COMPARATIVE DATA ON THE ACCUMULATION OF FIVE HEAVY METALS (CADMIUM, CHROMIUM, COPPER, NICKEL, LEAD) IN SOME MARINE SPECIES (MOLLUSKS, FISH) FROM THE ROMANIAN SECTOR OF THE BLACK SEA

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ABSTRACT

Information regarding bioaccumulation levels of heavy metals in marine organisms is very important, with many implications in various domains, like environment protection, public health, control of standards compliance or risk assessment. Taking into account the ability of marine biota to accumulate metals from their environment (seawater, sediments, food), their utilization as marine pollution bioindicators has been confirmed by numerous examples. A major aspect is represented by the numerous factors that could influence metals bioaccumulation, like food type, hydrochemical conditions, metals bioavailability, genetic differences, and physiological status. These factors could determine changes of metal concentrations that sometimes conceal the organism responses to temporal or spatial gradient of pollution.

The main interest of investigations was directed to understanding the spatial and temporal distribution patterns of heavy metals, through complex studies on some representative marine species from Romanian littoral. A long-term assessment was made (2001 – 2007) regarding heavy metals concentrations in

molluscs and fish species from various sites along the coastal zone. Metals were determined by using graphite furnace atomic absorption spectrometry (GF - AAS).
The results offered the opportunity to study heavy metals bioaccumulation mechanisms, which represent a major component in the process of assessment of the pollution effects upon marine ecosystem health. Investigations of metals bioaccumulation levels at molluscs and fish evinced not only important interspecific differences, due to trophic and ecologic peculiarities of each species, but also intraspecific variations caused by age, season or geographical location.

KEY WORDS: Black Sea, heavy metals, bioaccumulation, mollusks, fish

INTRODUCTION

In the past, the Black Sea was one of the most productive seas, pelagic and benthic organisms recording a remarkable abundance. Compared to this time, ecosystem ecology has been severely affected, a significant reduction of biodiversity being noticed (Gomoiu, 1981). In particular, the north-western part of the Black Sea ecosystem has suffered multiple and complex geo-morphological, sedimentological, physical-chemical and biological changes over time.

Isolation of the world ocean, associated with significantly river input (the Danube, Dnieper, Dniester) led the Black Sea particularly susceptible to the various anthropogenic pressures. Problems caused by eutrophication and pollution began in the second half of the '70s. Large quantities of inorganic and organic compounds were introduced into the sea annually, both by river and through discharges of sewage and industrial wastewaters, leading to dramatic changes at all levels of the ecosystem. Increased nutrients and hazardous substances in water have produced major changes in coastal ecosystems, having a major impact on biological diversity and legitimate utilizations of the sea (fishing, recreational activities) (Gomoiu, 2004).

It is estimated that currently one of the topics of high interest to the Black Sea is linked to estimation of the intensity of marine chemical pollution and its impact on marine organisms (Kostianoy et al, 2008).

Worldwide heavy metal pollution of the aquatic environment has been brought into attention by a number of serious incidents, including the implications on the human population, due to mercury, cadmium and other metals poisoning. It is well known the case of mercury pollution in Minamata Bay, Japan, due to industrial wastewater discharges into the sea. Thus, in 1956, about 2000 cases of alkyl-mercury poisoning caused by consumption of contaminated fish and shellfish (Mance, 1987) were reported among the local population. Such serious incidents have prompted many studies of marine pollution since the '60s - '70s.

Besides natural sources (erosion of rocks, volcanic emissions), heavy metals (arsenic, cadmium, copper, chromium, mercury, lead, nickel, tin, zinc) are released into the environment in large quantities from activities associated with mining, metallurgy, manufacture, fossil fuel combustion or waste incineration

It is considered that the lack of appropriate control measures in the riparian countries, particularly in the period before the '90s when industry recorded a peak of development was an important cause of pollution in the Black Sea (Mee, 2005). Certainly, besides the direct contribution of coastal activities (domestic and industrial wastewater, storm water), the pollutants generated in the hydrological basins of major rivers (the Danube, Dnieper, Dniester, Bug, Cuban, Don) flowing into the sea must not be neglected.

Along with terrestrial activities, shipping, oil and gas exploitation or discharge of dredged materials are themselves potential sources of pollution to the marine environment. Atmospheric transport of heavy metals is another major pathway by which these contaminants get into the marine environment.

Although anthropogenic sources are normal constituents of the marine environment, when they introduce additional quantities, metals enter the biogeochemical cycles and, as a result of their toxic potential, can interfere with the normal functioning of ecosystems. Metals present in sea water are most often associated with particulate matter and accumulate in sediments, where they can remain for long periods. Through complex interactions, metals can be immobilized, re-suspended or taken by marine organisms. Heavy metals are persistent environmental pollutants and even in the hypothetical situation of reducing anthropogenic contributions, metals accumulated over the years in sediments continue to threaten marine ecosystem health. It is a further argument for research activities dedicated to the monitoring of heavy metals levels in estuaries and coastal areas and assessing the effects of these contaminants on marine ecosystems

Living organisms have certain selectivity in the accumulation of metals, being necessary to distinguish between essential and non-essential metals. Essential metals such as copper, zinc, manganese, iron or cobalt are vital components of many enzymes and respiratory pigments. Carbonic anhydrase, carboxy-peptidase and several dehydrogenases contain zinc, pyruvate carboxylase contains manganese, hemocyanin contain s copper and hemoglobin iron. Consequently, marine organisms should provide metals for tissular metabolic and respiratory needs. Deficiency of these metals, but also accumulation over certain levels, produces harmful effects. Non-essential metals (lead, arsenic, mercury, cadmium) are highly toxic, even at very low levels, especially if they accumulate in the metabolically active sites. The organism has to limit the accumulation of toxic metals or to transform them in non-toxic forms. Toxic metals interfere with normal metabolic functions of essential elements. Their binding to protein macromolecules causes disrupting of the normal biological function. Metal catalyzed formation of free oxygen radicals is involved in the production of many pathological changes, including mutagenesis, carcinogenesis and aging (Depledge and Rainbow, 1990).

Thus, although metals are essential components of life, they become harmful when presented in excess. Increasing of environmental levels represents a problem for human and marine ecosystems health. Knowledge of the metals accumulation in marine organisms is of great importance, having implications in various fields such as environmental protection, public health, standards compliance, and risk assessment (UNEP, 1993).

Given the ability of marine organisms to accumulate in various ways metals from the environment (water, sediment and food), their use as bioindicators of marine pollution is supported by numerous examples from literature (Depledge, 1990, ICES 1991). An important aspect is the wide variety of factors that influence metal bioaccumulation, like type of food, hydrochemistry conditions, metal bioavailability, genetic differences, physiological state (Wang & Fisher, 1997). These factors determine variations of metal concentration that can sometimes mask the organism responses to temporal or spatial gradient of pollution.

Research interests were directed to spatial and temporal distribution patterns of heavy metals in marine ecosystem along Romanian littoral. Complex investigations were conducted on some molluscs and fish species, which followed intra- and interspecific variations. It was also intended to highlight the factors that influence tissue concentrations of metals.

Given the importance of discrimination between bioaccumulation changes in response to heavy metal pollution of the environment and natural variations (Depledge, 1990), a long term assessment of the metals concentrations in specimens of the same species from different geographical locations along the littoral zone was conducted. Another research direction pursued bioaccumulation differences in several types of tissues in marine organisms, in an attempt to decipher the mechanisms of metals uptake, storage and elimination.

MATERIAL AND METHODS

In the Black Sea molluscs are one of the most important and valuable group of benthos animals as they are widespread in the biotic area of the Pontic basin, dominating the total biomass of the benthos of the continental shelf, and represent an essentially trophic element (Gomoiu, 1976).

Bivalve molluscs meet the criteria for pollution bio-indicators species. Common mussels (*Mytilus sp.*) represent a well-studied group, being extensively used in monitoring programs. As filtering organisms, large volumes of water enter in contact with their body surface, causing the accumulation of pollutants. *Mytilus* was the subject of extensive studies in the global program Mussel Watch (Sericano et al., 1990)

Metal concentrations in *Mytilus galloprovincialis* varied in the following ranges: Cu 3.01 ± 0.90 (0.90 - 4.67) µg/g f.w.; Cd 0.79 ± 0.53 (0.08 - 2.58) µg/g f.w.; Pb 0.92 ± 0.81 (0.01 - 3.44) µg/g f.w.; Ni 2,37 ± 1,04 (0,72 - 4,78) µg/g f.w.; Cr 0.54 ± 0.19 (0.19 - 0.72) µg/g f.w. The order of bioaccumulation of elements in the sense of decreasing values, was: Cu > Ni > Pb > Cd > Cr. Similar research conducted in 1980 (Serbanescu et al., 1980) identified concentrations within the following limits: 1.36 - 1.57 µg/g f.w. Cu; 0.58 - 0.77 µg/g Cd; 0.01 - 0.12 µg/g Pb. In recent years a trend for cadmium stabilization and decreasing has been noted. Lead and copper do not show clear trends of evolution in one specific direction, as large fluctuations in concentration are observed over the years (Fig. 1).

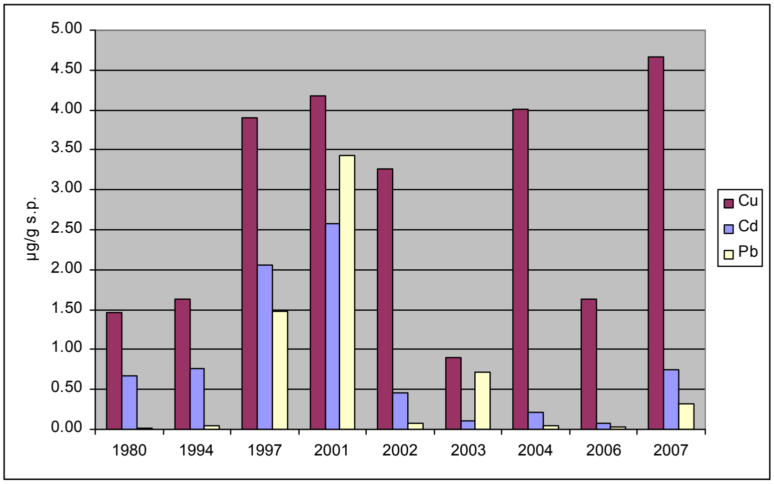


Fig. 1 - Annual variations in the concentrations of Cu, Cd and Pb in *Mytilus galloprovincialis* along the Romanian coast

For mussels (*Mytilus edulis*) from the North Sea and Baltic Sea the following threshold values corresponding to natural background concentrations of heavy metals have been proposed: Cu 2.0 µg/g f.w.; Cd 0.4 - 0.8 µg/g f.w.; Pb 0.4 - 1.0 µg/g f.w.; Ni 0.8 - 1.0 µg/g f.w.; Cr 0.4 - 0.6 µg/g f.w.; Hg 0.04 µg/g f.w.; Zn 24 - 40 µg/g f.w. (EPA, 2002). Investigations on the bioaccumulation of metals in mussels from different marine regions have reported various areas of variation, generally comparable to values observed at the Romanian seaside. In some cases, extreme values in mussels from highly contaminated locations were reported (Shulkin et al, 2003) (Table 1).

Table 1 - Heavy metal levels in mussels from different marine regions

Region	***Concentration (µg/g f.w.)***				
	Cu	**Cd**	**Pb**	**Ni**	***Cr***
Black Sea (personal data, 2001-2007)	**0.90 - 4.67**	**0.08 - 2.58**	**0.01 - 3.44**	**0.72 - 4.78**	***0.19 - 0.72***
Black Sea (Topcuoglu, 2002)	1.03 - 1.65	0.02 - 0.92	0.05 - 0.37	0.57 -3 .44	*0.06 - 1.08*
Aegean Sea (Sakellari et al., 2002)	0.57 - 1.03	0.23 - 0.34	0.92 - 1.94	0.42 - 0.49	*0.25 - 1.32*
Aegean Sea (Ugur et al, 2002)	1.03 - 6.92		1.18 - 1.61		
Mediterranean Sea (Conti & Cecchetti, 2003)	0.85 - 1.77	0.05 - 0.08	0.26 - 0.38		*0.08 - 0.20*

North Atlantic Ocean (Besada et al, 2002)	0.88 - 1.93	0.07 - 0.57	0.10 - 1.64		
North Atlantic Ocean (Ugur et al, 2002)	2.41 - 5.83		0.77 - 6.02		
Japan Sea (Shulkin et al, 2003)	*0.78 - 23.80*	*0.28 - 5.20*	*0.20 - 56.60*	*0.14 - 0.80*	

Investigations conducted in the period 2001 - 2007 on mussels from different geographical locations along the Romanian Black Sea coast indicated that copper and nickel levels showed no significant differences, ranging into narrow areas of values. In contrast, higher concentrations of cadmium and lead were measured at certain times in mussels from the vicinity of sewage discharge mouths from Constanta Nord, Eforie Sud and Mangalia, in correlation with metals levels in water and sediment. Unlike those sites, average values measured in Mamaia area were moderate (0.30 µg/g f.w. Cd şi 0.45 µg/g f.w. Pb), without major fluctuations over time, indicating a lower anthropogenic pressure (Fig. 2).

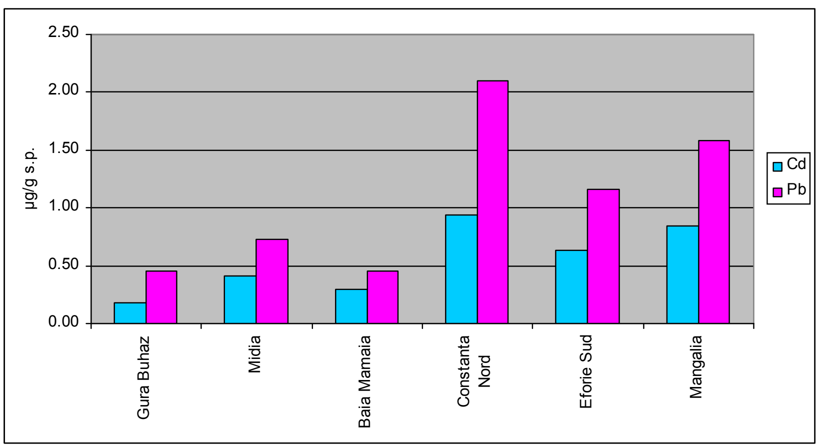


Fig. 2 - Comparative data on heavy metal concentrations in *Mytilus galloprovincialis* from different points of the coastline (2001-2007)

Values of metal accumulation in 4 species of mollusks encountered along Romanian littoral (filtrate bivalves *Mytilus galloprovincialis, Scapharca inaequivalvis*, *Mya arenaria* and predator gastropod *Rapana venosa*) were compared. Significant interspecific differences, due to the trophic and ecological features of each species, were evinced.

Rapana is encountered along the coastline upon the band that goes up to 10 m depth, both on rocky bottoms and on the sand. Also its presence is mentioned on muddy bottoms to depths up to 30 m. The preferred food of the gastropod is represented by the mussels. *Mytilus* is spread along the rocky coastline, but also on sedimentary bottoms from depths of up to 50-60 m. *Mya arenaria* occupies the sedimentary bottoms (sandy or muddy) up to 35 m depth. Having a long foot, *Mya* is deeply buried in sediment and is an excellent filter. *Scapharca inaequivalvis* also inhabit sandy bottoms, lives on the sediment surface and feeds also by filtering seston. Bivalve molluscs food is represented by planktonic and benthic microphytes, bacteria, particulate (detritus) or dissolved organic matter (Gomoiu, 1976).

Investigations upon species from Mamaia area revealed significant differences between concentrations of copper (ANOVA $df = 2, 33$; $F = 14.8158$; $p < 0.05$), in mussels being observed lower values compared with other species. Except for copper, metals bioaccumulation in Rapana venosa presented lower values for all elements, compared to the bivalve species. Concentrations of the metals accumulated in Rapana decreased in the order: Cu>Ni>Pb>Cr>Cd. The highest levels of copper, cadmium and nickel were measured in Scapharca. Concentrations of metals decreased in the order: Cu>Ni>Cd>Pb>Cr. Lead concentrations were similar in the two bivalve molluscs, whereas mussels were evinced by the largest accumulation of chromium (0,96 µg/g f.w. Cr). Accumulated metal concentrations in *Mytilus* from Mamaia area decreased in the order: Cu>Ni>Cr>Pb>Cd (Fig. 3).

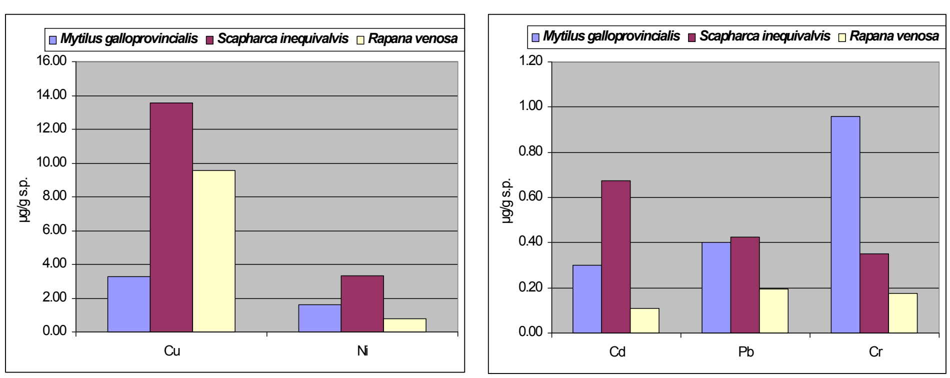


Fig. 3 - Metal concentrations in several species of marine molluscs (Mamaia area) (2001 - 2007)

In the northern sector of the coastline, *Rapana* concentrations of copper (18.15 µg/g f.w.) were significantly increased as compared to other species (ANOVA df = 3.17; FCu = 8.2187; $p < 0.05$), while cadmium and lead values were close to those recorded in *Mytilus*. Slightly higher accumulations of cadmium were determined in *Scapharca*, nickel and lead had no major interspecific differences (ANOVA df = 3, 17; FPb = 0.1954; FNi = 1,5479; $p<0{,}05$), and chromium showed maximum concentration in *Mya arenaria* (Fig. 4). Accumulated metal concentrations in molluscs from the northern sector decreased in the order: *Mytilus*: Cu>Ni>Cr>Cd≥Pb>V; *Scapharca*: Cu>Ni>Cd>V>Cr>Pb; *Rapana*: Cu>Ni>Cd>Cr>Pb>V; *Mya*: Cu>Ni>V>Cr>Cd>Pb. In the southern sector there was observed a slightly higher accumulation of cadmium and lead in *Mytilus*, in comparison with the other three species. Higher nickel, chromium and copper values were noted in *Mya arenaria*, while in *Scapharca*, unlike previous observations, metal concentrations were reduced (Fig. 5). Accumulated metal concentrations in molluscs from the southern sector decreased in the order: *Mytilus*: Cu>Ni>Pb>Cd>Cr; *Scapharca*: Cu>Ni>Cd>Cr>Pb; *Rapana*: Cu>Ni>Pb>Cd>Cr; *Mya*: Cu>Ni>Cr>Pb>Cd.

Generally, a higher potential for bioaccumulation of toxic heavy metals (Cd, Pb, Ni, Cr) in bivalve mollusks, compared with gastropods, was observed.

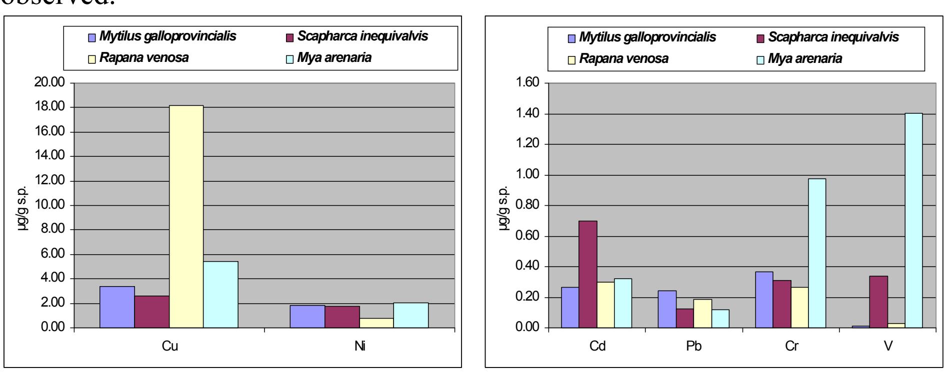


Fig. 4 - Metal concentrations in several species of marine molluscs (Northern sector) (2001 - 2007)

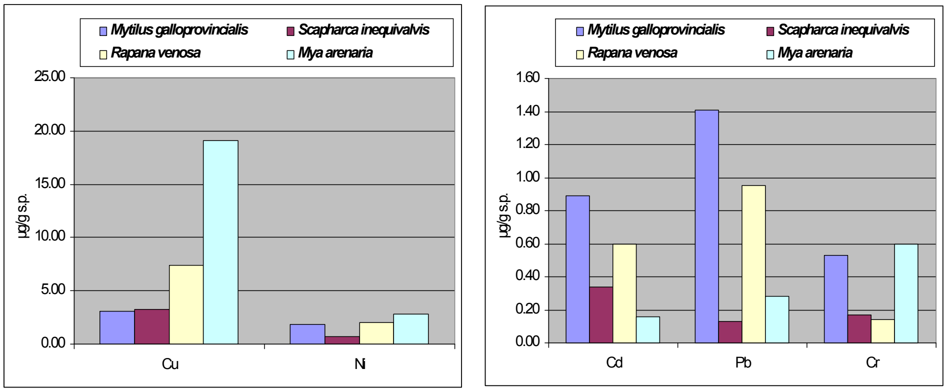


Fig. 5 - Metal concentrations in several species of marine molluscs (Southern sector) (2001 - 2007)

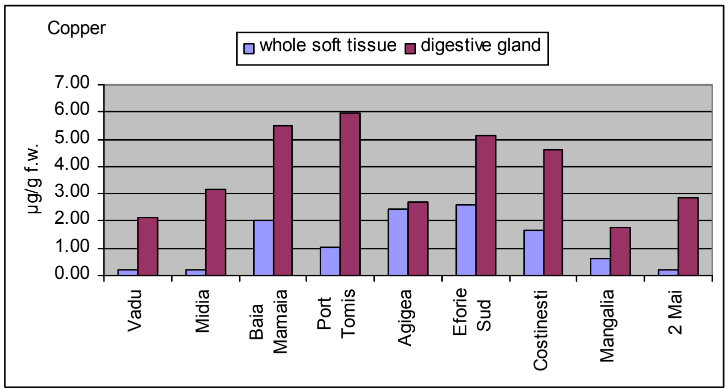
In the Mediterranean, values of metals accumulated in mussel decreased in the order: Zn>Cu>Pb>Cr>Cd, while in gastropods the sequence was Zn>Cu>Cd>Pb>Cr (Conti şi Cecchetti, 2003). Studies on metal accumulation in several species of molluscs of the Aegean (Sakellari et al., 2002) revealed significant species-specific differences.

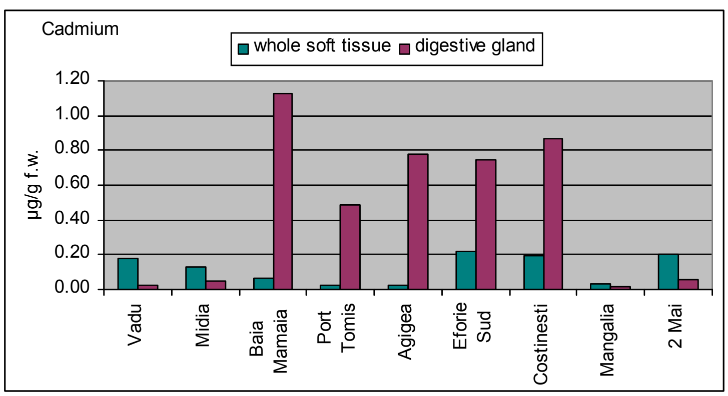
Studies on the effects of environmental variables and assimilation efficiency of metals in bivalve molluscs have shown the importance of factors such as food quantity and composition and concentration of metals in food. As bivalve molluscs can accumulate metals through sediment particles ingestion, their chemical composition also affects bioaccumulation. Thus, while iron oxides inhibit uptake of metals related to sedimentary particles, organic compounds (such as bacterial extracellular polymers and fulvic acids) or presence of benthic microalgae significantly enhances this process (Reinfelder, 1998).

Numerous studies have demonstrated that hepato-pancreas is the prevalent organ for the accumulation of various metals in bivalve molluscs (Adami et al, 2002). Investigations on the accumulation of copper, cadmium and lead in the digestive gland and whole soft tissue in mussels at the Romanian littoral confirmed this observation: in most cases, metals have higher values in the digestive gland (Fig. 6). Statistical tests for comparison showed significant differences between heavy metal concentrations in two tissues: copper (test t, unequal variances df = 19; $t_{Copper} = 2.3297$; $p < 0.05$); cadmium (test t, unequal variances df = 16; $t_{Cadmium} = 3.0843$; $p < 0.05$); lead (test t, equal variances df = 30; $t_{lead} = 2.3071$; $p < 0.05$). Excess of metals in the body is captured by metallothionein-like proteins, whose synthesis is induced in the digestive gland depending on the level and duration of exposure

(Raspor at al., 1989). Thus, the digestive gland may represent one type of indicator tissue for the long-term exposure.

Similar research on cephalopod molluscs have reported much higher concentrations in the liver compared to other tissues, suggesting that it is an organ in which metals are stored (Craig and Overnell, 2003).





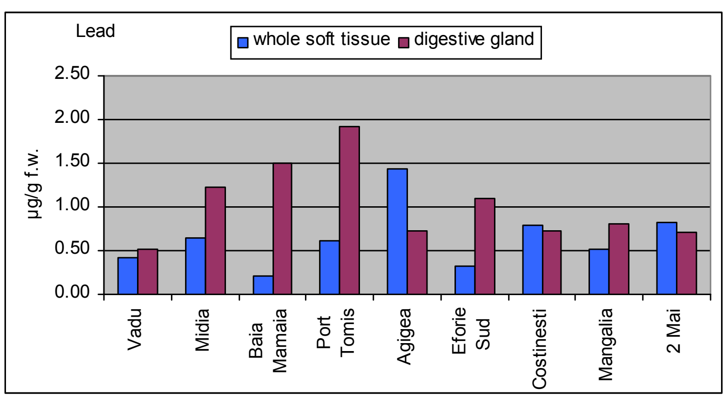


Fig. 6 - Heavy metal concentrations in whole soft tissue and hepatopancreas of mussels (Mytilus galloprovincialis) from different locations (2003 - 2004)

Molluscs, especially bivalves, can accumulate metals both in soft tissues and shells, numerous studies showing how the chemical composition of the shell may reflect human impact on ecosystems (Protasowicki et al., 2008). Although, generally, metals concentrate mainly in the soft tissue, there are also situations in which shells accumulate high levels of metals. Shells may be an indicator of changes in environmental pollution, presenting a lower variability compared with soft tissue and providing a historical record of metal content in the body throughout its life cycle.

Accumulation of metals in mollusc shells from the Romanian coast presented variations depending on the element and the species, generally highest concentrations being observed in *Mya arenaria*, and lowest in *Scapharca inequivalvis* (Fig. 7).

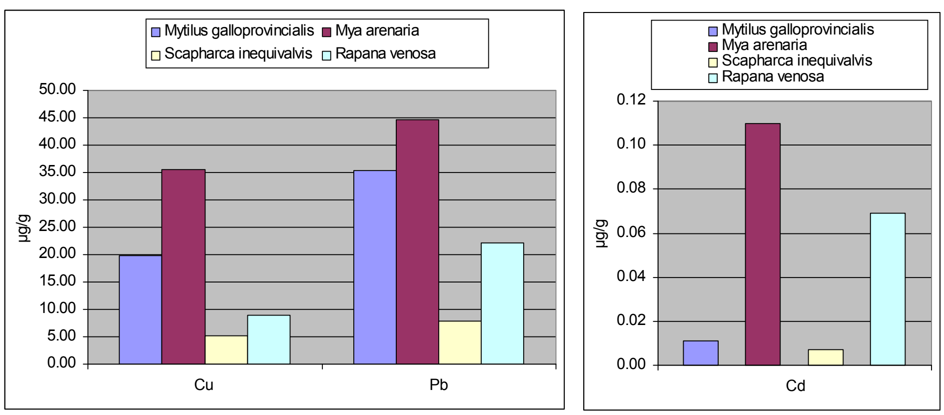


Fig. 7 - Heavy metal concentrations in marine mollusc shells from the Romanian Black Sea littoral (2003)

Regarding the partition of metals between soft tissues and shells, the following observations were made:

- Cd presented extremely low values in the shells in all 4 investigated species;
- Cu presented decreased values in the shell of *Rapana* and *Scapharca*, while *Mytilus* and *Mya arenaria* had similar concentrations in shell and soft tissue;
- Pb showed significantly higher accumulation in shells compared with soft tissue in all 4 species.

It is known that Pb, along with other metals, can substitute for calcium ions and thus incorporate into calcium carbonate crystals in the shell composition. It is assumed that by this mechanism any metal embedded in shell structure was uptaken from the environment and metabolized by the organism. Additional studies are needed on the relationship between the concentration of metals in the environment, partition ways between soft tissue and shell and the amounts of metals that can be removed from the system.

The vast majority (80%) of the investigated mussels did not exceed allowable values for cadmium and lead, recommended by EC Regulation no. 1881/2006 on the levels of certain metals in mollusks (1 µg/g f.w. Cd şi 1,50 µg/g f.w. Pb) (Fig. 8).

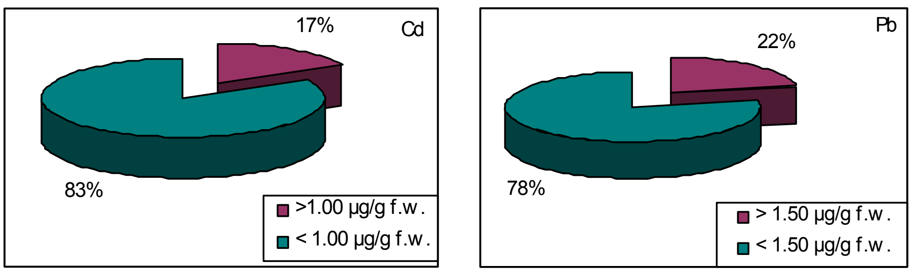


Fig. 8 - Percentage of Cd and Pb concentrations in *Mytilus galloprovincialis*

in relation to the limits set by EC Regulation no. 1881/2006 (2001-2007)

Similar observations were made for other species of marine molluscs investigated (Fig. 9; Fig. 10).

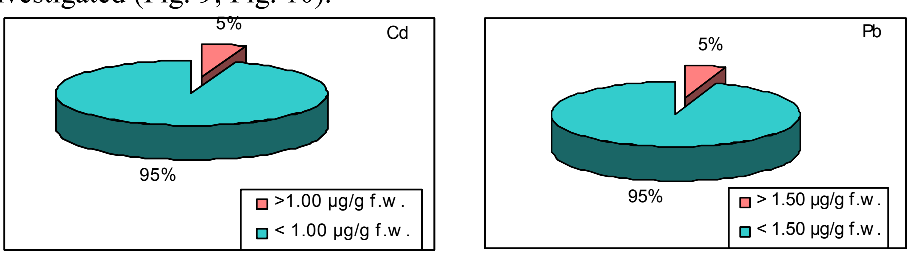


Fig. 9 - Percentage of Cd and Pb concentrations in *Rapana venosa* in relation to the limits set by EC Regulation no. 1881/2006 (2001-2007)

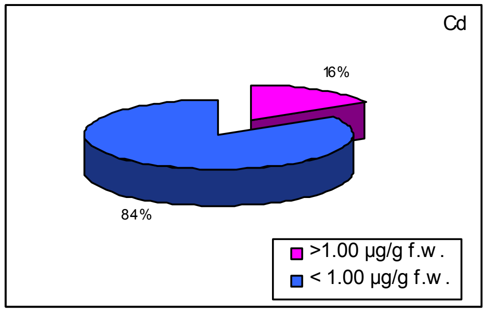


Fig. 10 - Cd concentrations in Scapharca inequivalvis percentage in relation to the limits set by EC Regulation no. 1881/2006 (2001 - 2007)

Marine fish

Studies on the presence of heavy metals in marine fish have contributed to the accumulation of new data on their levels in species of marine organisms with commercial significance, including implications for estimating the risk of consumer exposure to contaminants. Fish is an important food resource and a major component of the marine ecosystem, thus assessment of the contamination effects is particularly important. Investigations have revealed interspecific differences due to the trophic and ecological features of each species.

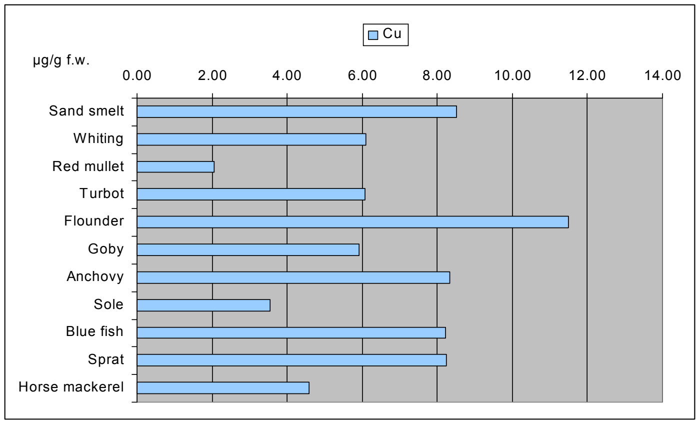
Values of metal accumulation in the dorsal muscle of marine fish ranged within various fields of concentration (Fig. 11). Copper did not register major interspecific differences (ANOVA df = 7, 60; F = 1.050096; $p < 0.50$). Flounder, goby, anchovy and sprat showed the highest average values for cadmium (1.06 - 1.40 µg/g f.w. Cd), while in the blue fish and horse mackerel were measured reduced values (0.31 - 0.49 µg/g f.w. Cd). Nickel showed slightly higher average concentrations in turbot, anchovy, blue fish and sprat.

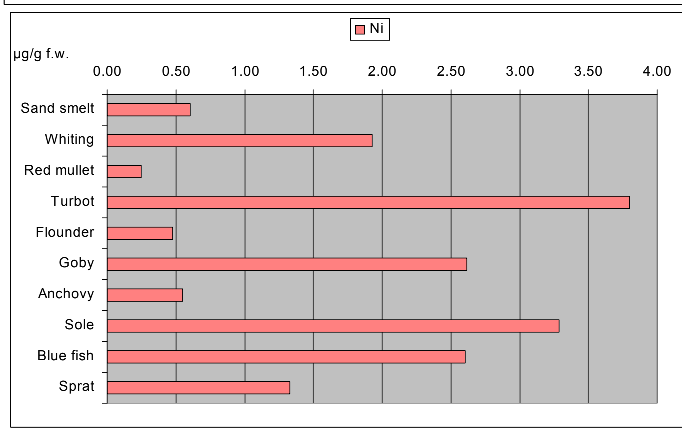
Benthos species of fish, through their association with sediment substrate, can directly uptake metals by ingestion of sediment particles or indirectly through consumption of benthic invertebrates (Bervoets & Blust, 2003). Differences in metal concentrations related to the feeding mode of benthic and pelagic fish were often highlighted. Investigations conducted on several fish species in the Aegean Sea or Antarctic Ocean have shown that benthic fish generally accumulate higher concentrations of heavy metals than pelagic fish (Bustamante et al., 2003). The presence of higher levels of accumulation in planctonivorous fish (anchovy, sprat) compared with predators fish may be explained on the basis of a higher efficiency of assimilation of metals from food.

In the Adriatic Sea, significant interspecific differences were found between anchovy (*Engraulis encrasicholus*) and sardine (*Sardina pilchardus*), increased metal concentrations observed in anchovy being explained on the basis of differences in the way of feeding or migration routes (Gilmartin şi Revelante, 1975). Recent investigations on the 5 species in the Black Sea revealed the lowest concentrations of metals in bonito (*Sarda sarda*), while the horse mackerel (*Trachurus trachurus*) presented the highest values (Tuzen, 2003).

Domains of values observed along the Romanian littoral are comparable with data reported in the literature on heavy metal concentrations in dorsal muscle of marine fish in the Black Sea and the Mediterranean.

Compared with recommended values of EC Regulation no. 1881/2006 which sets allowable concentrations of metals in fish meat 0.1 µg/g f.w. Cd şi 0.3 µg/g f.w. Pb), the percentage of samples that are below these limits is, depending on the species, between 30 to 55% for Cd and 20 - 80% for Pb.





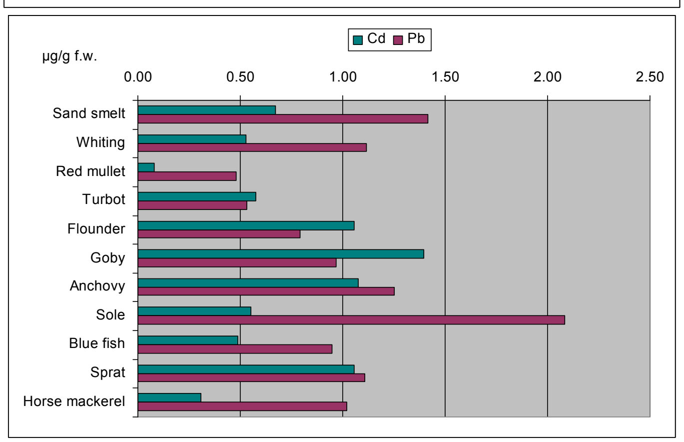


Fig. 11 - Heavy metal concentrations in dorsal muscle of marine fish from Romanian coastal area (2001 - 2006)

Metal accumulation in fish depends on the level of exposure (water, food) and physiological factors (age, metabolic activity), together with factors related to environment such as temperature, physical-chemical parameters, presence of other metals (Kim et al, 2004).

Sand smelt spawn (10-70 mm length) showed increased accumulation of copper and cadmium, compared with mature specimens (70 - 105 mm length) caught in the same season and location. Instead, lead increased with fish age. Likewise, it was observed that whiting juveniles (length 50 - 85 mm) accumulated high concentrations of copper, cadmium and lead compared to adults belonging to the length class of 90 - 180 mm. Young specimens (length 75 to 100 mm) of horse mackerel showed concentrations of cadmium and chromium higher than adults (length >115 mm). Other elements (copper, lead, nickel) increased with fish age (Fig. 12).

Increased accumulation of certain metals observed in fish juveniles can be explained by a better assimilation of metals present in their diet consisting of plankton and detritus. Similar investigations showed significant reductions in concentrations of Cu, Zn, Cd and Pb, with increasing length (age) of predators fish, suggesting that these trends are caused by variations in diet occurring over the ontological development. Adult fish are considered to have better capacity to regulate toxic metals (Cronin et al, 1998).

Metals accumulate in higher concentrations in the gills and digestive tract, compared with muscle tissue, which is not considered an active tissue in accumulating heavy metals (Yilmaz, 2003). In fish, it is considered that most toxic metals tend to accumulate in the liver or kidneys (ICES, 1991). Metallothioneins induction in these tissues is a form of detoxification and excretion of metals in fish (Roesijadi & Robinson, 1994; Kim et al, 2004).

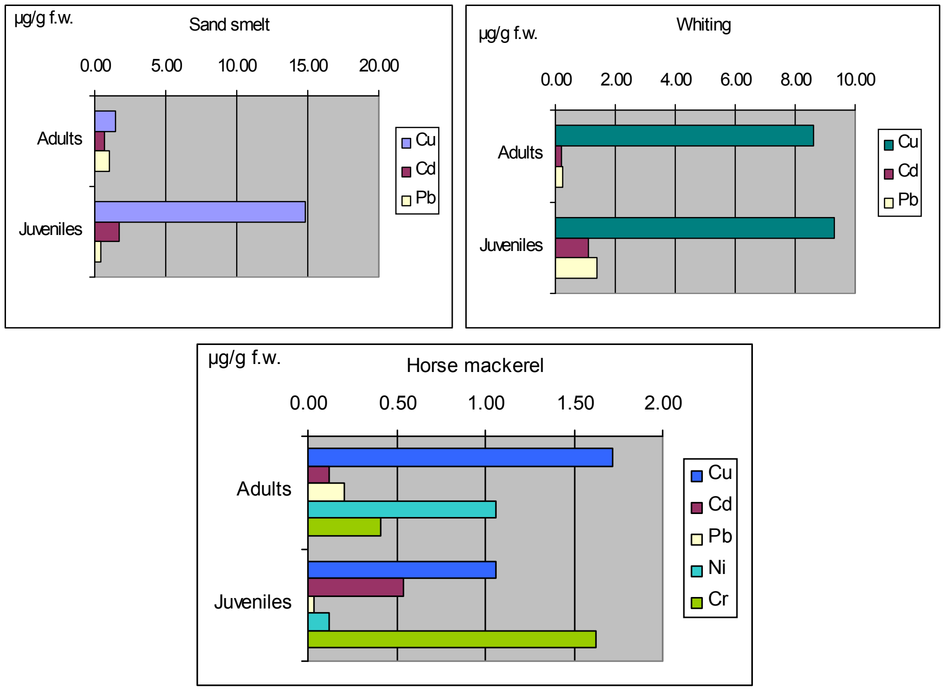


Fig. 12 - Intraspecific variation of metal concentrations in marine fish (2001-2006)

Accumulation patterns observed in fish from the Romanian coast were consistent with the above-mentioned observations. Tissues under direct exposure to contaminants (gills, skin), and those involved in detoxification (liver) showed an increased capacity for bioaccumulation of metals in comparison with muscle tissue (Fig. 13). The obtained results may contribute o understanding the mechanisms of uptake and accumulation of heavy metals.

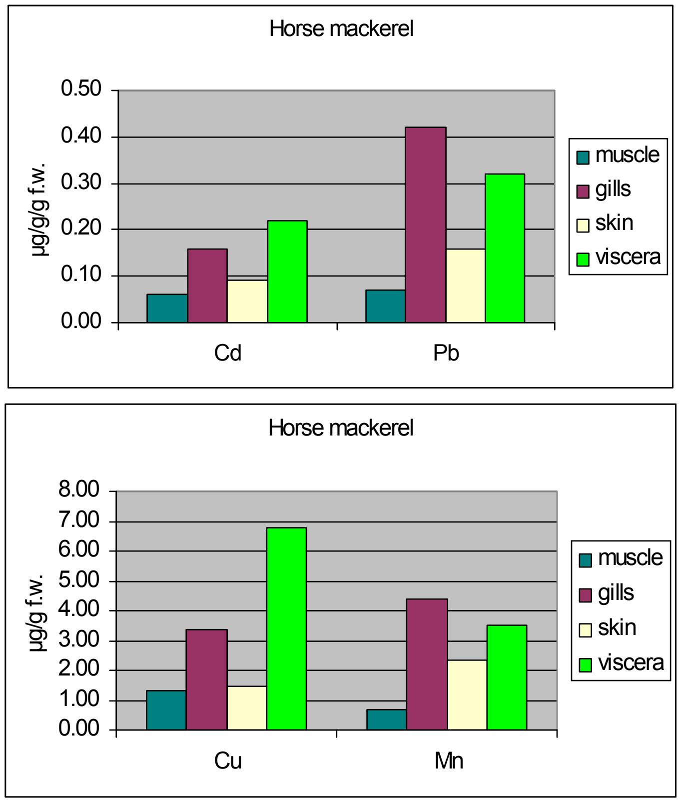


Fig. 13 - Heavy metal concentrations in tissues from horse mackerel from the Romanian littoral (2002 - 2003)

CONCLUSIONS

The study of heavy metal accumulation processes in different marine species revealed important interspecific differences due to trophic and ecological features, as well as intraspecific variation, depending on the stage of ontogenetic development, season or location of sampling.

The researches confirmed the potential of some marine species to be used as bioindicators of pollution. Bivalve molluscs showed a higher potential to accumulate toxic metals compared to gastropods.

Bioaccumulation model in various tissues and organs of molluscs and fish provides useful information for deciphering the mechanisms involved in detoxification. Metals accumulated in higher concentrations in tissues directly exposed (gills, skin) or involved in detoxification (liver, kidney) and less in muscle.

Compared with recommended values of EC Regulation no. 1881/2006 which sets allowable concentrations of metals in marine organisms, the percentage of samples that comply with the limits varies, depending on the species, between 75 - 95% for molluscs and 25 - 85% for fish.

Observations on marine organisms have provided an opportunity to study the mechanisms of bioaccumulation of heavy metals, which is an important component in assessing the effects of pollution on marine ecosystems.

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