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HEAVY METALS IN FISH FOR PUBLIC CONSUMPTION AND CONSUMER PROTECTION

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SYNOPSIS

The purpose of the study was to gather information and evaluate the status of Albanian fish products in terms of heavy metals, in order to protect consumer. Fish were selected based on life's condition (natural/ cultivated) and by size; small/medium. Two groups of fish samples (*Myllus* spp., *Merlucius merlucius)* were picked up in Albanian sea; two other species (*Dicentrarchus labrax* and *Sparus aurata)* were imported in. The level of heavy metals (Pb, Hg, Cd, Cr) was determined in muscle by using atomic absorption spectrophotometry (AAS).

INTRODUCTION

Fish is an important food source for the human body. Fish provides essential fatty acids like omega 3, proteins, vitamins and minerals. Despite it nutritional value the consumption of fish brings many times a potential hazard concern for the human consumers. Heavy metals enter into the aquatic environment mainly by anthropogenic source. Fish is at the top of the aquatic food chain, and during its life can accumulate large ammounts of toxic elements. Heavy metals are defined by their weight. To be classified as a heavy metal, it must have a specific gravity of 2.7. One category of toxic contaminants accumulated by fish are heavy metals such as lead (Pb), mercury (Hg), cadmium (Cd) and chrome (Cr). Any of these heavy metals can destroy life when they concentrate in the body above acceptable levels. Heavy metals have the tendency to accumulate in various organs and muscle tissue of fish. Contaminated fish enter into the human body through consumption and it causes health hazards. The purpose of this work was to gather information and evaluate the status of Albanian seafood products in terms of heavy metals in order to protect consumers. Secondly - to compare our results to EU maximum permitted levels of heavy metals in fish for human consumption.

MATERIALS AND METHODS

Four species of benthic fish such as *Mullus barbatus*, *Merlucius merlucius, Dicentrarchus labrax* and *Sparus aurata* were used in this study. Fish samples were collected in the period February – May 2010. Fish was collected from the central fish market of Tirana. All the analysis was done on the edible parts of the seafood products. A total of 71 samples were analysed for level of Pb, Hg, Cd and Cr by using atomic absorption spectophotometry (AAS). All samples were packet and transportet in a frezze container back into the laboratory. Samples were first identified, catallogated, get weight, and conservated at - 18º C. The samples were separated into two groups according to the weight: small fish size, mean weight of 158 g, and medium fish size, mean weight of 245 g. The samples were diveded into two groups depending of cultivation: natural and cultivated. Muscle tissue of samples was homogenized in a blender, they get dried at 100 ºC. One gramme of sample was weight and then treated with 10 ml of HNO_3 and 5 ml of concentrated H_2SO_4 and let in overnight. Next day they were dried at 150º C for at least, 30 minutes and 50 ml of it were put into a normal flask, and filled with destilated water. The heavy metals were measured by ICP-OES, Optima 2100 Dv produced by Perkin Elmer. The curves of calibration are presented in figures 1, 2, 3, 4.

RESULTS AND DISCUSSION

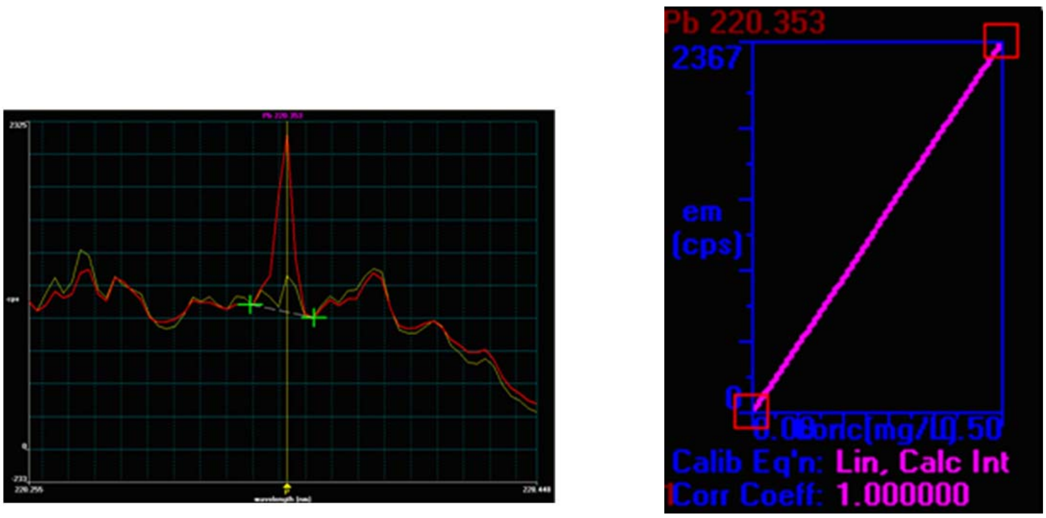

Figure 1: Calibration Curbe of lead (Pb).

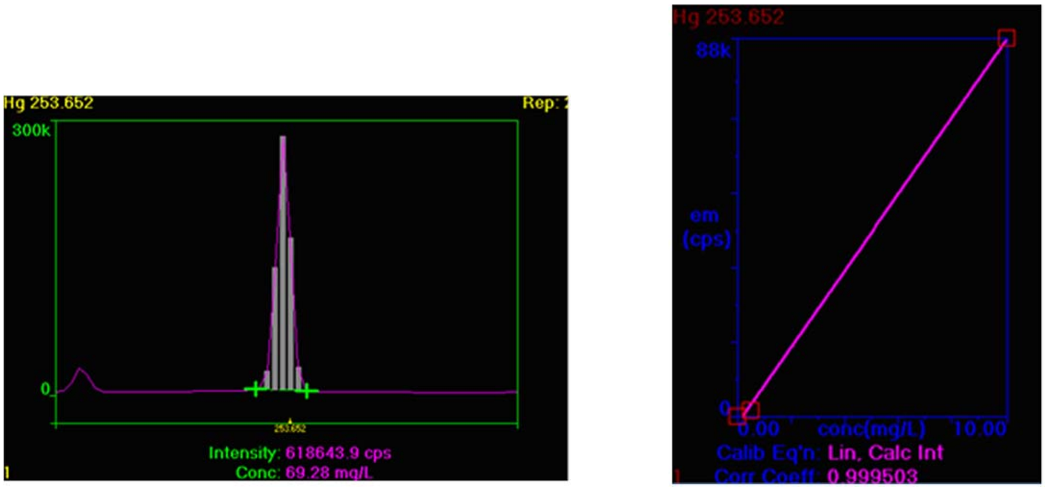

Figure 2: Calibration curbe of Mercury (Hg).

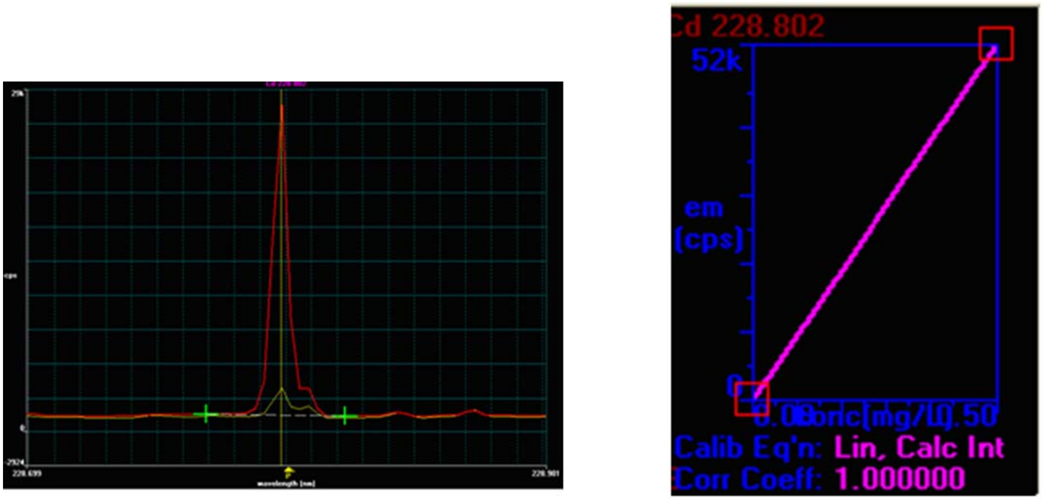

Figure 3: Calibration curbe of Cadmium (Cd).

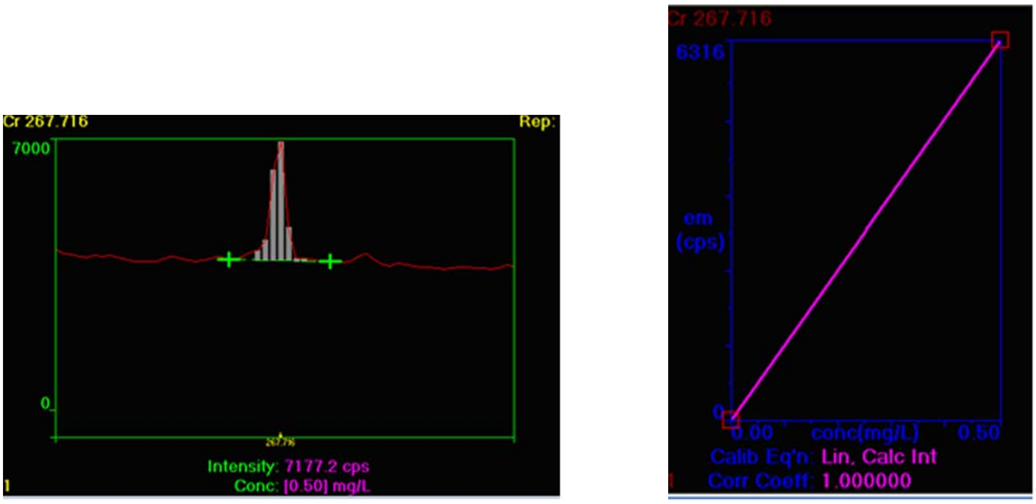

Figure 4: Calibration curbe of Chrome (Cr).

There are numerous heavy metals, some of which are highly toxic, like mercury, lead, arsenic, and cadmium. Fish accumulate toxic materials at various levels, depending on species, age, season, feeding habits, and so on. This study summarizes the results obtained in 2010 for the monitoring of various heavy metals in the edible part of fish used as meal for human consumption. The tables and graphs (Tabs. 1, 2, 3 and Fig. 5) show some of the main results from the analysis of heavy metals in seafood made during this study. The data is derived from the monitoring programme "Health fish - health consumer". The concentration of lead (Pb), mercury (Hg) and chrome (Cr) in the fish samples analyzed in the programme was always below the maximum limits set by the EU (Tabs. 1, 2, 3 and Fig. 5). There are means and standard deviation in followed results, according to fish sample size. The mean ± SE value of concentration of lead (mg/kg) in the muscle was 0.18 ±0.24 in small size and 0.07 ±0.01 in medium size. The mean ± SE value of concentration of mercury (mg/kg) was 0.83± 0.007in small size fish and 0.07 ±0.07 in medium size fish. The mean ± SE value of concentration of cadmium (mg/kg) in the muscle was 0.20 ± 0.15 in small size and 0.40 ± 0.16 in medium size. The mean ± SE value of concentration of chrome (mg/kg) was 0.26 ± 0.30 in small size fish and 0.10 ± 0.02 in medium size fish.

The mean value of lead, mercury and chrome were lower in case of medium fish size groups, mean value of cadmium was lower in case of small fish size group. These results are in agreement with our previous results obtained in a studying programme 2005-2008. The results reveal that these compounds are in very low amounts in fish and fish products and cadmium and chrome are actually below detection limits in *D. labrax and S. aurata*. *M. barbatus and M. merlucius* contain cadmium, as an undesirable substance, in concentration exceeding some times the maximum level set by the EU (0.05 mg/kg) (EC, 2001). Although, heavy metals in marine life in Albanian waters and in the seafood are in most instances found to occur at very low levels if at all detectable. All the fish species shown in the Tabs. 1 and 2 are carnivors and they live in the same habitat (benthic); fish species *Mullus barbatus* and *Merlucius merlucius* get cought in the Albainan marine water. *Dicentrarchus labrax* and *Sparus aurata* are cultivated species. None of the metals are biodegradable, and though they can change forms from solid, to liquid, to dust and gas, they never completely disappear**.** The ones that are toxic in even the some minute amounts create instant cellular destruction in any of their forms**.** Marine animals such as fish are able to readily absorb metals and their bodies regulate to accommodate their presence. They are easily stored in fatty tissue and will bio-accumulate if the fish is exposed to further contamination (Sindayigaya et al., 1994).

Table 1: Level of Pb and Hg in the muscle tissue (mg/kg wet weight).

	Heavy metals			
Fish species	Pb		Hg	
	S	M	S	M
M. barbatus	0.21 ±0.12***	nd	0.01 ± 0.03***	0.01± 0.01
M. merlucius	nd****	0.21 ± 0.004	0.03 ± 0.0002****	0.10 ± 0.02
D. labrax	0.16 ± 0.24*	0.02 ± 0.03	0.21± 0.02*	0.12 ± 0.14
S. aurata	nd	0.007 ±0.01	nd	nd
A±SD	**0.18 ±0.24**	**0.07 ±0.01**	**0.83± 0.007**	**0.07 ±0.07**

Table 2: Level of Cd and Cr in the muscle tissue (mg/kg wet weight).

	Heavy metals			
Fish species	Cd		Cr	
	S	M	S	M
M. barbatus	0.40 ± 0.27**	0.45 ± 0.32	0.40 ± 0.47*	0.08 ± 0.07
M. merlucius	0.22 ± 0.05**	0.36 ± 0.08	0.13 ± 0.04	0.13 ± 0.04
D. labrax	nd	nd	nd	nd
S. aurata	nd	nd	nd	nd
A±SD	**0.20 ± 0.15**	**0.40 ± 0.16**	**0.26± 0.30**	**0.10 ± 0.02**

S - Group of fish small weight of mean 158 g.
M - Group of fish medium weight of mean 245 g.
Significant differences of average between groups
**** P < 0.0001; *** P < 0.001; ** P < 0.01; * P<0.1

Table 3: Avarage values of heavy metal level
in fish different sized groups (mg/kg wet weight).

Fish size	Pb	Hg	Cd	Cr
Small	0.18	0.83	0.2	0.26
Medium	0.07	0.07	0.4	0.1

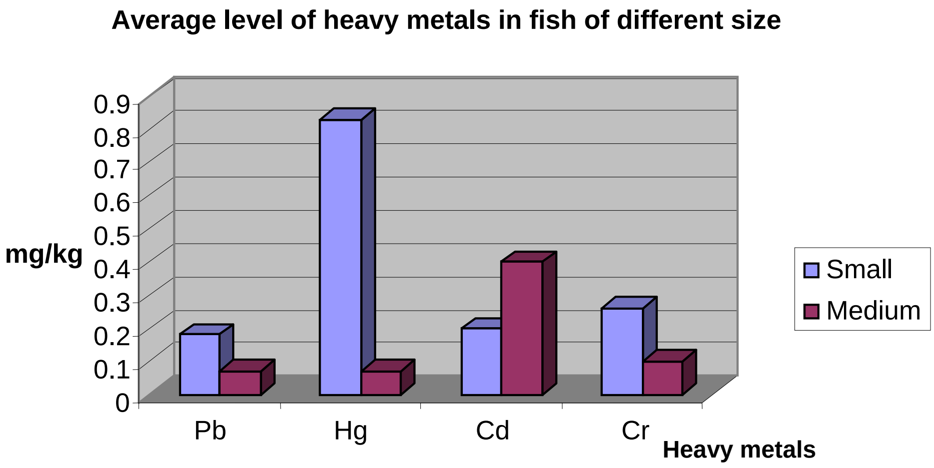

Figure 5: Avarage values of heavy metal level in fish different sized groups (mg/kg wet weight).

Rather, it is the more serious issue of our marine life being poisoned by toxic levels of metals, which are then passed up the food chain; it means a risk for human consumator. There are means and standard deviation in followed results, according to life condition of fish (Tab. 4, fig. 6). Fish species *Mullus barbatus* and *Merlucius merlucius* get cought in the Albainan marine water. The mean ± SE value of concentration of lead (mg/kg) in the muscle of *M. barbatus* was 0.21 ±0.12 and the mean ± SE value of concentration of mercury (mg/kg) of this fish was 0.01 ± 0.03. The mean ± SE value of concentration of cadmium (mg/kg) in the muscle of *M. barbatus* was 0.43 ± 0.27. The mean ± SE value of concentration of chrome (mg/kg) was 0.24 ± 0.17. The mean ± SE value of concentration of lead (mg/kg) in the muscle of *M. merlucius* was 0.11 ±0.002 and the mean ± SE value of concentration of mercury (mg/kg) of this fish was 0.06 ± 0.02. The mean ± SE value of concentration of cadmium (mg/kg) in the muscle of *M. merlucius* was 0.28 ± 0.05. The mean ± SE value of concentration of chrome (mg/kg) was 0.13 ± 0.04. *Dicentrarchus labrax* and *Sparus aurata* are cultivated species. The mean ± SE value of concentration of lead (mg/kg) in the muscle of *D. labrax* was 0.14 ± 0.12 and the mean ± SE value of concentration of mercury (mg/kg) of this fish was 0.165 ± 0.09. The concentration of cadmium (mg/kg) and chrome in the muscle of *D. labrax* and *S. aurata* were non detectible (nd).

Table 4: Avarage value of eavy metal concentration in two groups of fish (wild /cultivate) (mg/kg wet weight).

	Pb	Hg	Cd	Cr
Wild fish	0.1	0.037	0.35	0.18
Cultivated fish	0.06	0.16	nd	nd

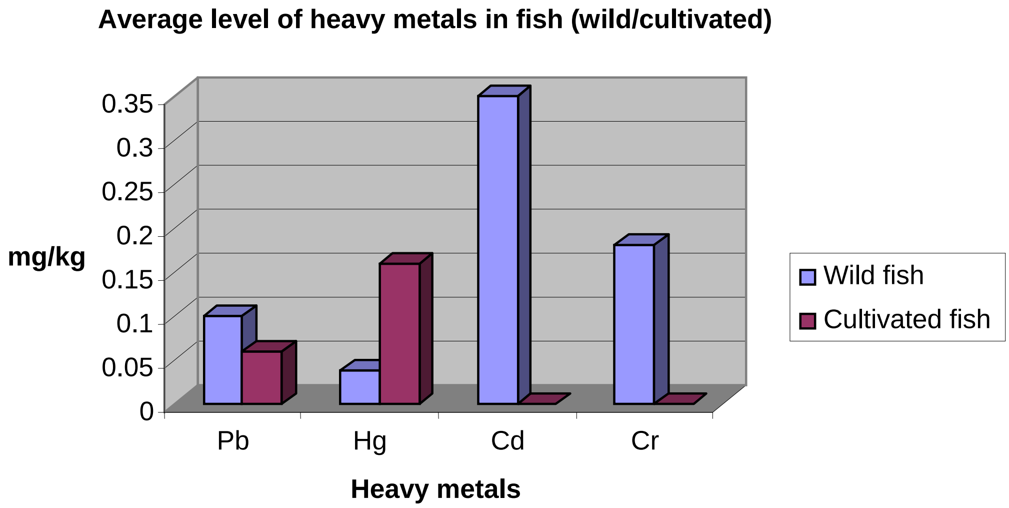

Figure 6: Avarage value of heavy metal concentration in two groups of fish (wild /cultivate) (mg/kg wet weight).

The mean value of lead and mercury were always below the maximum limits set by the EU in case of wild and cultivated groups (Pb - 0.30mg/kg, Hg -1.00mg/kg) (EC, 2001; Srebacon et al., 2007, Yilmaz, 2005). These results are expressed as upper bond level, that means when the concentration of a substance is measured to be below limit of detection (non detected) of the analytical method. Concentration of Pb has significant differences form *D. labrax samples* (p< 0.1) to *M. barbatus* (p < 0.001) and *M. merlucius* species (<0.0001). The higher values of Pb resulted in muscle tissue of *M. barbatus* (0.21 mg/kg) and *M. merlucius* (0.21 mg/kg) and the lower value resulted in *Sparus aurata* (0.007 mg/kg). They are two different species according to life condition; two first are wild fish and the last is a cultivated one**.** Mercury is one of the most lethal heavy metals. Its toxicity effects vary from the chemical form, dose, and route of ingestion, and with the exposed organism's species, sex, age and general condition (Eisler, 1987). It instantly damages every cell it touches and causes organ dysfunction, being particularly destructive to the brain, kidney and liver (Srebacon et al., 2007). The two main sources of mercury are amalgams and fish. In our study Hg presence is evident in most of analysed samples, except *S. aurata*. Concentration of Hg has significant differences form *D. labrax samples* (p< 0.1) to *M. barbatus* (p < 0.001) and *M. merlucius* species (<0.0001). The higher values of Hg resulted in muscle tissue of D. *labrax* of 158g weight (0.21 mg/kg) and lower level of it resulted in M. *barbatus* (0.01 mg/kg). Scientists today are concerned that people who eat fish contaminated with mercury will be put at risk**.** Cadmium is a heavy metal which has been found in quite high quantities in larger fish like tuna and swordfish. This is because the metal accumulates over time and also because these fish are higher up in the food chain and so will be eating already contaminated prey. Cadmium, bioaccumulates at all trophic levels, accumulating in the livers and kidneys of fish (Sindayigaya et al., 1994). It is stored in fat, which keeps it from circulating in the blood. Furthermore, as it can be seen, cadmium value, in wild fish, was several times higher than maximum limits set by EU in public consumed seafood (0.05 mg/kg) (EC, 2001). Concentration of Cd has significant differences form *M. barbatus samples* ($p < 0.01$) to *M. merlucius* ($p < 0.001$) and *M. merlucius* species of the same weight ($p <0.0001$). The higher values of Cd resulted in muscle tissue of medium weight of *Mullus barbatus* (0.45 mg/kg) and the lower level of it resulted in *M. merlucius* of small weight (0.22 mg/kg). Contrary our study, cadmium has sometimes been found to be rather high in crustaceans, fish liver and other internal organs, but not in fish flesh. This is thought to be due to natural sources and the volcanic nature of the land and not related to the activity of man. Concentration of Cr has significant differences only in *M. barbatus samples* ($p < 0.1$). The higher values of Cr resulted in muscle tissue of small weight group of *Mullus barbatus* (0.40 mg/kg) and the lower level of it resulted in the same *specie of medium weight group* (0.08 mg/kg). Differences between values of heavy metals presented in our study are depending on species, age, season, feeding habits, and so on. All fish species shown in the tables are carnivors and they live in the same habitat (benthic); fish species *Mullus barbatus* and *Merlucius merlucius* get cought in the Albainan marine water. *Dicentrarchus labrax* and *Sparus aurata* are cultivated. It is known that benthic fish can accumulate heavy metals some times more than pellagic fish; for this reason the maximim permitted levels imposed by EU for lead, mercury, cadmium and chrome are some times higher in pellagic one used as ichtic consume products (EU - No. 466/2001).

CONCLUSIONS

The contamination levels of heavy metals Pb, Hg, and Cr in samples of four kinds of fish in this study were lower than the maximim permitted levels imposed by EU. Level of Cd presented an exception in *Mullus barbatus* and *Merlucius merlucius* (both small and medium size fish groups). This preliminary evaluation of the status of the Albanian seafood products in terms of heavy metals as undesirable substances shown that consumers take a safe product. But, the study will be a long term one, which can only be reached through continuous monitoring. The information will be utilized for a risk assessment and the setting of maximum values that are now under consideration within EU (e.g. heavy metals).

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