ORIGINAL ARTICLES

HEAVY METALS IN MARINE ORGANISMS FROM ALBANIAN COASTAL WATERS

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ABSTRACT

BACKGROUND: Marine mussels and marine fishes are generally used as bioindicators of heavy metal pollution in coastal areas, because pollutants are potentially accumulated in marine organisms and sediments.

MATERIAL AND METHODS: Levels of mercury, cadmium, lead and chromium were determined in the soft issue of five types of marine organisms (*Mytilus galloprovincialis*, *Ruditapes decussatus, Donaxspp, Mullus barbatus, Sardina pilcardus*) collected along Albanian coast from Shengjin to Butrint , during two periods of time, 1990 – 1993 and 2002 – 2007. The analyses were performed using electrothermal atomic absorption and cold vapor atomic technique.

RESULTS: The concentration of heavy metals in marine organisms had resulted in very large range. The highest levels of heavy metals were obtained in samples collected near Vlora bay in central Albanian part of Adriatic Sea, where was allocated one chlorine soda plant, and the lowest concentrations were obtained in samples collected in northern part of country, Adriatic Sea, and in the southern part, Ionian Sea. The level of mercury varied from 0.02 – 0.410 mg/kg, the levels of lead and cadmium oscillated from 0.326 – 1.582 and 0.055 – 0.927 mg/kg. respectively.

CONCLUSIONS: Comparing the results obtained in first period of our study 1992 – 1993 with those of second period, ten years later, of 2002 – 2007, there was observed a slight decrease in concentrations of heavy metals in marine organisms, that is, in our opinion, related with the collapse of the industrial activities that polluted the sea water with heavy metals.

Keywords: pollution, heavy metals, marine mussels, marine fishes, coastal areas, atomic absorption spectrometry, biomonitoring.

BACKGROUND

Adriatic Sea is considered as the most polluted sea in Mediterranean areas. The main source of pollution were oil industry, paper industry and chemical industry.

Several studies have demonstrated that the concentrations of heavy metals in marine organisms can provide a time –integrated measure of the environment bioavailability of these contaminants (Philips, 1976, 1977, 1980)

However, the time-integration capacity of marine organisms may vary from different metals, and these bioindicators reflect the sea environmental condition over a period of time which increases if the biological half life of a particular metal is extended. Usually this aspect is not considered in monitoring studies, probably because the available data on heavy metals are scanty and often contradictory (Philips and Segar, 1986)

The role that heavy metals play as pollutants is widely recognized (Ballester, et al, 1980, Chester, 1975, Ober, et al, 1987). In the sea, pollutants are potentially accumulated in marine organisms and sediments, and subsequently transferred to man through the food chain.

Marine mussels and marine fishes are generally used as bioindicators of heavy metal pollution in coastal areas, because pollutants are potentially accumulated in marine organisms and sediments.

Factors known to influence metal concentrations and accumulation in these organisms include metal bioavailability, season of sampling, hydrodynamics of the environment, size, sex, changes in tissue composition, and reproductive cycle (Szefer et al., 2004). Seasonal variations have been related to a great extent to seasonal changes in flesh weight during the development of gonadic tissues (Rainbow, 2002; Szefer et al., 2004).

Of all the studies carried out up to know on the subject of heavy metals in the Adriatic and Ionian Sea, only three has been dedicated to Albanian Sea, (Corsi, Tabaku, Nuro, Beqiraj, Marku, etc 2011; Celo et al 1999; MWH Consulting, 2003) and this restricted to limited zone of Vlora bay

The purpose of this study was to evaluate and to compare the presence of some heavy metals chosen among those with highest pollution potential in marine organisms from Albanian coastal water collected in 1990-1993 and 2002-2007.

MATERIALS AND METHODS

The specimens that we used as bioindicators of heavy metal pollution in coastal areas were *Mytilus galloprovincialis, Mullus barbatus, Sardina pilcardus and Traschurus traschurus*. These specimens are species with relatively restricted migratory movements and are common in the Albanian Sea. Samples were collected in three stations situated along Albanian coast. Collected samples were placed in polyethylene bags and stored below -20°C pending analysis.

The soft part of the samples were carefully removed using a plastic knife and homogenized in a mixer to make up the sample from each sampling site. Homogenized samples were analyzed in triplicate.

Homogenized samples were analyzed for mercury using cold vapor AAS technique, after digestion with acid nitric and perhidrol in a hot-plate in 105° C, whereas for cadmium and lead the samples were digested with nitric acid and perchloric acid using a hot-plate in 150°C. Determination of cadmium and lead were performed by graphite furnace atomic spectrometry.

RESULTS

In tables 1-3 are presented results of analysis for mercury, lead and cadmium in organisms that were used as bioindicators of heavy metals pollution, obtained during the period of time 1990 – 1993 and 2002-2007.

Table 1. Hg content at different zones expressed in µg/kg wet weight.

Kind of products	Durres		Vlore		Sarande	
	1990-1993	2002-2007	1990-1993	2002-2007	1990-1993	2002-2007
Mytilus galloprovincialis	18.3±3.8	17.9±2.6	77.4±5.6	68.3±9.6	43.7±7.2	45.6±6.5
Mullus barbatus	88.8±7.1	86.2±4.2	172.3±4.8	125.2± 5.9	50.5±6.5	48.7±4.6
Sardina pilcardus	78.8±2.9	76.3±6.5	131.4±8.5	132.1±8.8	82.5±11.3	79,2±3.7
Trachurus trachurus	59.8±3.7	61.4±3.8	52.4±6.9	50.3±7.9	54.7±3.5	55.1±4.4

Table 2. Pb content at different zones expressed in µg/kg wet weight.

Kind of products	Vlore		Sarande	
	1990-1993	2002-2007	1990-1993	2002-2007
Mytilus galloprovincialis	502.1±20.3	493.2±16.1	424.8±26.9	454.4±75.6
Mullus barbatus	420±93.5	479±12.2	-	-
Trachurus trachurus	30.5±8.5	33.9±10.4	29.9±8.6	28.5±9.4

Table 3. Cd content at different zones expressed in µg/kg wet weight.

Kind of products	Vlore		Sarande	
	1990-1993	2002-2007	1990-1993	2002-2007
Mytilus galloprovincialis	531.2±20.6	489±18.5	420.4 ± 12.9	415.6 ± 20.8
Mullus barbatus	523.3±14.1	495.8±13.5	-	-
Trachurus trachurus	23.8-3.8	25.4±5.9	24.8 ± 7.5	22.5 ± 5.2

DISCUSSION

Metal pollution of the sea is less visible and direct than other types of marine pollution but its effects on marine ecosystems and humans are intense and very extensive. The toxic effects of heavy metals, particularly arsenic, mercury, cadmium and lead, have been broadly studied (Inskipand &Piotrowsiki, 1985; Kurieshyand D'siliva, 1993; Narvaes, 2002; Nishihara, Shimamato, Wen & Kondo, 1985)

Metal contaminations in food, especially in marine products, have been broadly investigated (Catsiki&Strogyloudi, 1999; Enomoto & Uchida, 1973; Liang, Cheung, & Wong, 1999; Uysal, 1980; Uysal, 1990). Tuna, as a predator,is able to concentrate large amount of heavy metals.Some of them are used for biomonitoring of environmental contamination (Schmitt & Brumbaugh, 1990).

The concentrations of mercury, lead and cadmium in *Mytilus galoprovincialis* from the Adriatic and Ionian Coast are of, 11.2 – 77.6, 380.4 – 545.1 and 434.8 – 560.9 µg/kg wet weight, respectively,and are similar to the results given in literature (Voegborlo, El-Methnani, & Abedin, 1999;Maanan 2007, Mol and Alakavuk 2011, Yilmaz 2003, Besada, 2002)

The mean concentration levels of mercury found in *Mytilus galloprovincialis* ranged from 18.3 in µg/kg wet weight in the Durres area to 77.4 in µg/kg wet weight in Vlora in the period 1990-1993, whereas for the period 2002-2007 the levels were oscillated from 17.9µg/kg to 68.3 µg/kg. Significantly higher levels of heavy metals were observed in mussels from Vlora Bay. .

The results obtained for the fish *Mullus barbatus* and *Trachurus trachurus* have shown that the mean mercury concentration have ranged from 88.8 µg/kg in Durres area to 172.3 µg/kg in Vlora area, where was allocated one chlorine soda plant. During the period of time 2002-2007 the results obtained for *Mullus barbatus* were oscillated from 86.2 – 125.2 µg/kg whereas for *Trachurus trachurus* the levels of mercury were oscillated between 50.3 – 61.4 µg/kg wet weight.

The significant heavy metal contamination in Vlora Bay has been already reported due to the presence of a soda production industry from 1978 to 1992: Due to the electrolytic method based on Hg, a huge amount of Hg has been discharged in the bay, which is reflected by the high levels detected in marine sediments (Celo et al., 1999; MWH Consulting, 2003)

According to the results obtained, the mercury levels in the samples of fishes and mussels from all sites of collected samples were found below the permissible levels (FAO, 1976; FDA, 2000; FDA, 2001)

The concentration of lead recorded at all sites ranged from 360.6 to 550.2 µg/kg for *Mullus barbatus* and for *Trachurus trachurus* 19.3-45.2 µg/kg.

Overall, heavy metals data seem to be similar to other low-impact areas, including the Adriatic Sea (Kljakovic´-Gas´pic´ et al., 2006; Lavilla et al., 2006; Martella, Nelli, and Bargagli, 1997; Orescanin et al.,2006)

The distribution of metals varies between fish species, depending on age, development status and other physiological factors (Kagi & Schaffer, 1998). Fish accumulate substantial concentrations of mercury in their tissues and thus can represent a major dietary source of this element for humans. Fish are the single largest sources of mercury and arsenic for man. Mercury is a known human toxicant and the primary sources of mercury contamination in man are through eating fish. Biotransformation of mercury and methyl mercuryformation constitute a dangerous problem for human health (Inskip & Piotrowsiki, 1985).

Statistical analysis of results by ANOVA showed no significant differences among all samples and periods of collected samples.

The levels of toxic elements in shellfish are related to age, sex, season and place (Kagi & Schaffer, 1998). It is also reported that cooking reduces the amount of some metals (Atta, El-Sebaie, Noaman & Kassab, 1997).

Few comparitive data are available from the same areas (Storelli, 2000; Orescanin 2006; but it seems that Albanian waterways are less contaminated than industrialized country waterways.

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