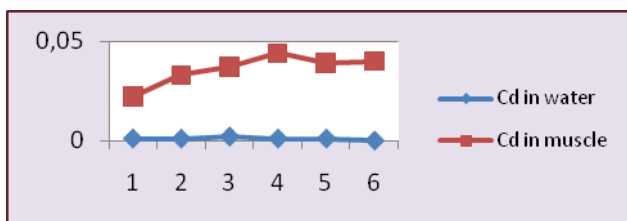


Figure 4: Comparison of average values of Cd in water and biota.

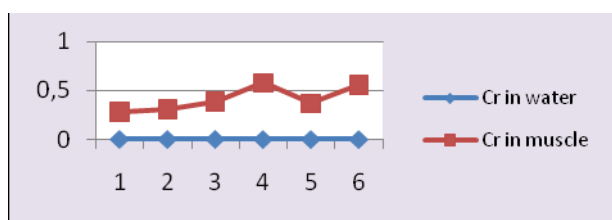


Figure 5: Comparison of average values of water and biota.

The graphic appearances of Cd and Cr values in water and Biota in figs. 3 and 4 clearly reflect the difference of accumulation of metals in water and Biota.

CONCLUSION

The results of this investigation showed that the water and fish of Durres bay were contaminated by heavy metals Cd and Cr. Fish liver exhibited higher tendency to accumulate both cadmium and chromium, in comparison with muscle. The accumulation of heavy metals is higher in fishes organism rather than in seawater. In this context, monitoring of fish and mollusk tissues serves as an important indicator of the level of contamination of water and sediment.

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