



<b>Analysis of Hazardous Substance Contamination of the Marine Ecosystem in the Romanian Black Sea Coast, Part of the Marine Strategy Framework Directive (2008/56/EEC) Implementation</b> <i>(Valentina Coatu, Daniela Țigănuș, Andra Oros, Luminița Lazăr)</i>	<b>“Cercetări Marine” Issue no. 43</b>  <b>Pages 174-186</b>	<b>2013</b>
---	--	-------------

## **ANALYSIS OF HAZARDOUS SUBSTANCE CONTAMINATION OF THE MARINE ECOSYSTEM IN THE ROMANIAN BLACK SEA COAST, PART OF THE MARINE STRATEGY FRAMEWORK DIRECTIVE (2008/56/EEC) IMPLEMENTATION**

**Valentina Coatu, Daniela Țigănuș, Andra Oros, Luminița Lazăr**

*NIRDEP - National Institute for Marine Research and Development  
“Grigore Antipa”, 300 Mamaia Blvd., 900581 Constanța, Romania,  
E-mail: [vcoatu@alpha.rmri.ro](mailto:vcoatu@alpha.rmri.ro)*

### **ABSTRACT**

The paper presents the contamination of the marine ecosystem with hazardous substances at the Romanian Black Sea coast. The assessment was done by analyzing the data obtained during 2006-2011, based on the indicators recommended by the Water Framework Directive (2000/60/EC), Marine Strategy Framework Directive (2008/56/EEC) and the parameters established by the Advisory Group on Monitoring and Assessment of Pollution of the Black Sea Commission. The distribution of contaminants (heavy metals, organochlorine pesticides, total petroleum hydrocarbons and polycyclic aromatic hydrocarbons) in the Black Sea marine ecosystem components show slightly increased concentrations in the water under the influence of the Danube and in the south, in certain areas subjected to different anthropogenic pressures (harbors, discharges of wastewater). Individual compounds concentrations show a decreasing trend in time, especially for organochlorine pesticides and polycyclic aromatic hydrocarbons.

**KEYWORDS:** Black Sea, heavy metals, organochlorine pesticides, polycyclic aromatic hydrocarbons

### **AIMS AND BACKGROUND**

The Black Sea ecosystem, as well as other European seas (Baltic, Mediterranean, Northeast Atlantic) underwent dramatic changes in all subsystems immediately after 1970 as a result of industrialization and intensive agriculture. Besides eutrophication, there were other forms of pollution, including oil pollution, coming from operational or accidental discharges from ships, pollution with other toxic substances such as pesticides (mostly



originating from agriculture and transported into the sea by the tributary rivers) and heavy metal pollution (ex. cadmium, copper, chromium, lead) from industry, that occupies an important place. The early 1990s period is regarded as a period of relaxation of human pressure, in relation, in particular, to the economic collapse of the socialist countries.

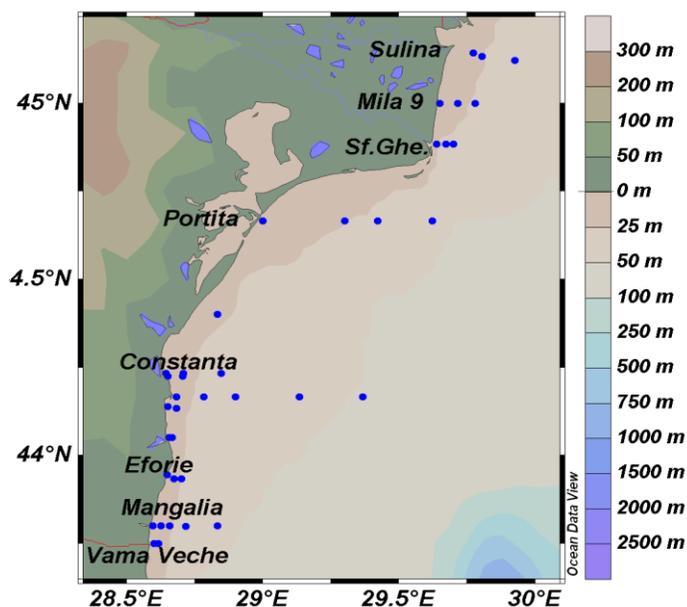
The objective of the paper is to assess the current state (2006 -2011) of the marine ecosystem in terms of contaminants concentration. This assessment is the starting point for developing a strategy to reduce marine pollution by decreasing or maintaining concentrations of hazardous substances within the limits stipulated by the current legislation, in the context of Romania's alignment with EU policies.

## **MATERIAL AND METHODS**

The status of the marine ecosystem in terms of contaminants was assessed based on the indicators recommended by the Water Framework Directive (2000/60/EC) and Marine Strategy Framework Directive (2008/56/CEE) and the parameters established by the Advisory Group on the Monitoring and Assessment of Pollution of the Black Sea Commission, as follows:

- presence of hazardous substances (heavy metals, chlorinated pesticides, polycyclic aromatic hydrocarbons) in surface seawater;
- contamination of surface sediments with hazardous substances (heavy metals, chlorinated pesticides, polycyclic aromatic hydrocarbons)
- bioaccumulation of hazardous substances (heavy metals, chlorinated pesticides) in marine molluscs.

The data were obtained in the frame of the monitoring program conducted during 2006-2011. Additionally, where data existed, comparisons with historical data were made in order to get the trendline of pollution with hazardous substances. The sampling of surface water, sediment and biota was carried-out with the research vessel "Steaua de Mare 1", with a frequency of 2-4 times/year. Samples were collected within a network of about 40 monitoring stations, located along the entire Romanian coast, between the Danube's mouth in Sulina and Vama Veche, with 5 - 30 m bottom depths (Fig.1).



**Fig. 1 - Map of monitoring network stations - Romanian Black Sea**

Total metals were determined in unfiltered seawater samples, previously acidified to pH 2 with nitric acid. Acid plays a role in the preservation, solubilization of metals which are in particulate form and also acts as matrix modifier, reducing the interference caused by salts.

For the determination of heavy metals in sediment, samples were dried by lyophilization and then homogenized. The further step was the treatment of the sample with concentrated acid (HNO<sub>3</sub> Suprapur), followed by digestion in a microwave oven. At the end of digestion, samples were taken in 100 ml volumetric flask with deionized water.

The analytical determination of the content of copper, cadmium, lead, nickel and chromium was performed by atomic absorption spectrometry using a SOLAAR model M6 Dual Zeeman, Thermo Electron - UNICAM equipment.

The extraction of organochlorine pesticides and polycyclic aromatic hydrocarbons from sediment samples was done with hexane, in a Soxhlet apparatus and from water sample with hexane/dichloromethane = 3/1, in a separating funnel. Further processing of the samples, both for water and sediment samples, followed the steps: concentration of the extracts to rotoevaporator, treatment of samples with copper to remove sulphur compounds, clean-up on florisil, respectively, alumina/silica column and concentration of the samples using the Kuderna- Denish concentrator and nitrogen flow.

The analytical determination of organochlorine pesticide content was made by the gas-chromatographic method, with a Perkin Elmer gas chromatograph CLARUS 500 equipped with electron capture detector.

The analytical determination of polycyclic aromatic hydrocarbons content was made by the gas-chromatographic method with a Perkin Elmer gas chromatograph CLARUS 500, equipped with mass spectrometer detector.

## RESULTS AND DISCUSSION

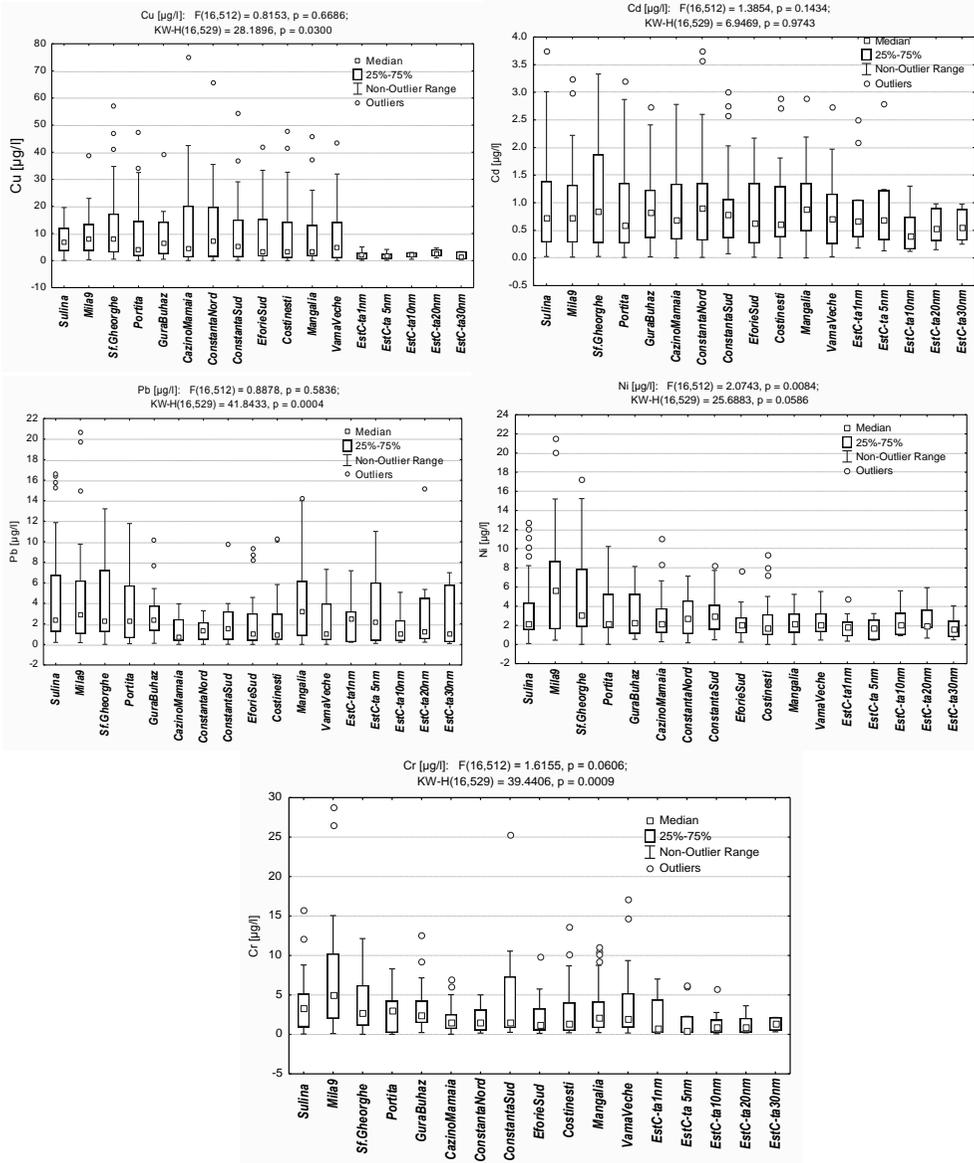
### *Status of heavy metal contamination*

The physical-chemical and hydrodynamic conditions of marine waters affect the transportation and distribution of heavy metals. Metals present in water can undergo chemical reactions, ion exchange or precipitation, after which they accumulate into the sediment, from where they can later be resumed in the water column. Due to all these factors, the concentrations of heavy metals in the marine environment are significantly influenced by variations in the physic-chemical parameters in the water column (pH, salinity, redox potential and concentration of organic ligands), spatial variations (depth, the distance from the mouth of the river or source of contamination) and temporal (season).

The range of heavy metals concentrations in water during 2006 - 2011 framed within the following limits: copper between 0.01 to 93.51 mg/L, cadmium between 0.01 to 18.32 mg/L, lead between 0.01 to 51.97 mg/L, nickel between 0.01 to 30.59 mg/L, chromium between 0.01 to 59.74 mg/L. In sediment, heavy metals concentrations varied within the following limits: copper between 0.53 to 147.84 mg/g, cadmium between 0.01 to 9.63 mg/g, lead between 0.10 to 300.78 mg/g, nickel between 0.40 to 211.73 mg/g, chrome between 1.34 to 231 mg/g.

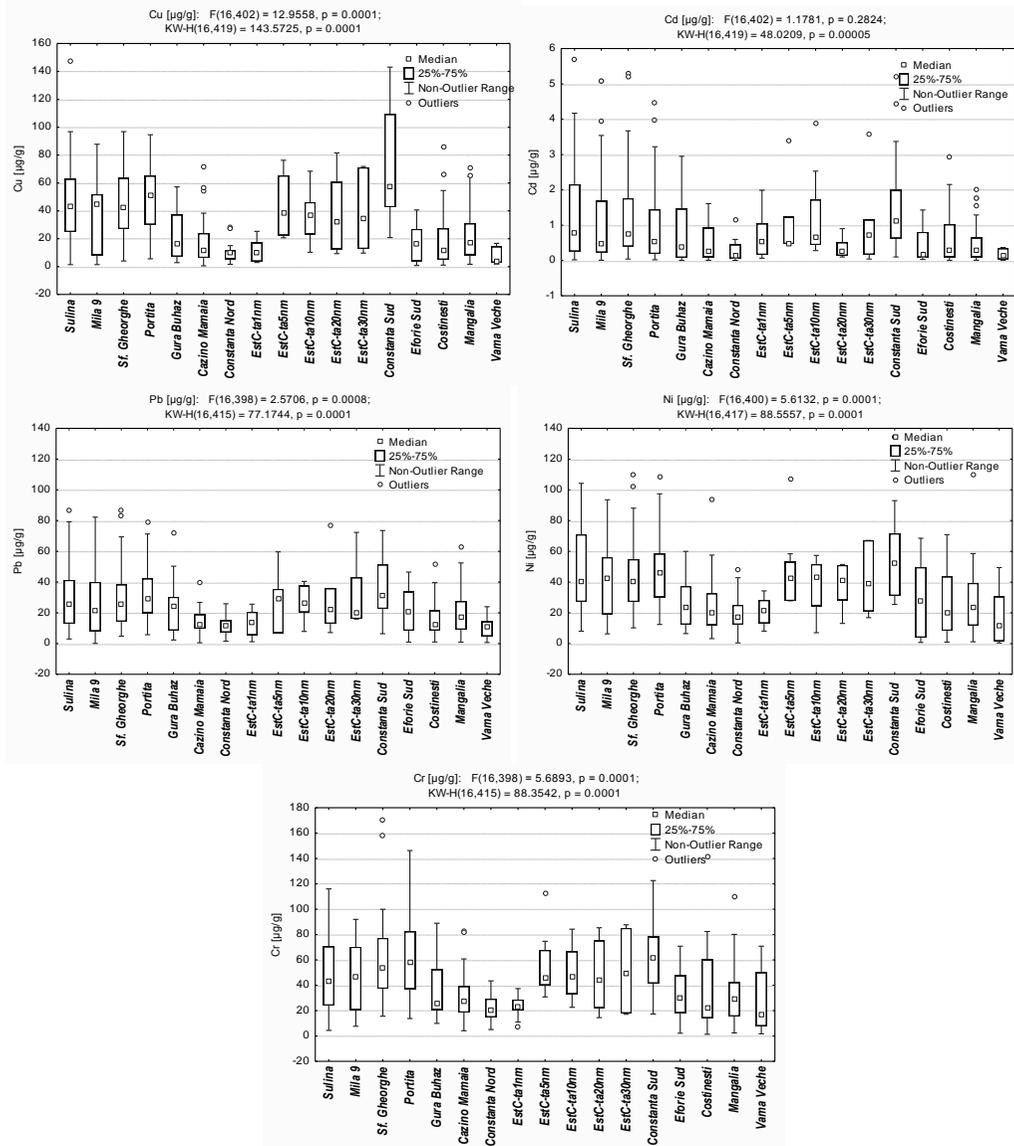
In relation to the quality standards recommended by national legislation (Order of the Minister of Environment and Water no. 161/2006 approving the Norms concerning the classification of surface water quality to determine the ecological status of water bodies), the percentage of samples investigated during 2006-2011 exceeding the proposed limits vary depending on element, zone or special hydrological events or sedimentary features, as follows: for water, 7.8% copper, 1.2% cadmium, 9.4% lead and 0% nickel and chrome and in sediment, 37.5% copper, 30.5%, cadmium, 5.5% lead, 39.3% nickel and 3.8% chromium.

In some cases, differences in the spatial distribution of heavy metal concentrations in marine waters highlight the contribution of the river input in the northern part (lead, nickel, chrome) and terrestrial sources of pollution in the southern sector (lead, chromium) (Mangalia, South Constanța). In comparison, the values observed in marine waters along the East Constanța profile that goes up to 30 Nn offshore are often reduced (copper, cadmium, chrome) (Fig. 2) .



**Fig. 2 - Spatial distribution of heavy metal concentrations in seawater along profiles monitored during 2006-2011**

The distribution of heavy metal concentrations in sediments is influenced by natural and anthropogenic sources and depends on the mineralogical features and grain size of the sediment [1]. Sediments with fine texture and a higher content of organic substances tend to accumulate high concentrations of heavy metals as compared to coarse sediments near the shore.



**Fig. 3 - Spatial distribution of heavy metal concentrations in sediments along profiles monitored during 2006-2011**

The presence of heavy metals in sediments from different geographical areas is characterized by a high degree of variability, depending on the element, sediment type, distance from shore and the influence of anthropogenic sources. Most metals showed increased accumulation in the area with river influence (Sulina - the harbor) and the aquatorium of the Constanța South Harbor, while the central sector (Gura Buhaz - Constanța North) and the southern area (Costinești - Vama Veche) are generally characterized by moderate values (Fig. 3)

The evolution of heavy metal concentrations in marine ecosystem components in the past decade shows various behaviors, depending on the matrix or element investigated. In general, the annual values calculated (median, percentiles 25 and 75) fall within normal multiannual variability, showing some trends of stabilization in recent years (e.g. nickel in water, copper, lead and chromium in the sediment, respectively). A slight upward trend in recent years has been observed for copper and lead in water, cadmium and nickel in sediment, respectively, while for chrome and cadmium in the seawater a small reduction was observed.

### ***Status of Polycyclic Aromatic Hydrocarbon contamination***

Polycyclic Aromatic Hydrocarbons (PAHs) with one or more condensed aromatic rings represent an important class of persistent organic pollutants. The number and position of the aromatic ring in the molecule determine the physical and chemical properties, the response to environmental factors and their interaction with the organisms. Solubility in water decreases with increasing PAHs molecular weight. One of the most important features is their affinity for lipids. These pollutants result from incomplete combustion of coal, oil, natural gas, timber. The main routes by which anthropogenic PAHs entry into the marine environment are atmospheric deposition, municipal and industrial discharges, direct flow of oil and petroleum products [2]. Once in the water, compounds that do not evaporate tend to adhere to the surface of organic and inorganic particles due to their strong hydrophobic character, they will be transported into the water column, and finally, will accumulate in the sediments.

Polycyclic Aromatic Hydrocarbons determined during 2006-2011 in water and sediment samples indicate the presence of 16 priority hazardous contaminants (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene, indeno(1,2,3-c,d)pyrene) in 90% of all samples taken in the area between Sulina - Vama Veche.

The total polycyclic aromatic hydrocarbons content ( $\Sigma$ PAHs) in water varied from 0.001 to 16.543. The highest concentrations were determined for naphthalene, anthracene, phenanthrene, fluoranthene and benzo[a]anthracene; the values of individual compounds exceed the maximum levels of the Order no.161/2006 (Table 1).

**Table 1 - PAH concentrations in water samples from the Romanian Black Sea coast during 2006-2011**

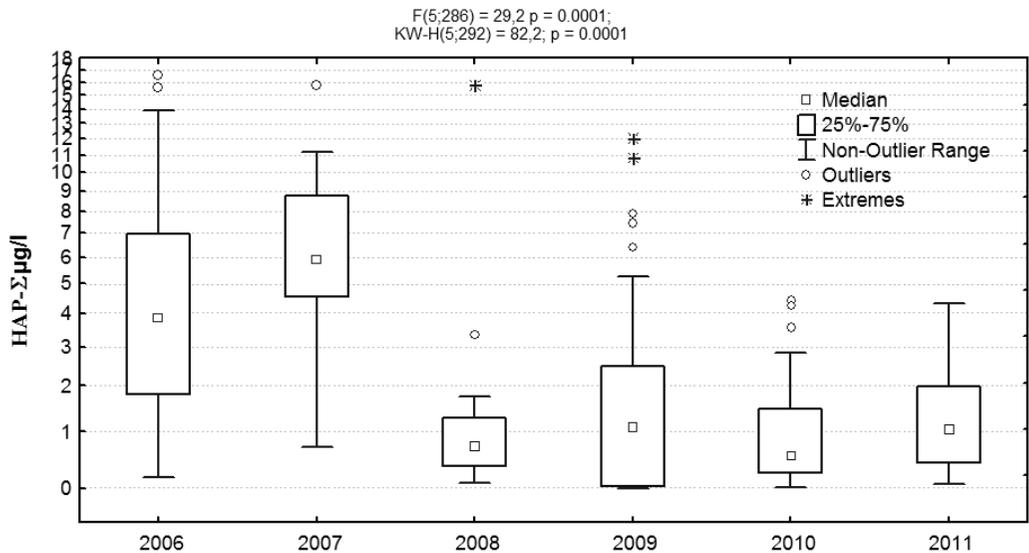
Compound	Maximum admissible level (µg/l) [3]	Mean (µg/l)	Minimum (µg/l)	Maximum (µg/l)
Naphthalene	2.400	1.1673	0.0010	10.1530
Phenanthrene	0.030	0.4676	0.0001	5.0835
Anthracene	0.063	1.3897	0.0008	9.0300
Fluoranthene	0.090	0.0823	0.0001	0.7552
Benzo[a]anthracene	0.010	0.0216	0.0001	0.6028
Benzo[b]fluoranthene	0.025	0.0125	0.0002	0.0442
Benzo[k]fluoranthene	0.025	0.0113	0.0001	0.0423
Benzo[a]pyrene	0.050	0.0176	0.0001	0.0942
Benzo(g,h,i)perylene	0.025	0.0070	0.0001	0.0547

The spatial distribution of total PAHs concentrations in water indicates no significant variations between the northern part, Sulina - Gura Buhaz (less urban area, under the influence of the Danube) and the southern part, Gura Buhaz - Vama Veche (densely populated, with many urban areas - resorts, harbors). Significant differences between the northern and southern Romanian coastline were observed only by analyzing the concentrations of the individual compounds; the main difference was observed for anthracene, for which a decreasing concentration gradient from north to south in the offshore waters was noticed.

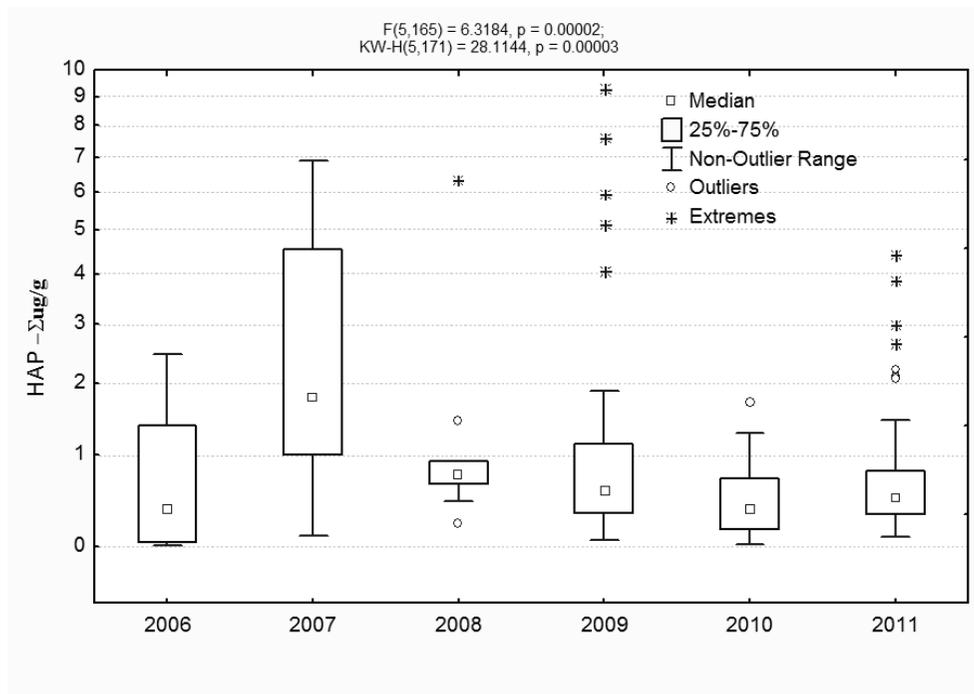
In sediment, the total PAHs concentrations during 2006 - 2011 ranged from 0.0026 to 16.425 µg/g. The total PAHs concentrations distribution in sediment indicates a very high pollution levels in 21% of the samples, in these sample values ranging between 2.0 and 10.0 µg/g.

The same as for waters, the total PAHs concentrations distribution in sediment shows no significant differences between the northern and southern sector of the Romanian seaside. On the other hand, the distribution of the concentrations of the individual compounds shows very significant differences between the two parts of the Romanian coast for fluoranthene, benzo[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[a]pyrene, benzo(g,h,i)perylene, indeno(1,2,3-c, d)pyrene and a decreasing gradient of pollutant concentration from north to south.

The evolution of  $\sum$ PAHs concentrations in the marine ecosystem components during 2006 - 2011 shows a downward trend for polycyclic aromatic hydrocarbons pollution. The highest values of total polycyclic aromatic hydrocarbons concentrations ( $\sum$ PAHs) were recorded during 2006 - 2007 (Fig. 4 and Fig. 5).



**Fig. 4 - Water comparative distribution of the total content of Polycyclic Aromatic Hydrocarbons - $\Sigma$ PAHs ( $\mu\text{g/l}$ ) in the Romanian sector of the Black Sea, 2006-2011**



**Fig. 5 - Sediment comparative distribution of the total content of Polycyclic Aromatic Hydrocarbons - $\Sigma$ PAHs ( $\mu\text{g/g}$ ) in the Romanian sector of the Black Sea, 2006-2011**



### ***Status of Organochlorine Pesticide contamination***

Organochlorine pesticides represent a class of persistent organic pollutants widely used since 1940 for pest control.

Persistent organic pollutants are chemical substances particularly harmful to human health and to the environment, carcinogenic and neurotoxic, affecting the functioning of the various systems of organisms, so in a certain dose they become lethal and, unlike other pollutants, resist degradation. POPs pollution is a cross-border problem, for which it is necessary to take action at the international level [4].

Representative compounds of this group include DDT, aldrin, dieldrin, endrin, heptachlor, lindane and hexachlorobenzene. These compounds are included in the list of POPs targeted by the Stockholm Convention, which aims to limit and ultimately permanently halt production, use, release and storage of these substances, but subject to other national conventions and regulations (International Convention on the Protection of the Black Sea Against Pollution, Order no. 161/2006 approving the Norms concerning the classification of surface waters quality to establish ecological status of water bodies, Directive 105/2008 of the European Commission on environmental quality standards in the field of water policy, Marine Strategy Framework Directive, Water Framework Directive).

Although in Romania the production and use of these compounds is banned since the 1970s - 1980s, they are found in the marine environment in significant concentrations. The most likely sources of contamination are the Danube and air transport (due to soil and water evaporation, as a result of using it in previous years or in other countries or from preservation deposits of these chemicals which have left considerable quantities) [5].

During 2006 - 2011, the dominant compounds in water and sediment were HCB, lindane, heptachlor and aldrin. The range of these compounds varied, in sediment, between the detection limit and 0.07 mg/g dry sediment and, in water, between the detection limit and 0.35 mg/L. The concentrations of other compounds investigated (dieldrin, endrin, DDE, DDD and DDT) varied, in sediment, between the detection limit and 0.005 mg/g dry sediment and, in water, between the detection limit and 0.02 mg/L.

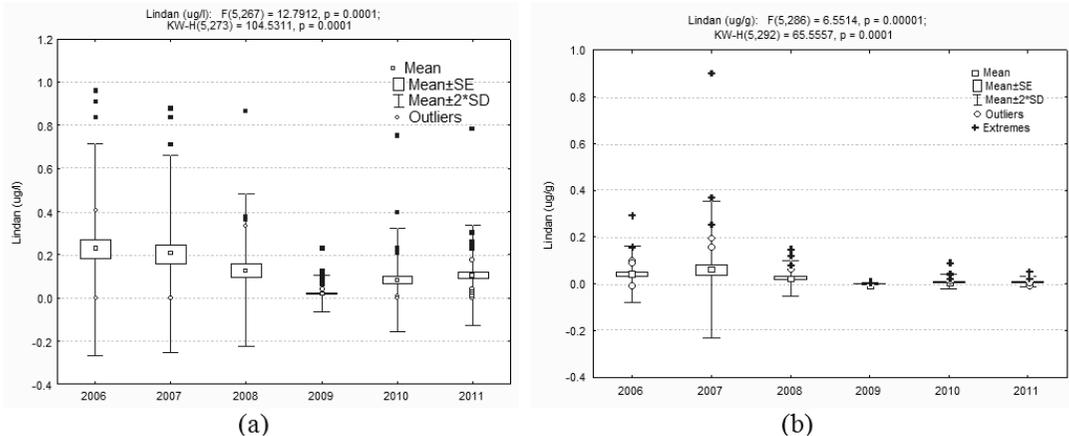
The concentrations of pesticides in water, calculated for this period, are higher compared with the maximum permitted levels stipulated by Directive 105/2008 of the European Commission on environmental quality standards in the field of water policy, in over 50% samples for HCB, lindane and cyclodienes pesticides (aldrin, dieldrin, endrin) and in more than 20% samples for DDT.

The first extensive investigation on sediment pollution in Romanian coastal waters of a broad pesticide spectrum was done in 1993. Samples were taken from 15 stations located along the Romanian coast, from the Danube Delta mouths to the Romanian southern border. Annual averages calculated in sediment during 2006-2011 are higher for HCB and lindane and comparable or lower for DDT and DDD, comparing to the concentrations measured in 1993 [6].

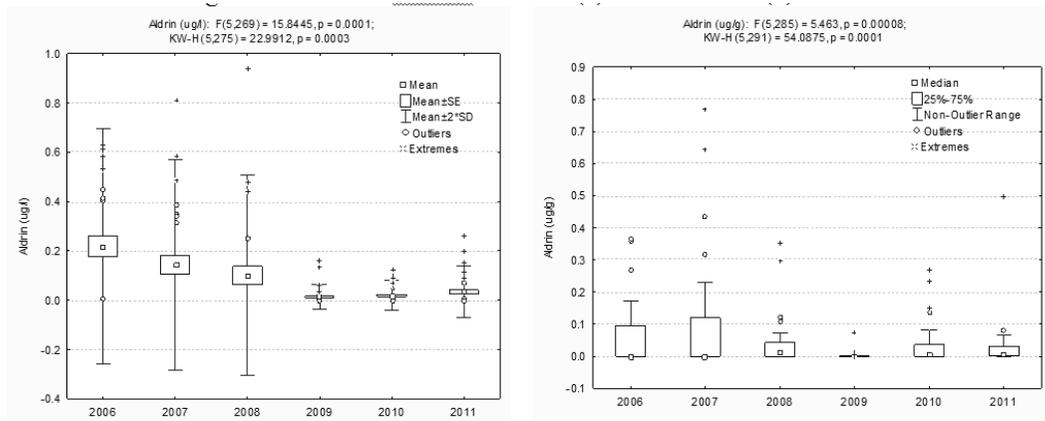
The spatial distribution of values in water and sediment shows no significant variations from north to south. There are not any significant variations for the pesticide levels in samples located on different isobaths, although, in water, extreme values are more numerous near the shore.

The temporal analysis of organochlorine pesticide levels highlighted the significant drop in recent years (2009 - 2011) of the values for lindane, aldrin and DDT, both in water

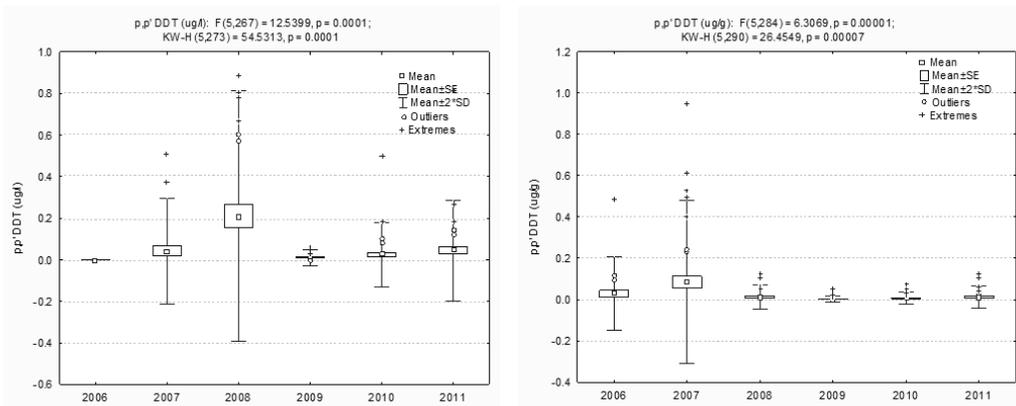
and sediment (Fig. 6, Fig. 7, Fig. 8). For the other compounds investigated, concentrations remain to the same extent of variation for the entire period.



**Fig. 6 - Variation of lindane in water (a) and sediment (b) during 2006 -2011**



**Fig. 7 - Variation of aldrin in water (a) and sediment (b) during 2006 -2011**



**Fig. 8 - Variation of DDT in water (a) and sediment (b) during 2006 -2011**

## CONCLUSIONS

Information resulting from investigations on heavy metals, polycyclic aromatic hydrocarbons and organochlorine pesticides provide a basis for characterizing the Romanian marine ecosystems in terms of levels of pollution with hazardous substances.

The concentrations of most heavy metals in water and sediment were generally classified as average annual value ranges, although some trends of decreasing or in other cases, increasing, were observed for certain items.

The distribution of hazardous substances in the Black Sea marine ecosystem components highlights the differences between different sectors of the coastline for heavy metals and polycyclic aromatic hydrocarbons, in general observing slightly increased concentrations in the water under the influence of the Danube and in the southern sector in certain areas subjected to various anthropogenic pressures (harbors, discharges of wastewater). The spatial distribution of organochlorine pesticides concentrations in water and sediment signals no significant variations from north to south. There are frequently overtakings of the quality standards in force.

Although research in recent years has shown tentative signs of recovery of the marine ecosystem quality, no firm conclusions can be drawn yet. It is necessary to study in more depth the extent to which pollution has affected the marine environment, the degree of reversibility of changes and how the ecosystem responds to anthropogenic pressure reduction.



## REFERENCES:

1. OSPAR, 1992. DGW Report nr. 92.033 - Background concentrations of natural compounds in rivers, seawater, atmosphere and mussels. RW Laane (ed). International Workshop on Background Concentrations of Natural Compounds, 6-10 April 1992, the Netherlands.
2. Polkowska, Z., Kot, A., Wiergowski, M., Wolska, L., Woowska, K. and Namienik, J.: 2000. Organic pollutants in precipitation: determination of pesticides and polycyclic aromatic hydrocarbons in Gdask, Poland, Atmos. Environ. 34, 1233-1245.
3. XXX Order of the Minister of Environment and Water 161/2006 approving the Norms concerning the classification of surface water quality to determine the ecological status of water bodies, M.O. Part I, no.511/13 June 2016
4. UNEP, 2005. Să salvăm lumea de POP: Ghid la Convenția de la Stockholm privind poluanții organici persistenți
5. XXX <http://apmvs.anpm.ro/pages/categorie/186>
6. Mee L.D., Topping G., 1998. Black Sea Pollution Assessment. Black Sea Environmental Series Vol.10, pp. 380.