

Pressures from land-based sources at Romanian Black Sea regarding eutrophication and contaminants

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ABSTRACT. The aim of the study was to identify the main land-based pressures at the Romanian Black Sea littoral by applying the DPSIR methodology to analyze them for the development of pressures indicators for eutrophication and contaminants. Thus, in addition to the major pressure exerted by the Danube, the main anthropogenic pressures identified in the Romanian coastal zone come from the development of many socio-economic activities in the area. The main sources of pollution are concentrated in the central-southern part of the littoral, an area where the main urban agglomerations and the related municipal and industrial activities are located. The comparative analysis of the Danube and other land-based sources (hot spots) flows shows that the aggregate flows of the municipal and industrial sources represent 0.04% of the total discharged in the Black Sea while the Danube flow, 99.96%. However, due to significantly different emissions and concentrations it is very important to quantify the local effect of the municipal and industrial sources on the Romanian coastal area. In the neighborhood of the land-based sources there is a risk of not achieving good environmental status (GES) for eutrophication and contaminants due to the pressures from ports (Midia, ConstanțaSud, Mangalia), wastewater discharges in the shallow waters (GuraBuhaz, EforieSud) and in the marine area in front of the Danube’s mouths (Sulina, Mila 9, Sf. Gheorghe). Increased bioaccumulation was usually observed in the areas under the anthropogenic impact.

KEYWORDS. marine pollution; anthropogenic impact; bioaccumulation.

I. INTRODUCTION

The marine ecosystem is extremely complex, with many-sided processes between its physical, chemical and biological features. The majority of human activities exerts pressures and the cumulative effects fluctuate based on their intensity, number and spatial and temporal distribution. Hence, the anthropogenic contribution of the Romanian Black Sea’s coastal zone, through the dynamics of the permanent (industrial, municipal, etc.), temporary (beaches rehabilitation, etc.) or seasonal (tourism which recorded in the summer season 2016 a 12% increasing comparing to 2015) brings major importance. Therefore, the pollution of the Black Sea’s Romanian littoral from land-based sources represents one the biggest threatens on its healthy. The risk to not achieve and maintain the good environmental status is, mostly, an elusive goal in the coastal zone, particularly near urban agglomerations and mouths of rivers. The regional and local efforts contributed to the quality improvement of the Black Sea waters affected by eutrophication in ’80s. Among these, are the Convention for the Protection of the Black Sea Against pollution (Bucharest, 1992) and European legislation - Water Framework Directive (2000/60/EEC), Shellfish Directive (79/923/EEC), Bathing Water Directive

(76/160/EEC), Nitrates Directive (91/676/EEC), Priority Substances Directive (76/464/EEC), Urban Wastewater Treatment Directive (91/271/EEC), Habitats Directive (92/43/EEC), Industrial Emissions Directive (2010/75/UE). All efforts to protect the marine environment are fully in line with the objectives of the Marine Strategy Framework Directive 2008/56/CE (MSFD), to adopt the essential measures to achieve or maintain the good status of the marine environment (GES) by 2020 at the latest. The strategy has a very ambitious goal of achieving good environmental status (GES) in European marine waters by 2020. MSFD is based on the concept of good environmental status, which involves both the protection of the marine environment and its rehabilitation, along with the sustainable use of marine resources. The monitoring and assessment of the status of the marine ecosystem must be based on the environmental indicators based on the reference level and the environmental objectives set and established on the basis of a good knowledge of the relationship between the state of the environment and the anthropic pressures.

II. METHODS

The study was done based on DPSIR analysis for pressures and impacts regarding eutrophication and contaminants according to Annex III (Table 2) from Marine Strategy Framework Directive. The analysis starts with drivers (human activities, economic sectors, population increasing/decreasing) which produce and may enhance pressures (nutrients and contaminants emissions) on the marine ecosystem. Therefore, the status of the environment (physical, chemical and biological features) is changing due to negative impact (changes of benthic habitats, oxygen deficiency, reduced transparency, biological effects) which requires an adequate response to establish the response in the form of measures to reduce adverse effects.

The scope of the study is the inventory of the main land-based sources from the Black Sea's Romanian littoral and their analysis to develop pressures indicators regarding eutrophication, hazardous substances and hydrocarbons for the MSFD implementation. The achievement of the scope was done using NIMRD data from the national monitoring program, national and international projects, data from Romanian Water Administration Dobrogea Littoral, literature and from the National Institute of Statistics and the International Commission for the Protection of the Danube River (ICPDR). These data are the base of environment quality regarding the marine space important also for Marine Spatial Planning data base preparing, including also in MARSPLAN BS Project.

III. RESULTS AND DISCUSSION

The entire Romanian littoral is subject of land-based sources of pollution. Thus, in the Northern part, the main comes from the Danube River which basin covers about 10% of the continent. With a length of 2780 km, catchment area of over 801,463 km² and annual average flow of about 6500 m³/s, the Danube, after the Volga, is the second longest river in Europe. 97.4% of Romania is located in the Danube river basin, which represents 29% of the Danube basin being the country with the largest area in the Danube Basin. Also, 37.7% of the length of the Danube is in Romania. Due to the physico-geographical distribution and character of the hydrological regime, the Danube is divided into three sections: the upper Danube (source - Vienna), the middle Danube (Vienna - Iron Gates) and the lower Danube (Iron Gates - Black Sea). The inferior lower Danube forms the border state with Serbia and Bulgaria to Romania. The lower Danube is characterized by a highly complex consisting of several sectors with specific characters. Important tributaries of the Danube are represented by Balkan rivers Timok, Lom, Ogosta, Iscar, Vit, Osam and Yantra on the right shore and Jiu, Olt, Vedea and Arges, Siret and Prut, on the left one. The Danube River is characterized by a high degree of

planning, due to hydraulic works carried out, due to land use for which they were created. The most important uses of the Danube are: power generation, agriculture (irrigation), navigation, urbanization, etc. All these uses are making as inevitable, the Danube as a natural receptor of pollutants.

Based on NASA, EOSDIS Worldwide web-site (<https://worldview.earthdata.nasa.gov>) in 16th of June 2017, On the Black Sea coast could be stressed the next image of pressures from the terrestrial part of the coast to the sea (Fig.1).

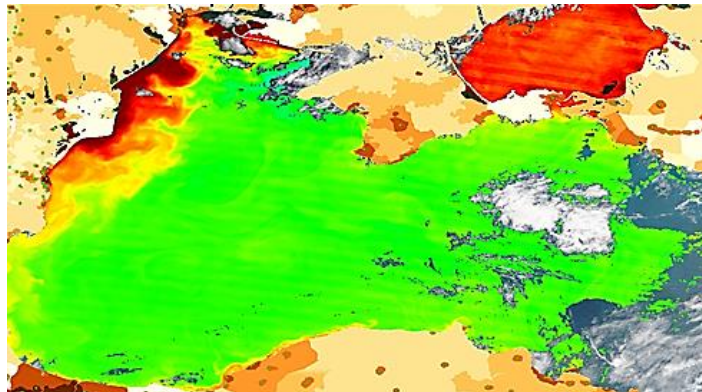


Fig. 1. Pressures from land to sea in the Black Sea (<https://worldview.earthdata.nasa.gov>)

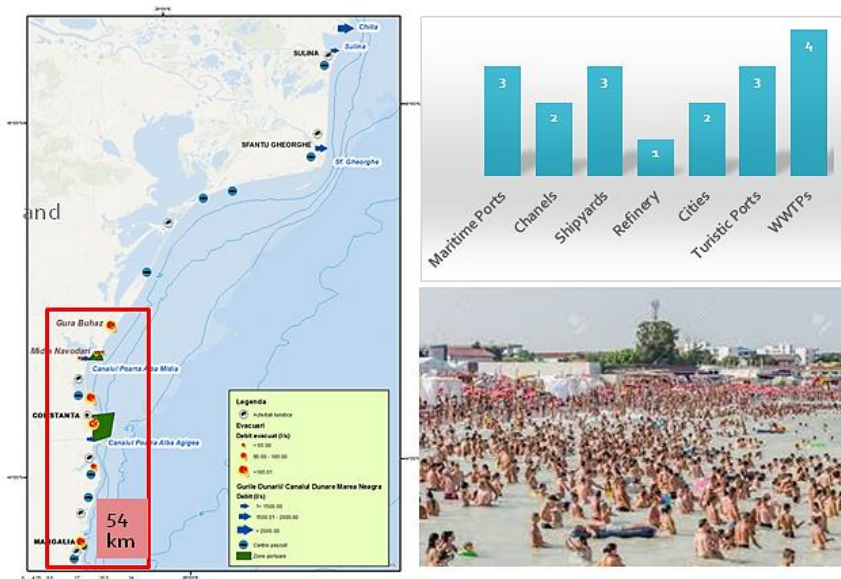


Fig. 2. Main sources of pollution of the Romanian Black Sea coast

Having more than 40 years of marine monitoring NIMRD can have on long-term and annually a general inventory on the whole marine network of 44 sampling station. Last years it shown that the main pressures from the coast to the sea (with worrying influence) are due to human activities (anthropogenous impact) and high demography during the summer season (Fig.2)

The DPSIR Analysis for the main pressures evaluation underlined drivers, pressures, state, impact, responses and the link between them (Fig.3).

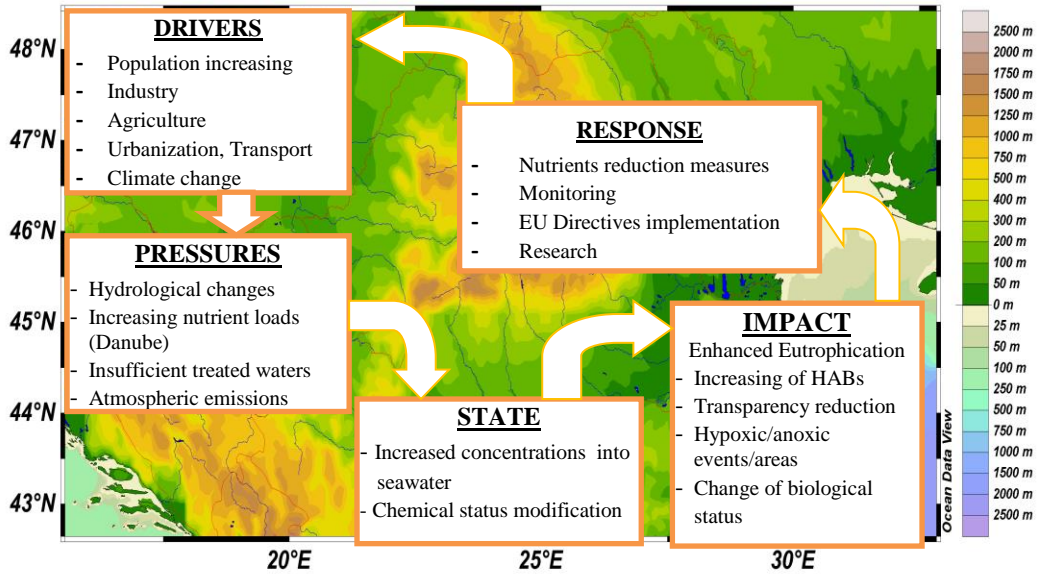


Fig. 3. The cycle of main pressures impact in the coastal-marine waters of Romania

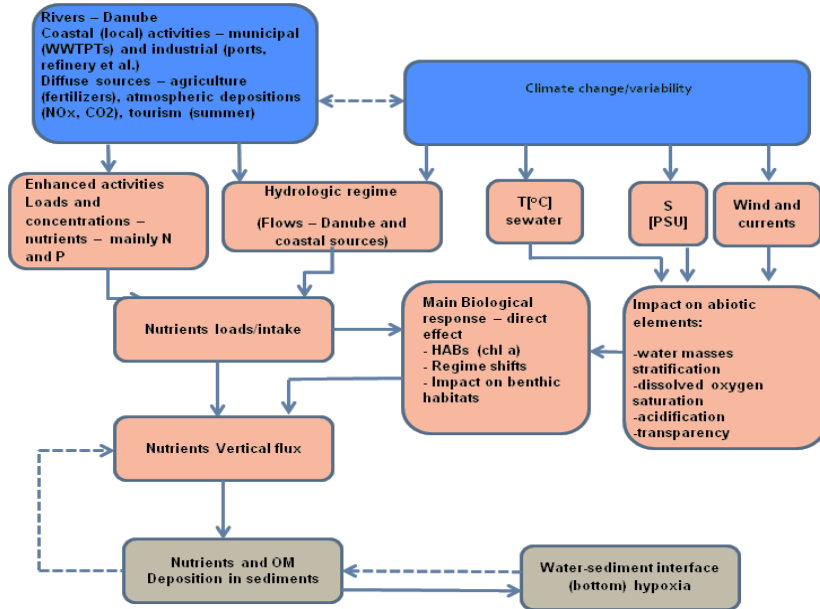


Fig. 4. The INTERACTIONS MODEL for climate affect on marine ecosystem components.

The INTERACTIONS MODEL (after Doney et al., 2012) is based on the local (coastal) overlapping of the anthropogenic and global pressures manifested by enhanced variability of the climate might affect on different pathways the functioning of the marine ecosystem's components (abiotic and biotic) at the Romanian littoral. (Fig.4).

In this context, the **Drivers** (represented by *Population increasing, Industry, Agriculture, Urbanization, Transport, Climate change*, etc.) have been evaluated as Diffuse and Point sources, according to ICPDR reports 2009-2012 –*Danube - main pathways of the nutrients*, and have been registered the following proportions (Fig.5).

Fig. 5. The main sources of pressures percentages at the Romanian Black Sea coast



- **diffuse sources** (TN – 84%; TP – 67%) - agriculture (N: 25%, P: 51%) and sewage (N: 42%, P: 28%)
- **point sources**– untreated waters (28%TN, 39%TP) from total.

By NIMRD “G.Antipa” own results (available data) the **Drivers** results shown like the next graphs (Fig.6 and 7)

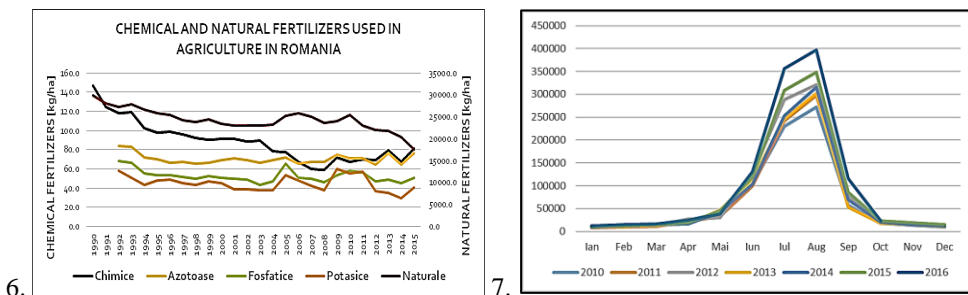


Fig. 6. Chemical fertilizers used in agriculture Fig. 7. Tourists in Constanta county, monthly averages, 2010-2016

The **Pressures** have been mainly represented by *Hydrological changes, Increasing nutrient loads of Danube, Insufficient treated waters, Atmospheric emissions.*

- The correlations between Danube's loads, kt/year (y) and seawater concentrations, μM (x), as annual means 2000-2014, are presented (Fig.8-11)

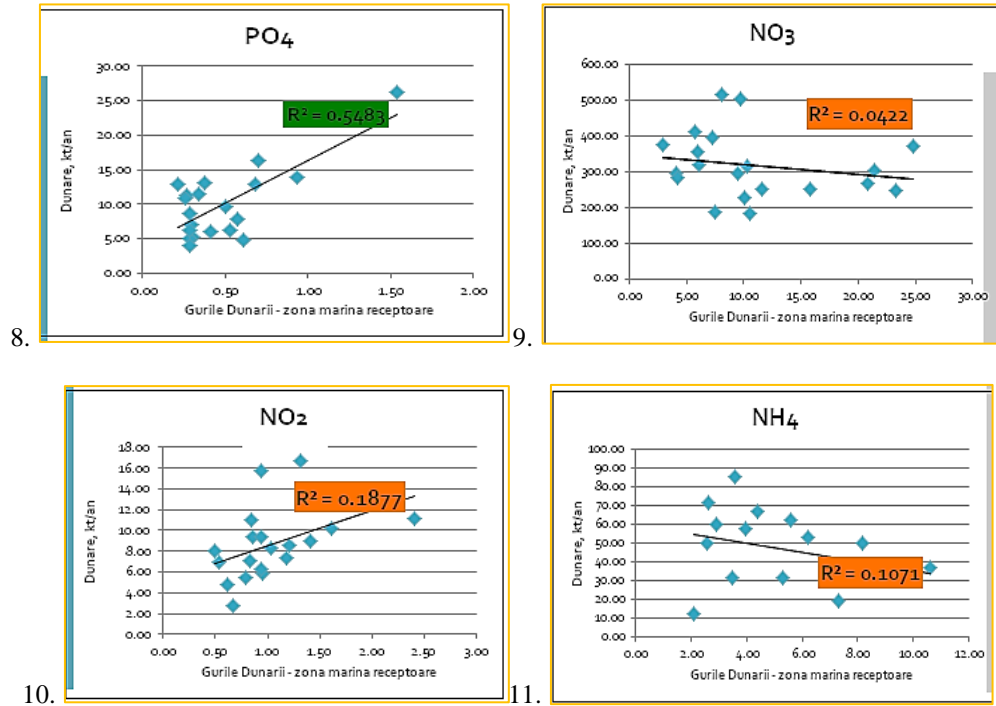
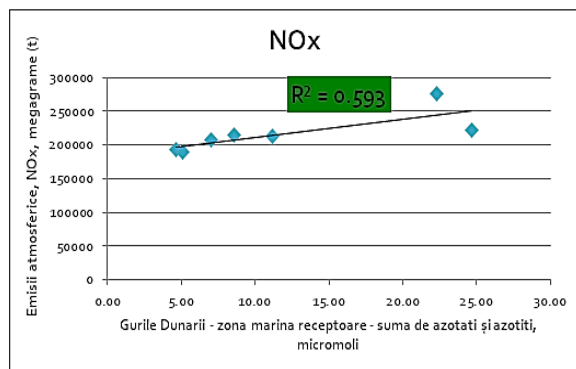


Fig. 8-11. Main Phosphates, Nitrates, Nitrites, Ammonium concentration in front of Danube Mouths

- The correlations between atmospheric emissions $\text{NO}_x(k)$ (y) and NO_x concentrations in seawater μM , 2008-2014 is also shown in the Fig. 12.



- Most continental Europe is confronted with overcoming critical levels for eutrophication.
- It is estimated that about 63% of the European ecosystems and 73% of the Natura 2000 network areas have been exposed to air pollution levels that exceed the eutrophication limits in 2010, the year of hypoxia with fish mortality at the Romanian seaside.

Fig. 12. Summ of Nitrogen compounds from the Danube Mouths

- The projections for 2020 indicate that exposure to eutrophication will remain widespread (EEA, 2016).

- The correlations between atmospheric emissions CO₂(kt) (y) and seawater Phytoplankton Biomass, mg/m³ (x), annual means, 1996-2008, is reflected in the next Fig.13.

According these, where evaluated the main pressures for the Romanian coast sectors. In front of Danube Delta marine side. the main registered pressures have been (Fig. 14.15)

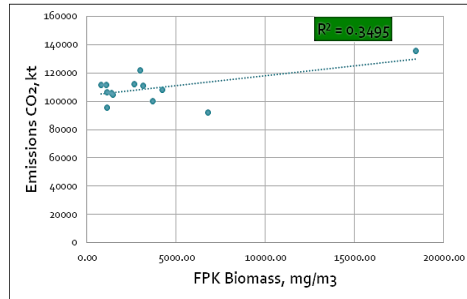


Fig. 13. The Phytoplankton Biomass correlated with CO₂ Emissions

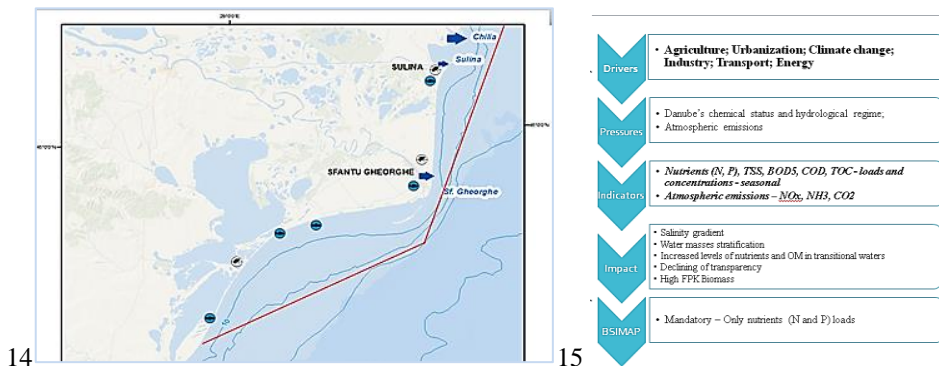


Fig. 14,15. The main pressures identified in the marine front of Danube Delta

The same variables were underlined in front of the central and southern parts of the Romanian coast. (Fig.16, 17)

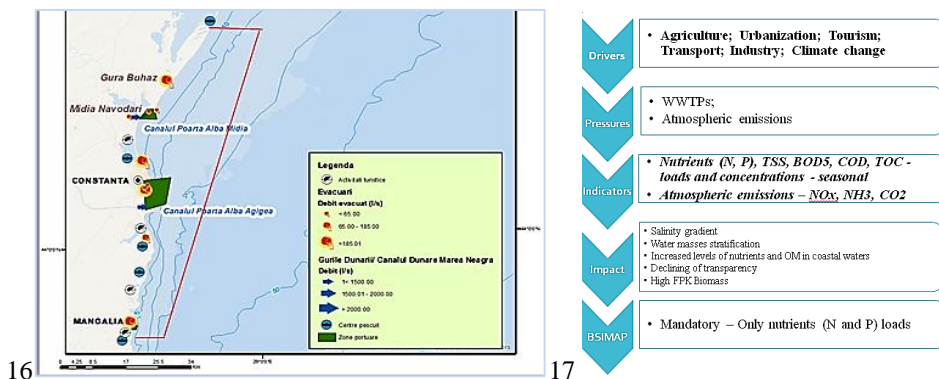
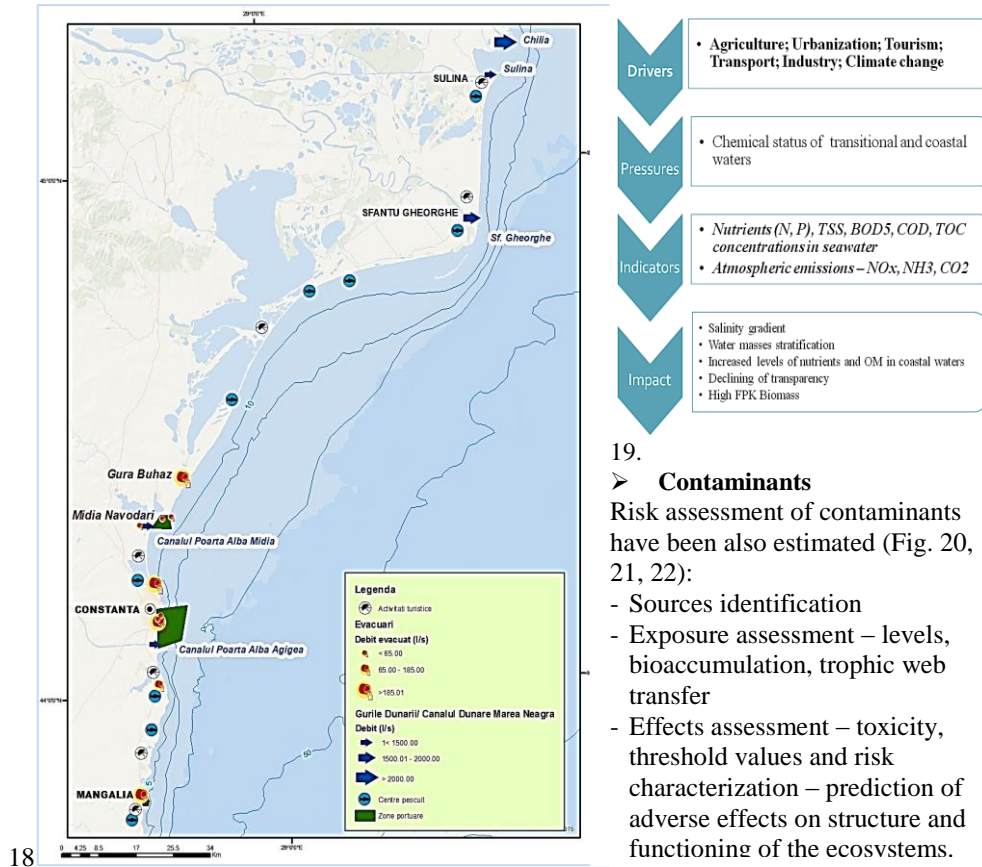


Fig. 16,17. The main pressures identified in the marine front of central and southern coast

These both delineation could give the real image of the whole pressures impact of the coastal areas, terrestrial waters outflow and emissions. Fig. 18, 19



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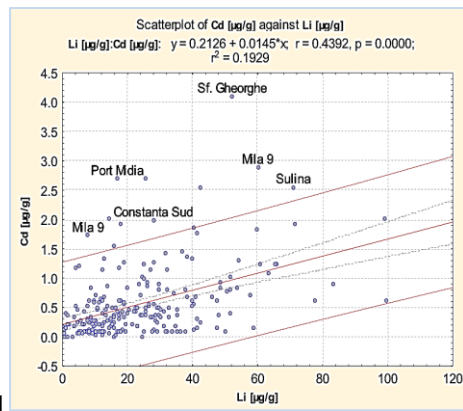
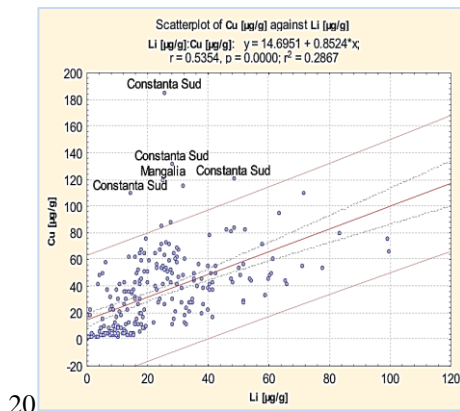
➤ **Contaminants**

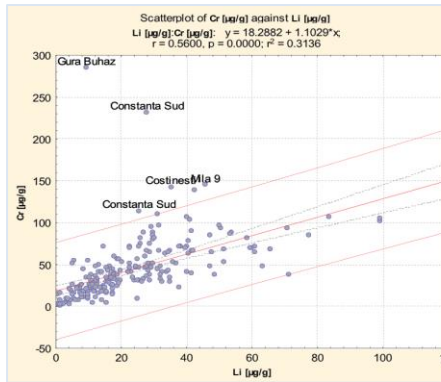
Risk assessment of contaminants have been also estimated (Fig. 20, 21, 22):

- Sources identification
- Exposure assessment – levels, bioaccumulation, trophic web transfer
- Effects assessment – toxicity, threshold values and risk characterization – prediction of adverse effects on structure and functioning of the ecosystems.

Fig. 18,19. The main pressures identified in the marine front of whole Romanian coast (Alina Spinu maps)

➤ **Sources and levels of sediments contamination were:**





Using diagrams Li/Cu, Li/Cr, Li/Cd it was assessed the levels of heavy metals enrichment of sediments along the Romanian littoral.

Contaminated sediments – ports (Midia, Constanța Sud, Midia), shallow waters nearby WWTPs (Gura Buhaz, Eforie Sud) and Danube’s mouths (Sulina, Mila 9, Sf. Gheorghe)

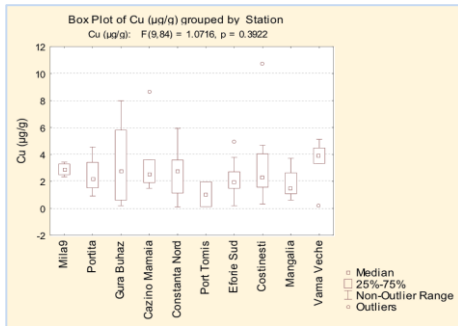
Fig. 20.21.22. The level of heavy metals from sediments along the Romanian littoral

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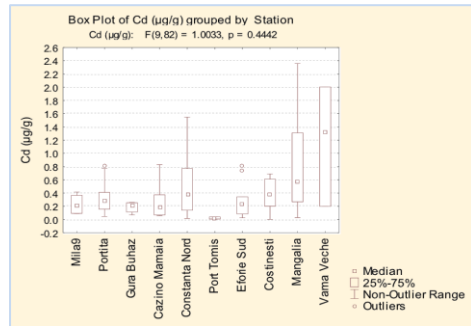
➤ **Bioaccumulation**

Long-term data (2002 – 2011) on heavy metals in *Mytilus galloprovincialis* revealed increased bioaccumulation approximately in the same areas Gura Buhaz (Cu, Ni), Constanța Nord (Cu, Cd, Pb), Eforie Sud (Ni, Cr), Mangalia (Cd, Pb), correlated with water and sediments concentrations. Fig. 23, 24, 25, 26.

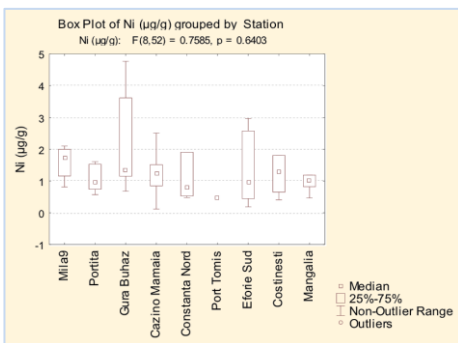
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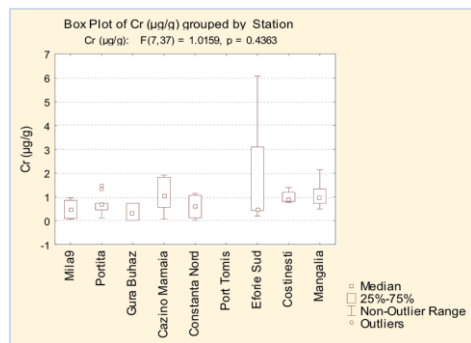
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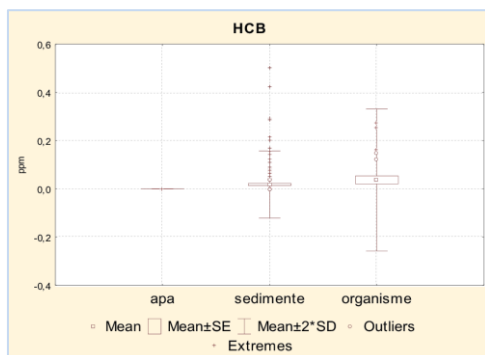
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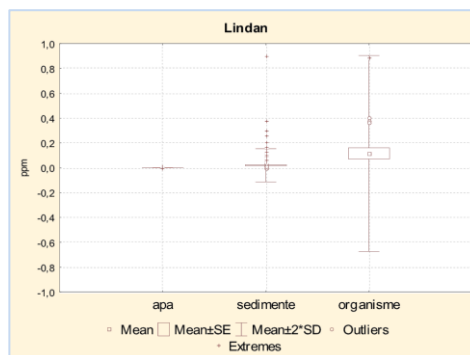
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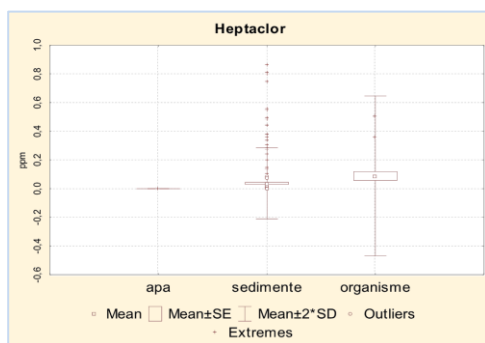
- **Pesticides.** Enhanced bioconcentration for HCB, lindane, heptaclor and DDT are presented (Fig. 27, 28, 29).



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29.

➤ **Biological Effect of Pollution**

- Biological effects are better assessed through biomarker analysis in sentinel organisms.
- Biomarkers are useful tools for the marine environment toxicity assessment. Some of the are included in the RSCs monitoring programs (OSPAR; MED POL, UNEP) (Lam and Gray, 2003; Viarengo et al., 2007).

- In Romania were done some investigations on general biomarkers - lysosomal membrane stability (Ciocan C, 1996-1997, Ciocan C, 2002) and oxidative enzymes (Coatu ș.a, 2001; Coatu ș.a, 2002; Coatu V. și Artenie V., 2002).
- Even we obtained few data there are no specific studies on biomarkers like metalothioneins, vitelogenin or glutathion transferase.

At the end, we have to mention that at the Romanian Black Sea coast there are as main sources of pollution the area from the Danube Branches front; Municipal sources related the Waste Waters Treatment Plants (WWTP): Constanta Nord (completely resported), WWTP ConstanțaSud (municipal and industrial), WWTP EforieSud, WWTP Mangalia; Industrial sources: RompetrolRafinare, Constanta Port, Midia Port, Mangalia Port; tourism areas during summer season: main Romanian resorts, Sulina, Sf. Gheorghe, Mamaia, Constanta, both Eforie, Olimp, Neptun, Aurora, Saturn, Mangalia, 2 Mai - VamaVeche.

IV. CONCLUSIONS

This paper presents the main evaluation regarding the transitional and marine waters pressures and quality.

In addition to the major pressure exerted by the Danube, the main anthropogenic pressures identified in the Romanian coastal zone come from the deepening of the various socio-economic

activities in the natural area of the coastal zone: agriculture and food industry, petrochemical industry, refineries, tourism and recreation, construction / holiday home districts in tourist areas, extension and modernization of existing tourist ports, ports and port activities (shipyards, warehousing, grain silos, oil and LPG terminals, etc.) and navigation.

The main sources of pollution are concentrated in the central-southern area of the Black Sea Romanian seaside, an area containing the main urban agglomerations and related industrial activities, along about 54 km, where has been developed a wide range of permanent economic activities.

Nearby the land based sources of pollution there is a risk of not achieving GES for nutrients and contaminants due to the higher values in the Danube mouths receiving area and the extremes permanently recorded in Constanta Sud station 5m and seasonally and punctually in the stations adjacent to the discharge areas of Eforie and Mangalia WWTPs.

Evidences of point sources and bioaccumulation of heavy metals and some pesticides in sediments and biota were found – initiating the biomonitoring program based on biomarkers.

All of these information are spatially represented, being extremely important for water quality improvement, pressures and pollution mitigation, attenuation, bio-potential preserving and recovery, sustainable development of the main maritime activities and uses.

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