Heavy Metal Pollution of the Romanian Coastal Area

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Black Sea pollution is an important issue which has significant effects on human health and aquatic life. Therefore, the pollution monitoring is very important. The aim of this study was to assess the marine ecosystem in terms of heavy metal contamination (Cu, Cd, Pb, Ni and Cr) at the Romanian coastal area in the 1996-2012 periods for Cu, Cd, Pb and in the 2004-2012 periods for Ni, Cr. The quantitative analysis of heavy metals is based on the information's provided by the National Institute for Marine Research and Development Grigore Antipa Constanta, as a result of research conducted within the integrated monitoring program. For this study were used the annual average concentrations recorded values of the heavy metals, on two areas of analysis: sea water and marine sediments. The obtained data were compared with the maximum allowable values for each category of analyzed heavy metals.

Keywords: heavy metal, sea water pollution, sediment, Black Sea

The metals enter in the marine environment from various sources, natural or manmade, in the form dissolved in water or as part of sediments [1-4]. The pollution general sources of the marine environment are: coastal cities and industries; wastewater and industrial residues; household waste and rainwater; shipping; the discharge of waste into the sea; wrecks; lost or discarded ammunition intended; offshore drilling platforms; atmospheric deposition [5-7].

Once broadcasts metals in aquatic ecosystems, they may follow different paths: it can dissolve in the water column, sediment deposit, volatilize into the atmosphere and accumulate in organisms.

The natural concentrations of some metals play an essential role in many biochemical processes, but in high concentrations can become toxic.

The metals bioaccumulation is an important process in the homeostatic regulation through the organisms obtains essential metals necessary to the biological functions, such as metabolic and enzymatic reactions. This process is defined as acquisition and net accumulation of a chemical substance by environmental organisms.

The study area is the Black Sea coast zone, between Sulina - Vama Veche (fig. 1, the red zone).

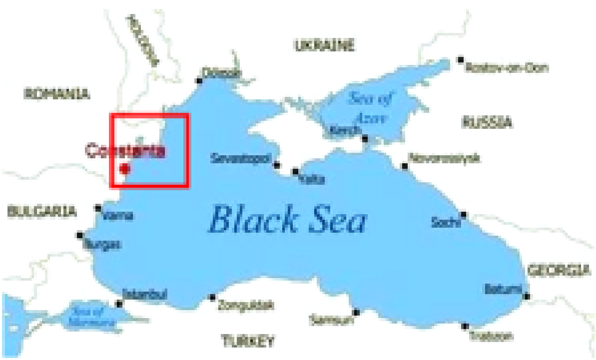

Fig. 1. Presentation of the studied zone

Experimental part

The monitoring of the transitional water quality, coastal and marine resources in the Romanian Black Sea littoral is conducted by the National Institute for Research and Development, *Grigore Antipa* Constanta.

The water and sediment samples were conducted with a frequency of 2-4 times per year and are performed by the research vessel *Steaua de mare (Sea Star) 1* (NIRMD, 2012) [4, 5].

Network monitoring extends along the Romanian littoral between Sulina and Vama Veche and includes a total of 39 stations (fig. 2), from 0 m depth horizon to 50 m depth horizon [3-6]. The stations were chosen based on the presence of terrestrial pollution sources, sensitivity of the area, the specific use of these areas (beaches, areas of mussel culture) and specific hydrological conditions [9].

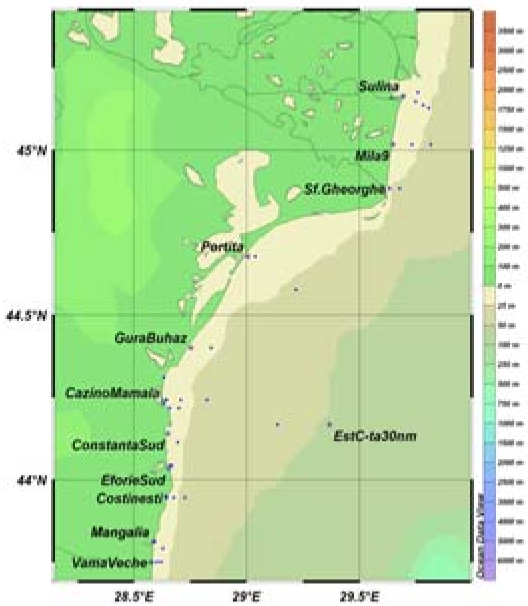

Fig. 2. Location of the sampling stations [9]

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The concentrations of heavy metals in water and sediment were determined by atomic absorption spectrometry with graphite furnace (GF-AAS), using the ATI Unique 939Z spectrometer and correction specialist SOLAAR M6 DUAL Zeeman Thermo Electron device [9].

In order to determine the total content of dissolved and suspended metals in water samples were collected from the surface of plastic bottles, clean and without filtration, they have been acidified with nitric acid (HNO_3), until the pH reached a value of 2 and preserved at a temperature of 40^0C. The nitric acid dissolves the metals from the suspended forms and has change matrix role, minimizing the interference between metals [8].

The sediment samples, collected by dredging the seabed, were dried in an oven at 105^0C and well mixed. In this process a fraction less than 2 mm was removed. The dried sediment was weighed and treated with 5 ml of nitric acid (65% concentration), HNO_3 Merck supra pure [10].

The digestion process took place in a hot digester, Microwave digestion system - Speed wave type MWS-3 Bergdorf. At the end of this process, the samples were diluted with unionized water up to 100 mL.

Results and discussions

The quantitative analysis of heavy metals was conducted based on the informations provided by the National Institute for Marine Research and Development *Grigore Antipa* Constanta, as a result of the research conducted within the integrated monitoring program.

In this work the annual average concentrations recorded values of the heavy metals were used, on three areas of analysis: sea water and sediment, which were compared with the maximum allowable values (table I) for each category of analyzed heavy metals.

In the following figures is represented the mean annual concentrations of studied heavy metals.

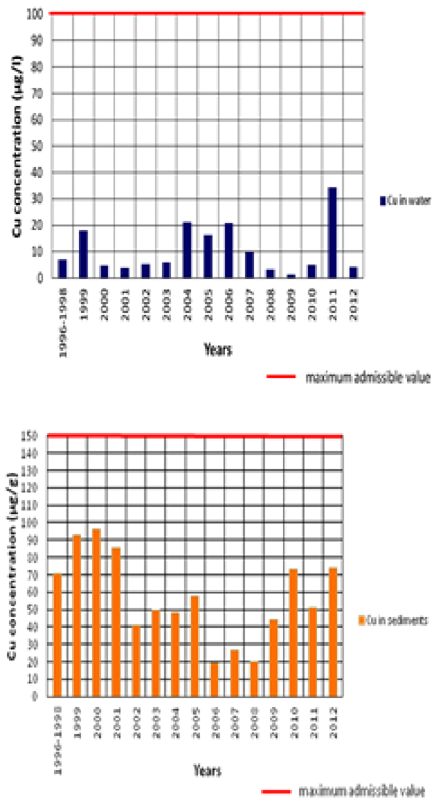

Fig. 3. The evolution in time of the mean concentrations of copper in water column and sediments

The figure 3 shows that the concentrations of copper in water and sediments have a variable trend and are very small compare to the maximum admissible limit.

The maximum value in water was observed in 2011 (34.47 µg/L) and in sediments in 2000 (96 µg/g).

The minimum value in water is observed in 2009 (1.43 µg/L) and in sediments in 2006 (19.36 µg/g).

For cadmium, the figure 4 shows that in 1996-1999 the concentrations of cadmium in sediments are over the maximum admissible limit. The other concentrations are less than the maximum admissible limit. The maximum value of cadmium was registered in 1999 (14.5 µgL in water columns and 62.7 µg/L in sediments) and the minimum value in 2001 (0.45µg/g) in water columns and 2008 in sediments.

Table 1

THE MAXIMUM ALLOWABLE VALUES (ORDER NO. 1888/2007 FOR SEA WATER AND SEDIMENTS)

Heavy metal	Sea water		Sediments	
	U.M.	Maximum allowable values	U.M.	Maximum allowable values
Cd	µg/L	20	µg/g	20
Cr	µg/L	100	µg/g	100
Cu	µg/L	100	µg/g	150
Ni	µg/L	50	µg/g	100
Pb	µg/L	20	µg/g	100

In the case of lead, all concentrations are less than maximum admissible value in the both situation (in water column and sediments), excepting the concentrations of lead in water which correspond to years 1999, 2000 and 2011 when they exceeded the maximum admissible limit (fig. 5).

Concerning the nickel concentrations in water, the fig. 6 shows that all values are much lower than the maximum limit. In sediments, all values of concentrations are below of the maximum admissible value, except in 2011 when was registered 106.34 µg/g (fig. 6).

The annual average concentrations of chrome are all lower than the maximum limit (fig. 7). The maximum value in water (15.01 µg/L) was recorded in 2004 and in sediments in 2011 (87.55 µg/g).

The basic statistics (mean, standard deviation, maximum, minimum, kutosis and the skewness) are presented in table 2.

We observe that the series distributions are not homogenous.

In the case of water, the value of skewness varies between 0.79 and 1.89 and the kurtosis from -0.9 to 2.77.

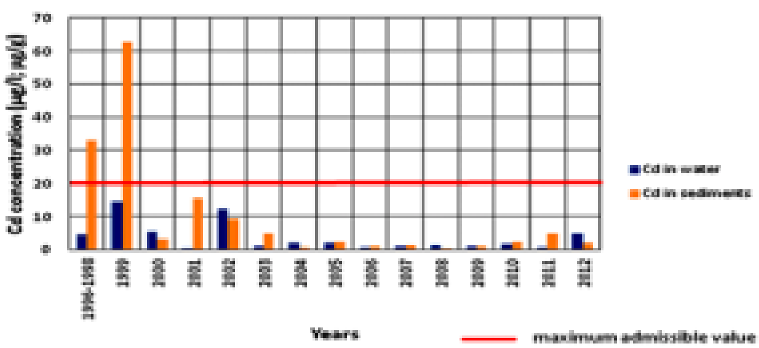

Fig. 4. The evolution in time of the mean concentrations of cadmium in water and sediments

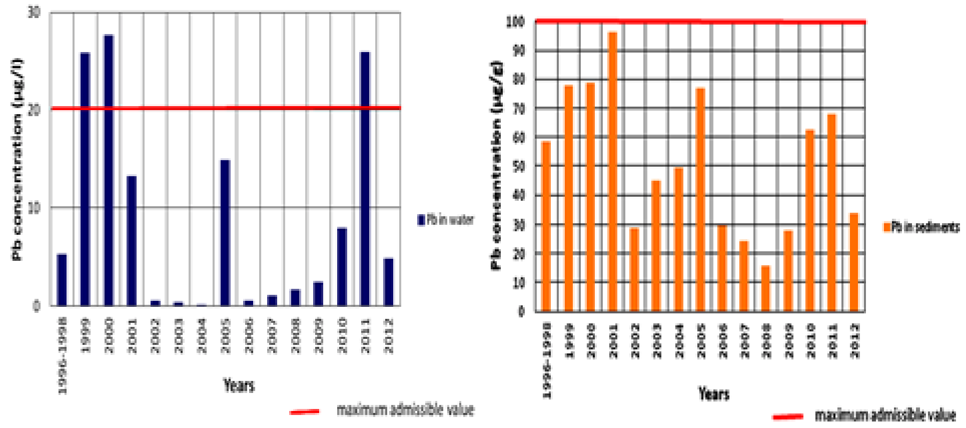

Fig. 5. The evolution in time of the mean concentrations of lead in water and sediments

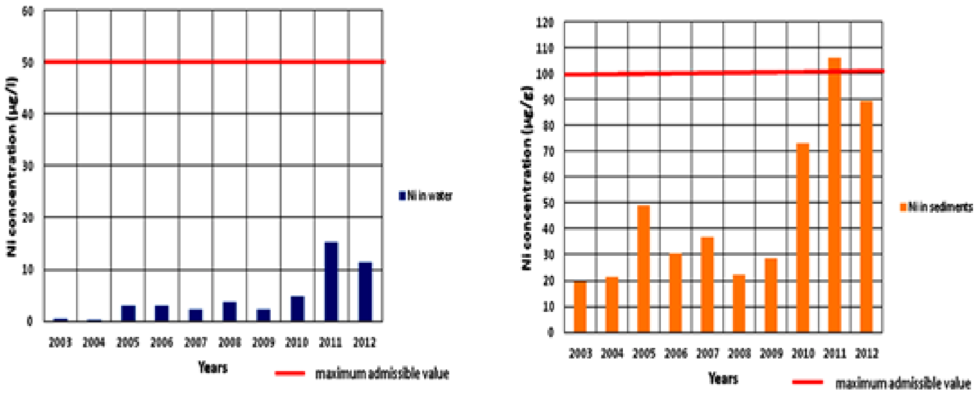

Fig. 6. The evolution in time of the mean concentrations of nickel in water and sediments

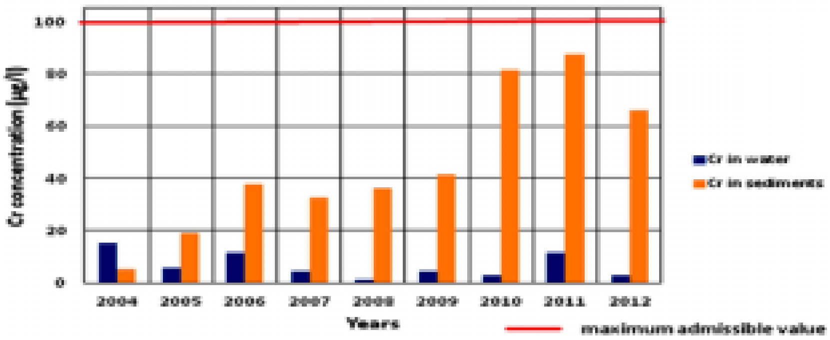

Fig. 7. The evolution in time of the mean concentrations of chrome in water and sediments

Table 2
THE BASIC STATISTICS OF STUDIED HEAVY METALS

Element	Water Column					Sediments				
	Mean±SD	Max	Min	Kurtosis	Skewness	Mean±SD	Max	Min	Kurtosis	Skewness
Cu	10.81±9.32	34.47	1.43	1.43	1.36	56.69±24.86	96.00	19.36	-0.99	0.05
Cd	3.54±4.30	14.50	0.45	2.77	1.89	9.59±16.99	62.70	0.38	7.17	2.65
Pb	8.87±10.22	27.70	0.15	-0.48	1.03	51.63±24.56	96.40	15.74	-1.16	0.23
Ni	4.65±4.88	15.30	0.32	1.74	1.60	47.74±31.17	106.34	19.70	-0.41	1.01
Cr	6.55±4.85	15.01	1.29	-0.90	0.79	45.24±27.62	87.55	5.32	-0.84	0.36

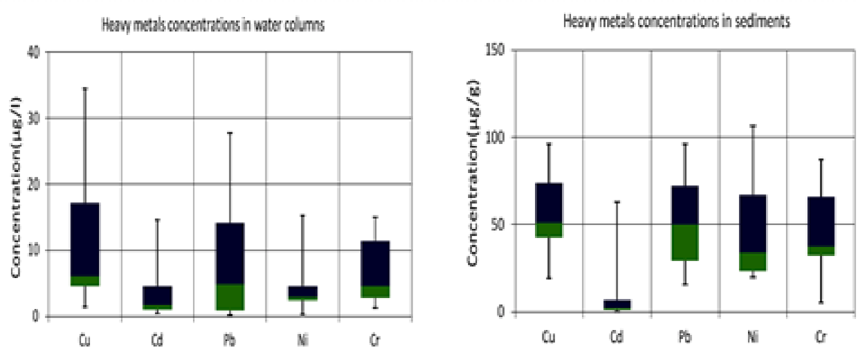

Fig. 8. Boxplots of the heavy metals series

In sediments, the value of skewness varies between 0.05 and 2.65 and the kurtosis from -1.16 to 7.17.

These values are represented in the box plots from figure 8 where: top of upper whisker is the maximum value of the sample; Top of box - 75th percentile of the sample; Line through the box- Median of the sample; Bottom of the box-25th percentile of the sample; Bottom of the lower whisker- Minimum of the sample.

The figure 8 shows that the order of elements accumulation in the sense of decreasing values, is: in water, Cu > Pb > Cr > Ni > Cd and in sediments, Cu > Pb > Ni > Cr > Cd.

Comparing to the Turkish Black Sea coast, the results of heavy metal levels measured in seawater and sediment in Zonguldak, indicate that Cd, Cu, Zn and Pb concentrations in sea water and Cd, Cu, Cr and Pb concentrations in sediments are high, possibly caused by fly ash from coal combustion and wastes from cement and lime plants in the area.

In sediment samples taken from Zonguldak coasts, heavy metal pollution especially cadmium, chromium and lead levels were very high like the other Black sea countries [11].

Conclusions

The results of this work presented above demonstrated clearly that the Romanian Black Sea coast is not facing heavy metal pollution. This conclusion is based on the annual average concentrations recorded values of the heavy metals, on two areas of analysis: sea water and marine sediments.

Considering the last ten years, all annual average concentrations of heavy metals in sea water and marine sediments are below the maximum allowable value, except 2011 when were recorded exceeding at lead in water and nickel in sediments.

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