

Monitoring and Assessment of Heavy Metals in the Romanian Black Sea Ecosystem during 2006-2018, in the Context of Marine Strategy Framework Directive (MSFD) 2008/56/EC Implementation <i>(Andra Oros)</i>	“Cercetări Marine” Issue no. 49 Pages 8 - 33	2019
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MONITORING AND ASSESSMENT OF HEAVY METALS IN THE ROMANIAN BLACK SEA ECOSYSTEM DURING 2006 - 2018, IN THE CONTEXT OF MARINE STRATEGY FRAMEWORK DIRECTIVE (MSFD) 2008/56/EC IMPLEMENTATION

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ABSTRACT

The current paper provides an overview of the heavy metals monitoring data (2006 - 2018), matrices and proposed threshold values used for the assessment of the Descriptors 8 and 9 during MSFD reporting cycles: Initial assessment (2012), and updates of the MSFD Articles 8, 9 and 10 (2018). Compiled information helps evaluate long-term trends and actual state of Black Sea Romanian waters with respect to these contaminants and to identify aspects that need further development, in order to achieve consistency with the MSFD Commission Decision (EU 2017/848) and also harmonization at regional and European level regarding the assessment methodologies of good ecological status (GES).

Key-Words: heavy metals, pollution monitoring, Black Sea, GES

AIMS AND BACKGROUND

Heavy metal contamination of the marine environment may be correlated with urban or industrial sources such as factories, thermoelectric plants, port activities, sewage treatment stations. The influence of rivers on coastal areas is significant, constituting a major source of metals, especially in particulate forms, extreme hydrological events (floods) contributing to the intensification of this input (Sakson et al., 2018). Atmospheric fluxes, demonstrating both natural and anthropogenic influences, are also considered to have an important contribution for European seas, both in coastal and basin areas, depending on the variability of the meteorological and local climatic conditions. Biogeochemical processes and natural levels of metals in the marine environment depend on numerous factors, such as sedimentary rock

type, oxygen content, currents, salinity, pH, etc. The spread of metals in water, sediment and atmosphere results from their presence in the earth crust. In their natural concentrations metals play an essential role in many biochemical processes in living organisms, but any concentration that exceeds the background, as a result of anthropogenic activities, can become toxic (OSPAR, 1992).

The general sources of pollution of the marine environment are represented by: cities and coastal industries, urban and industrial waste waters, landfills, rainwater, shipping, waste dumping, wrecks, lost or intentionally discarded ammunition, marine drilling platforms, atmospheric deposits (UNEP, 2002; 2006). Metals are transported either in dissolved forms in water or as an integral part of particulate matter. Once in the aquatic environment, they can follow several paths: dissolved in the water column, stored in sediment, volatilized in the atmosphere, accumulated in aquatic organisms. Metals are also generated as a result of natural rocks erosion processes. This process is intensified as a result of mining extractive activities which thus expose various minerals containing metals. Leakage from mining waste dumps and resting ponds introduce substantial amounts of metals into water resources. Any activity involving extraction or processing of metals is a source of fine metallic particles dispersed in the atmosphere. Rust and other forms of corrosion lead to the spread in the environment of metals, during the use or storage of various metallic equipment. The combustion of fossil fuels or of various categories of waste also produces the release into the atmosphere of metals. The largest deposition of metal particles is evident in the vicinity of mines, or other categories of metal processing activities, which are major emission sources (Fashola et al., 2016). But most of the particles are so small, they can be transported over enormous distances by the wind. Also, road transport is responsible for major emissions of lead, following the use of fuels containing as an additive lead compound. Metals released into the atmosphere are deposited at ground level, where they remain in the long run. Under certain conditions, for example when lowering pH, soil metals are solubilized and end up in neighboring water resources.

As observed in many marine areas, even if the emissions of metals are reduced or even halted, the sediments in the immediate vicinity of the sources remain polluted long after the end of the emissions, restoring the ecosystem being a long-term process. In addition, the metals in the sedimentary layers can return in the water column. The physico-chemical and hydrodynamic conditions in marine waters influence the transport and distribution pathways of heavy metals (Hazrat et al., 2019). Metals present in water may undergo complexing reactions, ionic exchanges or precipitation, as a result of which they accumulate in the sedimentary substrate, from which they can subsequently return in the water column. Due to all these factors, the

concentrations of heavy metals in marine water are significantly influenced by spatial (depth, proximity to the mouth of the river or contamination source) or temporal (season) variations.

Coastal sediment has a lower degree of variability than the water column. However, metals are not permanently fixed in the sediment. The variation of physico-chemical parameters in the water column (pH, salinity, redox potential and organic ligands concentration) causes the release of metals from sediment into the water column. The assimilation of metals by biota is conditioned by several physico-chemical and biological processes that determine solubilization and their bioavailability (Wang & Fisher, 1997). High concentrations of metals in the environment affect biota through their bioaccumulation capacity, transferring along the food chain and finally reaching human consumers. In the situation where additional quantities of heavy metals are introduced into the marine environment from various sources, they penetrate into the biogeochemical cycles and interfere with the normal functioning of ecosystems. Marine organisms are continuously exposed to variable concentrations of metals in marine water, especially in coastal areas affected by anthropogenic activities.

Living organisms have a certain selectivity in the accumulation of metals, a distinction must be made between the essential and the non-essentials metals. Essential metals such as copper, zinc, manganese, iron or cobalt are vital components of many enzymes and respiratory pigments. As a consequence, marine organisms must provide metal tissues in sufficient quantities for metabolic and respiratory needs. Deficiency of these metals, but also accumulation above certain levels, produce harmful effects (White & Rainbow, 1985). Non-essential metals (lead, arsenic, mercury, cadmium) are very toxic, even at very low levels, especially if they accumulate at the level of active metabolic sites. The organism is obliged to limit the accumulation of non-essential metals or to convert them into non-toxic forms. Toxic metals interfere with the normal metabolic functions of essential elements. A disturbance of normal biological function is caused by binding to protein macromolecules. The metals catalyzed formation of free oxygen radicals is involved in the production of many pathological changes, including mutagenesis, carcinogenesis and ageing (Depledge & Rainbow, 1990). Thus, although metals are essential components of life, they become harmful when they are present in excess. Increasing bioavailable levels in the marine environment is a problem for human health and marine ecosystems.

The Marine Strategy Framework Directive (MSFD, 2008/56/EC) provides for regular updates of the marine strategies by EU Member States (MS) every six years. The article 17(2) requires reporting on articles 8 (Initial Assessment), 9 (determination of the Good Environmental Status) and 10 (establishment of targets) to be updated in 2018. The current paper provides

an overview of the substances (heavy metals), matrices and threshold values that were used for the assessment of the Descriptor 8 and 9 during MSFD reporting cycles (Initial Assessment, 2012 and IA update, 2018) for the Romanian Black Sea waters. This compilation helps evaluate existing gaps as well as to identify aspects that need further harmonization at regional and European level (Golumbeanu et. al., 2014). It also helps understand which issues should be addressed to achieve consistency with the new MSFD Commission Decision (EU 2017/848).

According to the revised MSFD Commission Decision (EU 2017/848), Member States have to consider the Priority Substances (PS) and River Basin Specific Pollutants (RBSP) already identified under the Water Framework Directive (WFD, 2000/60/EC), and establish, through regional cooperation, a list of additional contaminants that may give rise to pollution effects. For each contaminant under criterion D8C1, MS shall express its concentration, the matrix used for monitoring (water, sediment, biota), whether the threshold values set have been achieved, and the proportion of contaminants assessed which have achieved the threshold values. For the contaminants already identified under the WFD, the threshold values should be the values set in accordance with that Directive. For contaminants measured in a matrix for which no value is set under the WFD, as well as for additional contaminants, the threshold values for a specified matrix should be established through regional cooperation. It is important to highlight that some European countries do not report compliance with a threshold value, but provide integrated assessments across time (for trends) and space (from individual monitoring stations to the classified area) in order to reach a conclusion on the status of their marine waters (Tornerio et al., 2019).

EXPERIMENTAL

Romania, as an EU Member State, must fulfil the obligations laid down in the Marine Strategy Framework Directive (MSFD), namely to make every effort to improve and maintain the good state of the Black Sea marine ecosystem. In 2012, Romania elaborated the first report on the state of the marine Black Sea ecosystem under the provisions of art. 8 - Evaluation, art. 9 - Determination of Good ecological status (GES) and art. 10 - Setting environmental objectives. The following stages of the first implementation cycle in achieving the good ecological status of the Black Sea were updating the national monitoring programme according to art. 11 (2014) and elaboration of the National programme of measures (articles 13 and 14). In 2018, the report on the ecological status of the marine Black Sea ecosystem according to the requirements of article 17 of the Marine Strategy Framework Directive (2008/56/EC) takes into account Commission Decision

2017/848/EU on the criteria and the methodological standards on good environmental status, replacing Commission Decision 2010/477/EU, and Commission Directive 2017/845/EU, which amends annex III to the MSFD (Boicenco et al., 2018).

The Initial Evaluation report, 2012 (Boicenco et al., 2012), chapter contaminants – heavy metals, was based on data from the monitoring programme during the period 2006-2011, as well as on previously available data, period 2000-2005 (Oros et. al., 2003). In 2018, the report on state of the marine Black Sea ecosystem according MSFD Art. 17 (Boicenco et al., 2018), Descriptors 8 and 9, contaminants – heavy metals, was made on the basis of monitoring data from 2012 – 2017, compared with the previous evaluation period (2006 – 2011) (Oros & Gomoiu, 2012; Coatu et. al, 2015).

The national monitoring network initially started (over 30 years ago) with a number of about 29 stations, most of which were within 1 mile from shore (bathymetric strip 0 – 20 m) (transitional and coastal waters), except for the reference transect East Constanta, which stretched up to 30 nautical miles offshore. Starting with the year 2009 the network was extended (up to 40 stations), by prolonging the existing 13 transects, along the isobaths of 30, 40 or 50 m (up to the limit of 12 nm, and in some cases beyond it), to ensure the data necessary for the initial assessment of Romanian marine waters according MSFD requirements. In 2014, along with the revision of the monitoring program, the NIMRD national network of marine monitoring was further expanded, covering the transitional, coastal and marine waters (territorial waters and part of the EEZ). Currently the network is represented by 45 permanent stations, having transects that reach up to 100 m deep, respectively 65 nautical miles from the base line (Fig. 1), thus responding to the implementation requirements of MSFD, providing relevant information for the Report on the ecological status of the marine Black Sea ecosystem according to the requirements of art. 17 in 2018.

Assessment of ecological status based on criteria and indicators according to Decision 2017/848/EU for the period 2012-2017 was carried out on the following assessment areas (Fig. 2) (Boicenco et al., 2018):

- BLK_RO_RG_TT03_ Variable salinity waters – located in the north sector, under the direct influence of the Danube, from the mouths of the river into the Black Sea, to the south, to Portita, up to the depths of 30 m;
- BLK_RO_RG_CT_ Coastal waters - from the central to the south sector (Portita – Vama Veche), from the base line to the 30 m isobath;
- BLK_RO_RG_MT01_Marine waters – the marine waters area from 30 m isobath to 200 m;
- BLK_RO_RG_MT02 – offshore waters – no data available.

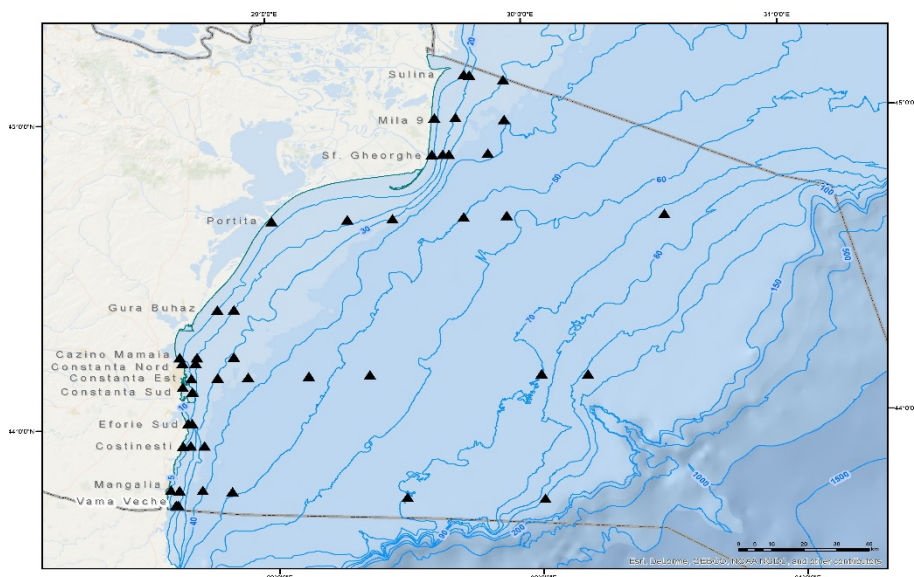


Fig. 1. Integrated monitoring network of Romanian marine waters.

The monitoring of heavy metals in the period 2006 - 2018 was carried out by analysis of 952 seawater samples (surface horizon), 866 surface sediments and 143 samples of mollusks (*Mytilus galloprovincialis*, *Rapana venosa*), taken from 45 monitoring stations, arranged on 13 transects along the Romanian shoreline, bathymetric strip 0-100 m. Research expeditions were conducted with the NIMRD R/V ship *Steaua de Mare 1* (with an average frequency of 2 times/year) for sampling water (Nansen bathometer), superficial sediment (Van Veen boden-greifer) and biota (beam trawl) for the analysis of contaminants (heavy metals and organic pollutants). Preliminary processing of samples was carried out according to the recommended reference methods in the study of marine pollution (UNEP, 1993; 1995).

Heavy metals were determined in unfiltered marine water samples, acidified up to pH = 2 with HNO₃ Ultrapur. Nitric acid is used not only for the preservation of samples and solubilization of particulate metals, but also as a matrix modifier, diminishing the interferences caused by salts.

Sediments and marine organisms were freeze-dried by lyophilization (Lyophilizer Labconco-FreeZone 2,5 Plus) and then well homogenized, and in the case of sediment the coarse fragments (> 0.5 mm) were removed by sieving. Further processing of samples consisted of treatment with concentrated acid (HNO₃ 65%) followed by the process of digestion in the microwave oven (Microwave Digestion System BERGHOF MW4). At the

end of mineralization, the samples were resumed in the 100 ml flask, with deionized water (Water purification System Simplicity 185, Millipore).

The analytical determination of the copper, cadmium, lead, nickel, and chromium was carried out by atomic absorption spectrometry method (GF-AAS), using a M6 DUAL Zeeman, Thermo Electron – Unicam model. Calibration was performed with working standards for each element, starting from stock solutions of 1000 µg/L (Merck). The work domains are as follows: Cu 0-50 µg/L; Cd 0-10 µg/L; Pb 0-25 µg/L; Ni 0-50 µg/L; Cr 0-50 µg/L. At least 3 instrumental readings have been performed for each sample, with average value reported.

Standard procedures for the analysis of heavy metals, recommended in marine pollution studies (IAEA-MEL, Monaco, 1999) and the Manual "Methods of Seawater Analysis" (Grasshoff, 1999) have been applied.

In the case of Descriptor 8, good ecological coverage was defined on the basis of criterion D8C1, for which indicators, targets and environmental objectives were defined (Tab. 1, Tab. 2).

Table 1. Summary of criteria associated with Descriptor 8, Commission decision 2017/848.

DESCRIPTOR		CRITERIA	Primary/ Secondary
D8	Concentrations of contaminants are at levels that do not cause pollution effects.	D8C1 In coastal and territorial waters, concentrations of contaminants shall not exceed the threshold values.	Primary
		D8C2 Species health and Habitat status (such as species composition and relative abundance in chronic pollution locations) are not affected by contaminants. Including cumulative and synergic effects.	Secondary
		D8C3 Spatial expansion and duration of significant events of acute pollution are minimized.	Primary
		D8C4 The adverse effects of significant events of acute pollution on the health of species and habitat status (such as species composition and relative abundance) are minimized and where possible eliminated.	Secondary

Table 2. Overview of good ecological status and environmental objectives for Descriptor 8 - contaminants - heavy metals.

Criteria (2017/848/EU): D8C1 In coastal and territorial waters, concentrations of contaminants do not exceed the threshold values.

PROPOSED INDICATOR	GES	PROPOSED TARGET	ENVIRONMENTAL OBJECTIVES
Heavy metals concentration in surface marine sediments	Concentrations of contaminants relevant to the marine environment, measured in the appropriate matrices (water, sediment or biota), are lower than the concentrations at which negative effects may occur or demonstrate a downward trend. – Coastal waters (up to 12 nautical miles):	The ' 75th percentile of the concentrations of heavy metals measured in sediments is less than the levels from which adverse effects are expected (ERLs; Ord.161/2006)	Status Objective: Concentrations of contaminants in water, sediment and biota do not present increasing trends. Pressure Objective: The loads of contaminants in the marine environment are reduced. Impact Objective: The percentage of water samples, sediments and biota that exceed the values proposed as a limit for good ecological status for contaminants is reduced (< 25%).
Concentration of heavy metals in marine waters	concentrations of contaminants relevant to the marine environment, measured in the appropriate compartments (water, sediment or biota) comply with the EQS environmental quality standards used in the WFD 12 nm zone (for priority substances) or the area of 1 nm (for all other substances). – Offshore waters (1 or 12 nautical miles, respectively): concentrations of contaminants relevant to the marine environment, measured in appropriate compartments (water, sediment or biota) comply with environmental quality standards or demonstrate a downward trend.	The ' 75th percentile of the concentrations of heavy metals measured in marine waters is less than the levels from which adverse effects are expected (Directive 2013/39/EU; /Ord.161/2006)	

In the case of Descriptor 9, good ecological status was defined on the basis of criterion D9C1, for which indicators, targets and environmental objectives were defined (Tab. 3, Tab. 4).

Table 3. Summary of criteria associated with Descriptor 9, Commission decision 2017/848

DESCRIPTOR	CRITERIA	PRIMARY/SECONDARY
D9	Contaminants in fish and other seafood for human consumption shall not exceed the levels established by the European Union legislation or other relevant standards.	D9C1 The level of contaminants in edible tissues (muscle, liver, or other soft parts, where appropriate) of seafood (including fish, crustacean, mollusks, seaweed and other marine plants), caught or harvested from the natural environment (excluding fish from mariculture) do not exceed the maximum levels established.

Table 4. Overview of good ecological status and environmental objectives for Descriptor 9- contaminants in fish and other seafood for human consumption

Criteria (2017/848/EU): D9C1 The level of contaminants in edible tissues (muscle, liver, or other soft parts, where appropriate) of seafood (including fish, crustacean, mollusks, seaweed and other marine plants), caught or harvested from the natural environment (excluding fish from mariculture) do not exceed the maximum levels established.

PROPOSED INDICATOR	GES	PROPOSED TARGET	ENVIRONMENTAL OBJECTIVES	
Contaminants levels (heavy metals) in fish and mollusks	The concentration of contaminants does not exceed the levels regulated by the European legislation: EC Regulation no.1881/2006 laying down maximum levels for certain contaminants in foodstuffs (including mollusks and fish), with subsequent modifications.	Percentile ' 75th of the concentrations of heavy metals measured in fish and mollusks is less than the levels regulated by European legislation	Seafood	Maximum admissible levels (mg/kg w.w.)
			Lead	
			Fish dorsal muscle	0.30
			Bivalve mollusks	1.5
			Cadmium	
			Fish dorsal muscle (depending of specie)	0.050; 0.10; 0.20;0.30
			Bivalve mollusks	1.0

Available data on the concentration of contaminants – heavy metals in relevant matrices: water, sediment and biota, during the evaluated period, were centralized, processed, analyzed statistically and evaluated in relation to the proposed target values for defining good ecological status. The definition of good ecological status (GES) for the D8C1 criterion was made by inventorying the methodologies used at national, regional, European level;

choosing the relevant methodology for the analyzed contaminants group; determination of the background values and target values (Coatu et. al, 2018). As there are no target values for contaminants in sediments and biota established by European legislation, the methodology involved a stage of inventory of literature and methodologies adopted in other marine regions (NOAA, 1999; OSPAR, 2009; UNEP MAP, 2011) and statistical processing of long-term monitoring data for the validation of the proposed target values: ERL and ERM (Effect Range Low and Effect Range Median) describing the toxic potential of heavy metal and organic pollutants content in sediments on marine organisms (Long et al., 1995). For seawater, environmental quality standards are regulated for a part of the elements (cadmium, lead, nickel, mercury, some organic pollutants) by Directive 2013/39/EU.

For descriptor D9, evaluation was based on the D9C1 criterion. Data available during the evaluation period on the concentration of contaminants in mollusks of commercial interest (*Rapana venosa* and *Mytilus galloprovincialis*), collected from the marine areas were centralized, processed, analyzed statistically and evaluated in relation to the proposed target values for defining good ecological status. The definition of good ecological status (GES) for Criterion D9C1 was made on the basis of the maximum allowable concentrations imposed by the legislation in force (EC Regulation no. 1881/2006, with subsequent amendments).

Thresholds values/reference levels

The standards and threshold values considered for the assessment of contaminants under MSFD D8 and D9 are (Tornero et al., 2019):

- EU-wide Environmental Quality Standards (EQS) laid down in part A of annex I to Directive 2000/60/EC as amended by Directives 2008/105/EC and 2013/39/EU. The EQS is the concentration of a particular pollutant or group of pollutants in water, sediment or biota which should not be exceeded in order to protect human health and the environment. EQS are set as a maximum allowable concentration (MAC-EQS) or an annual average (AA-EQS), protecting aquatic organisms from acute and chronic effects, respectively. Water EQS are expressed as total concentrations in the whole water sample except in the case of metals (cadmium, lead, mercury and nickel) where the water EQS refer to the dissolved concentration, i.e. the dissolved phase of a water sample obtained by filtration through a 0.45 µm filter or any equivalent pre-treatment, or, where specifically indicated, to the bioavailable concentration.
- Maximum levels for certain contaminants in foodstuffs set in the Commission Regulation (EC) No. 1881/2006 and amendments in order to prevent contaminated foodstuff from being placed on the market.

- Effects Range-Low (ERL) values developed by the United States Environmental Protection Agency (US EPA) for assessing the ecological significance of sediment concentrations. ERL is the lower tenth percentile of the data set of concentrations in sediments, which were associated with biological effects. Adverse effects on organisms are rarely observed when concentrations fall below the ERL value.
- National EQS. MS are to establish national EQSs according to the procedure described in the WFD guidance document no. 27 (European Commission, 2011 and 2018 revision). Alternatively, to water EQSs, MS can also set sediment or biota EQSs, as long as they provide at least the same level of protection (Tornero et al., 2019).

RESULTS AND DISCUSSION

The pressures suffered by the Black Sea over time make it an environmentally vulnerable unit, especially because this sea is semi-closed and too small to self-balance ecologically. Thus, the saturation point of contaminants discharged into the sea will be achieved faster than in the case of oceans. For example, high levels of heavy metals currently measured in the Mediterranean indicate non-stationary geochemical cycles resulting from an increase in external inputs (Saliot A., 2005). In addition, the almost total absence of tides does not allow the dilution of contaminants and prevents natural purging phenomena encountered in larger water bodies (e.g. in the oceans). Also, the Black Sea, like Mediterranean Sea, shows a deficiency in the movement of deep-sea water masses and surface currents that "turn into circles" in these almost closed basins. The consequence of these specific characteristics is that the response of small semi-closed seas to environmental disruptions resulting from anthropogenic pressures is faster than in the oceans.

Initial Assessment, period 2006 – 2011

Heavy metals concentrations in marine water observed in the period 2006-2011 recorded the following average values and variation ranges: copper 10.02 ± 13.77 µg/L (0.01-93.51 µg/L); cadmium 0.99 ± 1.26 µg/L (0.01-18,32 µg/L); lead 3.78 ± 6.03 µg/L (0.01-51.97 µg/L); nickel 3.65 ± 4.40 µg/L (0.01-30.59 µg/L); chromium 3.84 ± 6.26 µg/L (0.01-59.74 µg/L). In relation to water environmental quality standards recommended by national legislation (Ord. 161/2006 for the approval of the normative on the classification of surface water quality in order to establish the ecological status of water bodies), the percentage of samples investigated in the period 2006-2011 exceeding the proposed limits varied depending on the element, area, season, special hydrological events, as follows: copper 7.8%; cadmium 1.2%; lead 9.4%; nickel and chromium 0%.

The accumulation of heavy metals in superficial marine sediments investigated in the period 2006 – 2011 was characterized by the following mean values and variation ranges: copper $33.05 \pm 27.54 \mu\text{g/g}$ (0.53 – 147.84 $\mu\text{g/g}$); cadmium $1.03 \pm 1.52 \mu\text{g/g}$ (0.01-9.63 $\mu\text{g/g}$); lead $26.71 \pm 26.16 \mu\text{g/g}$ (0.10-300.78 $\mu\text{g/g}$); nickel $36.54 \pm 25.93 \mu\text{g/g}$ (0.40 – 211.73 $\mu\text{g/g}$); chromium $44.58 \pm 31.08 \mu\text{g/g}$ (1.34 – 231 $\mu\text{g/g}$). In relation to the quality standards for marine sediments recommended by national legislation (Ord. 161/2006 for the approval of the normative on the classification of surface water quality in order to establish the ecological status of water bodies), the percentage of samples investigated in the period 2006-2011 exceeding the proposed limits varies depending on the element, area, sedimentary characteristics, as follows: copper 37.5%; cadmium 30.5%; lead 5.5%; nickel 39.3% and chromium 3.8%.

The bioaccumulation of heavy metals in marine mollusks investigated in the period 2006 - 2011 was characterized by the following average values and variation ranges:

-*Mytilus galloprovincialis*: copper $2.61 \pm 1.80 \mu\text{g/g}$ (0.91 – 10.77 $\mu\text{g/g}$); cadmium $0.36 \pm 0.39 \mu\text{g/g}$ (0.05 – 1.98 $\mu\text{g/g}$); lead $0.98 \pm 1.78 \mu\text{g/g}$ (0.02 – 10.29 $\mu\text{g/g}$); nickel $1.05 \pm 0.55 \mu\text{g/g}$ (0.11 – 2.66 $\mu\text{g/g}$); chromium $0.97 \pm 1.13 \mu\text{g/g}$ (0.01 – 6.07 $\mu\text{g/g}$).

-*Rapana venosa*: copper $16.26 \pm 6.71 \mu\text{g/g}$ (2.44 – 29.89 $\mu\text{g/g}$); cadmium $0.86 \pm 0.89 \mu\text{g/g}$ (0.03 – 3.74 $\mu\text{g/g}$); lead $1.71 \pm 3.27 \mu\text{g/g}$ (0.02 – 15.67 $\mu\text{g/g}$); nickel $1.76 \pm 4.14 \mu\text{g/g}$ (0.09 – 19.55 $\mu\text{g/g}$); chromium $0.90 \pm 1.10 \mu\text{g/g}$ (0.03 – 4.19 $\mu\text{g/g}$).

The vast majority of mussels samples investigated in the period 2006 – 2011 presented the accumulation values of heavy metals included in the normal areas of variability, as follows: copper 95% values < 5 $\mu\text{g/g}$; cadmium 93% values < 1 $\mu\text{g/g}$; lead 78% values < 1.5 $\mu\text{g/g}$; nickel 94% values < 2 $\mu\text{g/g}$; chromium 93% values < 2 $\mu\text{g/g}$.

The differences in spatial distribution of heavy metals concentrations in marine waters during 2006 – 2011 highlighted in some cases the Danube contribution in the northern sector (lead, nickel, chromium), as well as land-based sources of pollution in the southern sector (lead, chromium) (Mangalia, Constanta South). In comparison, the values observed in marine waters along the East Constanta profile, which goes up to 30 nm offshore, were often diminished (copper, cadmium, chromium).

The distribution of heavy metal concentrations in sediment is influenced by the contribution of natural and anthropogenic sources and depends on the mineralogical and granulometric characteristics of sediments (OSPAR, 1992). The finer-textured sediment, with a higher content of organic substance, tend to accumulate higher concentrations of heavy metals, compared to coarse sediment near the shoreline. The presence of heavy metals in sediments from different geographic sectors in the period 2006 – 2011 was

characterized by a high degree of variability, depending on the element, the type of sediment, the distance from the shore and the influence of anthropogenic sources. Most metals had increased accumulations in the area of the river influence (Sulina – Portita), as well as in the port of Constanta South, while the central sector (Gura Buhaz – Constanta Nord), as well as in the southern extremity (Costinesti – Vama Veche) are generally characterized by moderate values.

Assessment period: 2012-2017

The evaluation of the heavy metals indicator in water, following data processing for the period 2012-2017, reflected in the vast majority of cases a good ecological state. The percentage exceeding the quality standards for heavy metals was insignificant, below the threshold of 25% determined for GES, excluding cadmium in the waters with variable salinity, where 26% of the samples presented slight overheads of the regulated value (Tab. 5).

Table 5. Assessment of ecological status of the assessment areas for heavy metals in water in the period 2012 - 2017

Assessment area	Compounds	Percentile 75 th value (µg/L)	Threshold value (µg/L)	Percentage of samples higher than threshold value (%)	Ecological status
Marine waters	Copper	6.31	30.00	3	Good
	Cadmium	1.14	1.50	13	Good
	Lead	7.43	14.00	4	Good
	Nickel	3.78	34.00	2	Good
	Chromium	3.21	100.00	0	Good
Coastal waters	Copper	4.21	30.00	7	Good
	Cadmium	1.06	1.50	14	Good
	Lead	6.06	14.00	5	Good
	Nickel	3.79	34.00	1	Good
	Chromium	2.74	100.00	0	Good
Variable salinity waters	Copper	6.53	30.00	3	Good
	Cadmium	1.61	1.50	26	Bad/Moderate
	Lead	6.45	14.00	8	Good
	Nickel	3.78	34.00	0	Good
	Chromium	5.35	100.00	0	Good

The assessment of the heavy metals indicator in sediment, following data processing for the period 2012-2017, reflected in the vast majority of cases a good ecological state. However, copper revealed a bad condition in sediments from marine and variable salinity waters, cadmium in variable

salinity areas, and nickel in all areas investigated. (Tab. 6, Fig. 2). Sediments accumulate over time contaminants from the water column, and heavy metals concentrations are dependent on the granulometry of sediment, as well as the organic substance content. It should be mentioned, however, that especially in the case of nickel, the concentrations characterizing the natural background can normally be higher in marine sediments from the Black Sea area (Secieru, 2002), compared to the recommended threshold values, therefore in the case of heavy metals in sediment, the integrated assessment of the ecological status at the level of indicators must be made with caution and taking into account the specifics of the area.

The analysis of the data for the period 2012 – 2017 shows that toxic heavy metals (cadmium, lead) had in marine mollusks of commercial interest a good ecological status, the 75th percentile value being below the maximum allowable values for human consumption provided in European legislation. In the case of lead, there was no surpassing of the maximum allowable value in the mollusks analyzed during the period 2012 – 2017, while in the case of cadmium there were surpasses of the threshold value in 3% of the investigated samples.

Table 6. Assessment of ecological status of assessment areas for heavy metals in sediment in the period 2012-2017

Assessment area	Compounds	Percentile 75 th value (µg/L)	Threshold value (µg/L)	Percentage of samples higher than threshold value (%)	Ecological status
Marine waters	Copper	51.08	40.00	35	Bad
	Cadmium	1.15	1.20	23	Good
	Lead	15.19	47.00	3	Good
	Nickel	78.09	35.00	73	Bad
	Chromium	69.74	81.00	11	Good
Coastal waters	Copper	22.30	40.00	14	Good
	Cadmium	0.73	1.20	16	Good
	Lead	11.33	47.00	2	Good
	Nickel	44.15	35.00	39	Bad
	Chromium	38.44	81.00	3	Good
Variable salinity waters	Copper	44.25	40.00	29	Bad
	Cadmium	1.27	1.20	28	Bad
	Lead	18.49	47.00	2	Good
	Nickel	87.47	35.00	70	Bad
	Chromium	69.42	81.00	14	Good

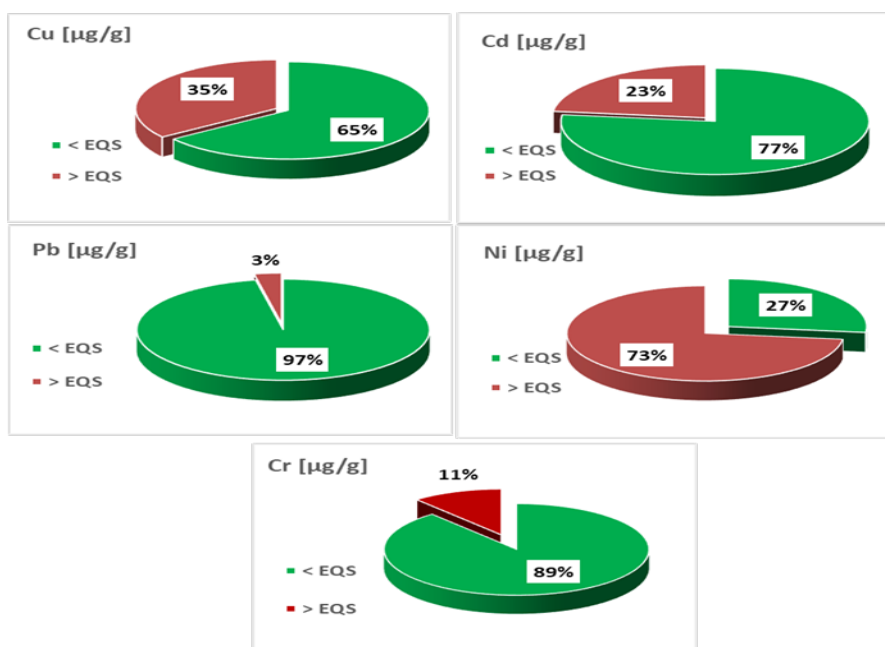


Fig. 2. Assessment of the state of marine sediments based on the heavy metals indicator, 2012-2017.

Current status of Romanian Black Sea waters with respect to contaminants – heavy metals

Metals are removed from sea water by passive deposition, i.e. the combined process of superficial adsorption on a wide variety of surfaces with high affinity associated with particulate material, followed by the deposition of particles. A large part of this particulate material (together with the associated metals) is recycled either in the water column or in superficial sediments. Weak-bound metals can be released from the surface of the particles that are deposited, replenishing the stock of dissolved metals. Marine sediments can also act as a source of metals by releasing them back into the water column above. The primary flow processes between sediments and the water column are re-suspension and deposition, bioturbation, advection, upwelling/downwelling, diagenetic processes and diffusion. Due to these remobilization processes, the effects of metal pollution on the local environment and organisms can be substantial and lengthy, even in the situation of restoration efforts (Richir J and Gobert S., 2016).

Heavy metals concentrations determined in 2018 in marine waters (surface horizon) have been included in their vast majority in normal areas of variability, with the following average values: 14.94 ± 6.34 μg/L Cu; $1.06 \pm$

0.38 µg/L Cd; 12.21 ± 5.12 µg/L Pb; 11.78 ± 4.98 µg/L Ni; 8.81 ± 4.51 µg/L Cr. (Tab. 7).

Table 7. Heavy metals concentrations in marine surface waters in 2018

	Average	Median	Percentile – 25th	Percentile – 75th	Std.Dev.	EQS
Cu [µg/l]	14.941	13.290	11.285	19.395	6.338	30.000
Cd [µg/l]	1.062	0.945	0.790	1.240	0.382	1.500
Pb [µg/l]	12.214	10.210	8.475	15.240	5.116	14.000
Ni [µg/l]	11.783	12.105	8.310	14.920	4.979	34.000
Cr [µg/l]	8.814	8.945	4.510	12.740	4.514	100.000

The distribution of the concentrations of most of the elements showed a pronounced gradient on the north – south direction, demonstrating the importance of the Danube's input. Also, most metals (Pb, Ni, Cr) presented some degree of enrichment around the port areas (Constanta, Mangalia), apparently the result of localized influences (sewage stations, port activities, naval traffic, etc.) (Fig. 3).

Numerous studies on biogeochemical processes and distribution of heavy metals in the Black Sea have demonstrated the importance of the supply of metals and nutrients of the Danube and other localized sources, together with the influence of the redox cycles of Mn and Fe complexes. For example, Cu and Ni were found in higher concentrations in the area of the Black Sea continental shelf than in the oxic layer of the deep-sea basin, reflecting the significant impact of the river and anthropogenic contributions on this semi-closed sea. High concentrations of dissolved lead observed in surface waters of the offshore area were attributed to atmospheric inputs combined with a less efficient capture of metals in these waters depleted in particulate matter (Tankere S.P.C., 2001).

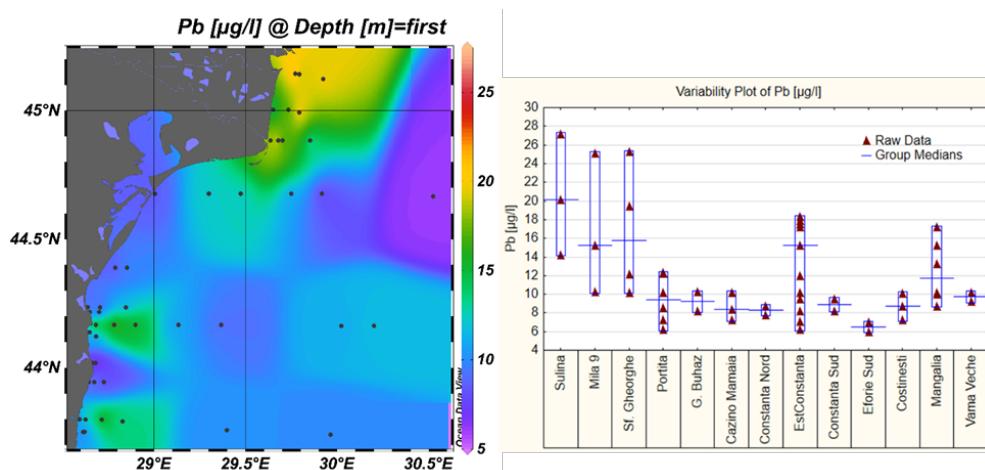


Fig. 3. Lead distribution in marine waters along the Romanian coastline in 2018.

The state of the marine waters in 2018, in relation to the quality standards for marine waters (EQS) (Directive 39/2013, Ord. 161/2006) was good, considering that the percentage of samples higher than EQS was below 25% of the total monitored water samples: Cu (1%) , Cd (15%), Ni and Cr (0%). The criterion for good ecological status (GES) was slightly exceeded in the case of Pb, where 32% of samples exceeding EQS (14 µg/L Pb) were noticed (Fig. 4).

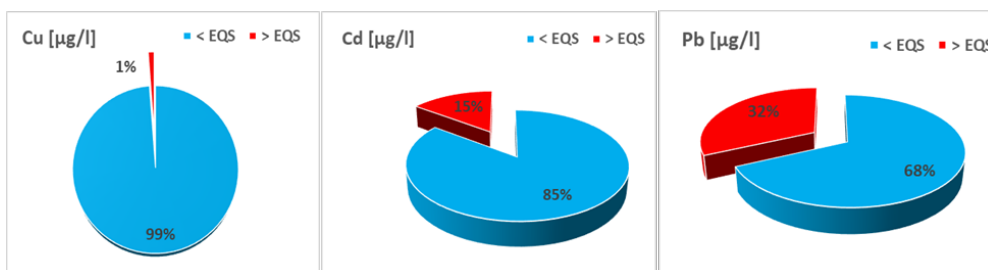


Fig. 4. Status of marine waters in 2018 relative to quality standards (EQS) for heavy metals.

Measurements of heavy metals only in marine water are not conclusive for assessing the state of the ecosystem, due to high variability, fluctuating inputs and low residency time. With a combined action of adsorption, hydrolysis and co-precipitation, only a small fraction of the free metal ions remains dissolved in water, while a large amount of them is deposited in sediment. However, when environmental conditions are changed, sediments can be transformed from heavy metal deposits into sources for the water column. Therefore, the content of heavy metals in sediment is monitored to provide vital information for environmental risk assessment (Zhuang W., Gao X., 2014).

The concentrations of heavy metals determined in 2018 in superficial marine sediments have been included in their vast majority in normal areas of variation, the average concentrations being the following: 24.57 ± 12.98 µg/g Cu; 0.25 ± 0.29 µg/g Cd; 10.43 ± 6.09 µg/g Pb; 72.10 ± 27.59 µg/g Ni; 23.92 ± 10.48 µg/g Cr (Tab. 8).

Table 8. Heavy metals concentrations in marine sediments in 2018

	Average	Median	Percentile – 25th	Percentile – 75th	Std.Dev.	EQS
Cu [µg/g]	24.571	24.425	13.690	33.040	12.987	40.000
Cd [µg/g]	0.251	0.160	0.061	0.325	0.298	1.200
Pb [µg/g]	10.431	9.705	4.810	14.710	6.092	47.000
Ni [µg/g]	72.102	70.805	50.195	90.745	27.594	35.000
Cr [µg/g]	23.921	25.310	11.870	33.140	10.481	81.000

Most of the investigated elements recorded higher accumulation values in sediments from higher depths (bathymetric strip 30 – 100 m), both in the north and in the south of the coastline. There were also noted accumulation trends in certain stations on the Portita transect, depths 20 – 30 m, for Cu, Pb and Ni, Casino Mamaia 30 m, for Pb and Ni, Costinesti 30 m for Cd and Ni, as well as in the vicinity of Constanta Port. Also, Ni, an element with great affinity for fine particles and the organic substance in the sediment, was found in high concentrations including in the sediments in front of the Danube, depths 5 – 30 m. Excluding the above mentioned situations, in coastal sediment (bathymetric strip between 5 – 30 m), moderate concentrations of heavy metals were recorded (Fig. 5).

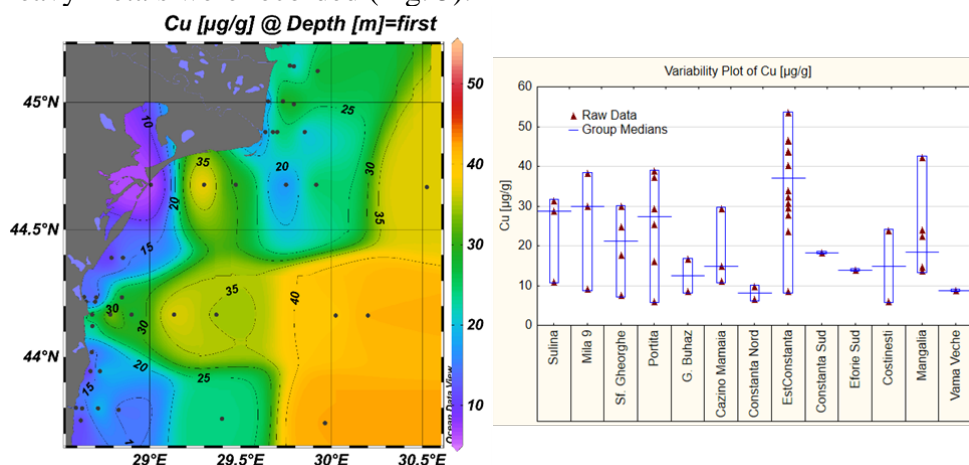


Fig. 5. Copper distribution in marine sediments along the Romanian coastline in 2018.

The status of marine sediments in 2018, in relation to quality standards for marine sediment (ERL) is good, considering that the percentage of EQS exceedances is located below 25% of the total samples of sediment monitored: Cu (15%), Cd (1%) Pb and Cr (0%). The criterion for Good Ecological Status (GES) is exceeded in the case of Ni, where most samples exceeded the EQS (35 μg/g Ni) (Fig. 6). However, in the case of nickel, it is considered that the background values could be naturally higher in the Black Sea sediments (Oros A, et al., 2016).

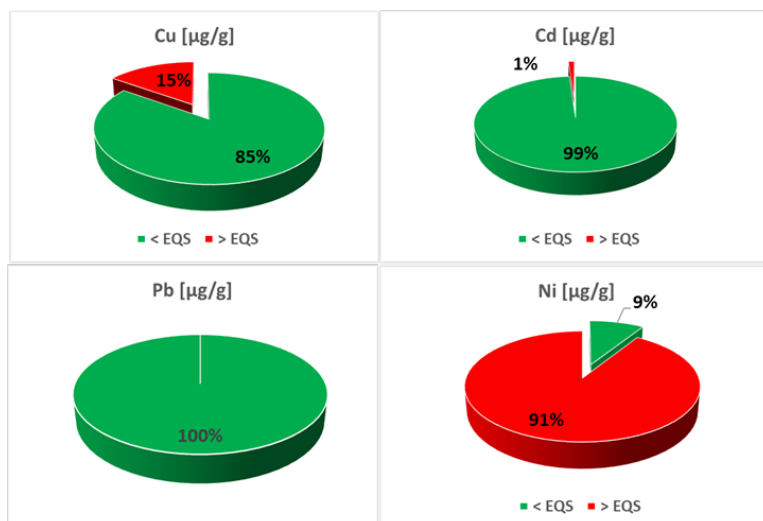


Fig. 6. Status of marine sediments in 2018 relative to environment quality standards (EQS) for heavy metals.

In relation to the permissible levels for contaminants in marine mollusks (EC Regulation No. 1881/2006), cadmium and lead concentrations were below the threshold value in the three species of mollusks which were investigated in 2018. An overtake of the regulated value for the Cd was noted at *Rapana*, but it is explicable considering that the total tissue (muscle and viscera) has been analyzed.

The results of investigations carried out in 2018 on heavy metals in water, sediment and biota demonstrate distribution differences between different sectors of the Romanian coastline, reflecting the potential impact of natural or anthropogenic pressures, generated by coastal or offshore sources and activities.

The evolution of the average annual concentrations of heavy metals in marine water in the period 2006 – 2018 demonstrates slight stability trends and maintenance between similar variability ranges for Cu and Cd, but also some increasing trends in 2018 for Pb, and Cr compared to previous years. In sediment, the evolution of the average annual concentrations of heavy metals in the period 2006 – 2018 demonstrates maintaining in similar areas of variability, even with slight decrease trends for Cu, Cd and Pb in 2018, compared to previous years (Fig. 7, Fig. 8).

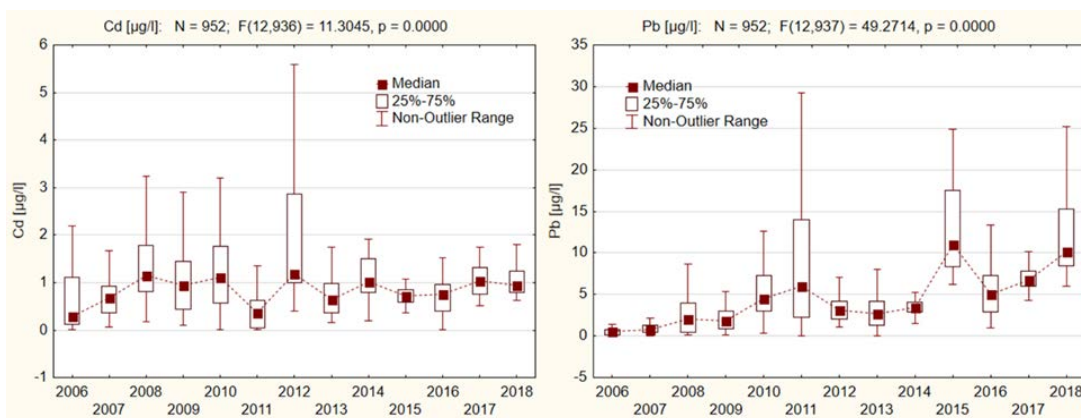


Fig. 7. Trends in the evolution of the heavy metals concentrations during 2006 – 2018 in marine waters.

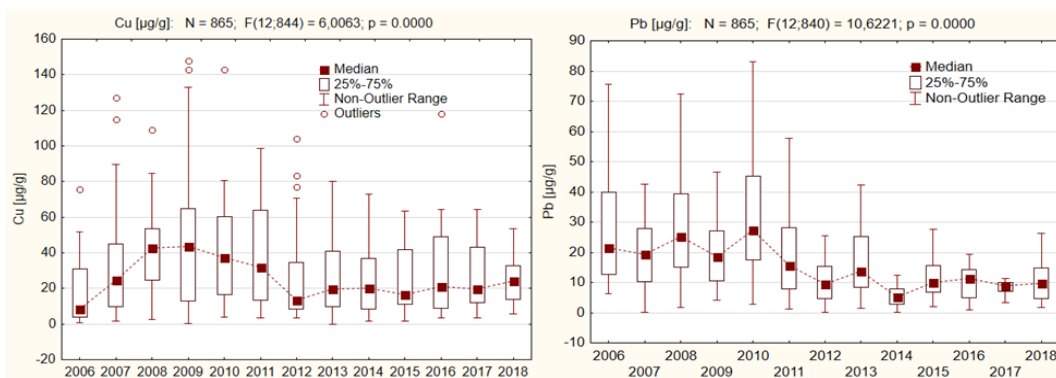


Fig. 8. Trends in the evolution of the heavy metals concentrations during 2006 – 2018 in sediments.

CONCLUSIONS

The distribution of heavy metals in the components of the marine Black Sea ecosystem highlights the differences between different areas of the coastline, generally observing slightly increased concentrations in the marine area under the influence of the Danube, but also in the southern sector in certain areas subjected to various anthropogenic pressures (ports, waste water discharges). The concentrations of most heavy metals in water, sediment and biota have generally been within the limits of multiannual average values, although some decreasing or, in other cases, increasing, have been noted for certain elements and matrices.

The information resulting from investigations into the presence of heavy metals provides a basis for characterization of Romanian marine

ecosystems in terms of heavy metal pollution levels. Although the research of the last years has shown timid/slight signs of restoring of the quality of the marine ecosystem, no firm conclusions can be drawn yet. It is necessary to study more in-depth the extent to which pollution has affected the marine environment, the degree of reversibility of the changes produced and the mode of response of the ecosystem to the reduction of anthropogenic pressure.

Information was gathered and analyzed in order to evaluate current status and to identify existing gaps, for a better understanding on where efforts should be focused further to improve knowledge in the field of marine pollution. Nevertheless, the results provided here could be a good starting point to evaluate the current situation, to suggest some improvements for contaminants monitoring and support further work on implementing MSFD, Descriptors 8 and 9.

With respect to Descriptor 8, criteria D8C1, the program is fully adequate for data/information collection to assess the distance to GES, as it is defined at present. More research is needed dedicated to: methods to study hazardous substances combined effect on organisms and the ecosystem; new elements and hazardous substances to be included in monitoring surveys; new biota matrices (highly mobile species - fish, mammals, birds) have to be included in the program for a better understanding of the effects at the higher levels of the food-web; development of new sampling and observation techniques (passive sampling, in situ voltammetry, satellite images, etc.); new modeling techniques (e.g. biogeochemical modeling, bioaccumulation modeling, etc.) to be developed; tools for the integrative assessment of contaminants status need to be implemented (e.g. CHASE) (Andersen et al., 2016).

As for Descriptor 9, criteria D9C1, the program is also considered to be adequate in terms of providing data and information needed to assess GES. Presently, the program provides quite enough data for assessing GES, but some improvements have to be made so that the program could be considered fully adequate for giving a more robust GES assessment. More data/information is needed either in terms of additional determinants (As, Hg, etc.) or matrix (more commercial fish species– to be selected more species target). Also, the program has to be improved in terms of data collection. The concentrations below the regulatory levels are not necessarily indicators of good environmental status, since environmental effects might be present at lower concentrations. In this respect, the MSFD – Task Group 9 recommends aggregation between descriptors 8 and 9 for more robust GES definition. The program has to be developed for more data/information acquisition (data regarding the number of contaminants for which exceeding levels have been detected in parallel, origin of the contamination, etc.) or increased knowledge

(e.g. possible relations between contaminants in water/sediment and biota, new analytical procedures, improved QA/QC, etc.).

At European level, MSFD Expert Network on Contaminants, an informal network established by the Joint Research Centre (JRC) to support the MSFD implementation, works towards comparable MSFD Descriptor 8 and 9 assessments, compiling information related to substances, matrices and threshold values/reference levels (Tornero et al., 2019), aiming at equal levels of protection across European Seas. This is part of a process to help regulators to assess relevant contaminants in their jurisdictional area, thus aiming at EU national authorities but also at Regional Sea Conventions in the shared marine regions.

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