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Black Sea
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Anthropogenic pressures and impacts on the Black Sea coastal ecosystem

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EDITURA CD PRESS
www.cdpress.ro

BUCUREȘTI, 2021

Descrierea CIP a Bibliotecii Naţionale a României
Anthropogenic pressures and impacts on the Black Sea coastal ecosystem / Luminiţa Lazăr, Laura Boicenco, Yuriy Denga, ... –
Bucureşti : CD Press, 2021
ISBN 978-606-528-529-3

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This document is based on the activities of the ANEMONE project (Assessing the vulnerability of the Black Sea marine ecosystem to human pressures) with the financial support from the Joint Operational Programme Black Sea Basin 2014-2020.

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For bibliographic purposes, this document should be cited as:

ANEMONE Deliverable 2.1, 2021. “Anthropogenic pressures and impacts on the Black Sea coastal ecosystem”, Lazăr L. [Eds], Ed. CD PRESS, 167 pp.

ISBN 978-606-528-529-3

Cover page design by new7ducks/ Freepik. Cover page photo by NIMRD.

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Acronyms

AAS-ET	atomic absorption spectrometry
AMBI	AZTI Marine Biotic Index
ANEMONE	Assessing the vulnerability of the Black Sea marine ecosystem to human pressures
BEAST	Black Sea Eutrophication Assessment Tool
BOD	Biological Oxygen Demand
BS	Black Sea
BSIMAP	Black Sea Integrated Monitoring and Assessment Programme
CHASE	Contaminants Status Assessment Tool
CIS	Cooled Injection System
COD	Chemical Oxygen Demand
CR	contamination ratio
CTD	Instrument for measuring conductivity, temperature, and depth
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DIN	Dissolved Inorganic Nitrogen
DMA	Direct Mercury Analyzer
DO	Dissolved oxygen
EAC	Environmental Assessment Criteria
EBM	Ecosystem-Based Management
EC	European Commission
ECD	Electron capture detector
EEA	European Environmental Agency
EF	enrichment factors
EI	electron ionization
EPA	Environmental Protection Agency
EQS	Environmental Quality Standard
ERL	Effect Range Low
ERM	Effect Range Medium
EU	European Union
EUR	European
EUT_Ratio	eutrophication ratio
GC-ECD	Gas chromatography with an electron-capture detector
GC-MS	Gas Chromatography - Spectrometry
GC-MSMS	Gas Chromatography - Tandem Mass Spectrometry
GES	Good Environmental Status
GF-AAS	Graphite furnace – atomic absorption spectrometry method
HAB	Harmful Algal Blooms
HCH	Hexachlorocyclohexane
HEAT	HELCOM Eutrophication Assessment Tool
HELCOM	The Baltic Marine Environment Protection Commission
HF	hydrogen fluoride
IAEA	International Atomic Energy Agency
ICES	The International Council for the Exploration of the Sea
ICPMS	inductively Coupled Plasma Mass Spectroscopy
IOC	International Oceanographic Commission
JRC	Joint Research Center
KED	Kinetic Energy Discrimination

LAT	Latitude
LBS	Land Based Sources
LONG	Longitude
LPG	Liquefied petroleum gas
MAC	Maximum allowable concentration
MISIS	MSFD Guiding Improvements in the Black Sea Integrated Monitoring System
MPS	MultiPurpose Sampler
MSFD	Marine Strategy Framework Directive
ND	Not Detected
NEAT	Nested Environmental Status Assessment Tool
NIMRD	National Institute for Marine Research and Development "Grigore Antipa", Romania
NIVA	Norwegian Institute for Water Research
NMDS	Non-metric multidimensional scaling
NOAA	National Oceanic and Atmospheric Administration
NPMS	National Preventive Mechanisms
NW	Northwest
OECD	Organisation for Economic Co-operation and Development
OHI	Ocean Health Index
OOAO	One-Out-All-Out-principle
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic (the 'OSPAR Convention')
PAH	Polyaromatic hydrocarbons
PCB	Polychlorinated biphenyls
PLE	accelerated pressure extraction
POP	Persistent Organic Pollutants
PRIMER	Plymouth Routines in Multivariate Ecological Research - software
PSU	Practical Salinity Units
PTFE	Polytetrafluoroethylene
PTV	Programmable temperature vaporizing inlet
RO	Romania
SAU	Spatial Assessment Unit
SD	Standard deviation
SDD	Secchi disk depth
SE	Standard error
SIMPER	Similarity Percentage analysis
SNU-FF	Sinop University Fisheries Faculty
TBT	Tributyltin
TDS	Thermal Desorption System
TDU	Thermal Desorption Unit
TM	Trace metals
TN	Total Nitrogen
TOC	Total organic carbon
TP	Total Phosphorus
TPH	Total Petroleum Hydrocarbons
TR	Turkey
TRIX	Trophic Index
TSS	Total suspended solids
TUBI	Turkish Benthic index
TÜBİTAK	Scientific and Technological Research Council of Turkey (Turkish: Türkiye Bilimsel ve Teknolojik Araştırma Kurumu, TÜBİTAK)
TÜBİTAK-MRC	Scientific and Technological Research Council of Turkey - Marmara Research Center
TUDAV	Turkish Marine Research Foundation
UA	Ukraine
UM	Unit of Measure
UNEP MAP	United Nations Environment Programme / Mediterranean Action Plan
UNESCO	United Nations Educational, Scientific and Cultural Organization
US	United States of America
USA	United States of America
UV-VIS	Ultraviolet–visible spectroscopy
UWWTD	Urban Wastewater Treatment Directive
WC	Water Column
WFD	Water Framework Directive
WORMS	World Register of Marine Species
WWTP	Wastewater Treatment Plant

Executive summary

Large and growing human populations on the coastal fringe of all continents is the most important pressure on coastal ecosystems, particularly to the human activities generating wastes, including sewage, to coastal waters (Koop & Hutchings, 1996). Degradation of marine and coastal ecosystems can be seen in the Baltic, Black and Mediterranean Seas and the North-East Atlantic and even Arctic Oceans. Effects on the environment are a consequence of meeting our immediate human needs. However, they impact species and habitats that have evolved over thousands, if not millions, of years — sometimes irreversibly. These impacts are related to the high and increasing population densities along Europe's coasts, fishing, agricultural and industrial chemical pollution, tourism developments, shipping, renewable energy infrastructures and other maritime activities. Although Europe's seas are productive, they cannot be considered healthy, clean, or undisturbed[1]. Effects on the marine environment from discharges may take many years or even decades to become manifest (Koop & Hutchings, 1996).

The coastal zone of the Black Sea riparian countries represents an extremely complex social-ecological system, which is developing and functioning under the pressure of interdependent political, social, environmental, economic, cultural, governance, and other factors. The economic activities directly connected to the Black Sea comprised the following key sectors: shipping and ports, fishery, tourism, and oil&gas related activities. There is a quite intense expansion of urbanized areas and related infrastructures in all Black Sea countries. Thus, the built-up areas almost doubled within the 10 km strip buffer zone located along the Black Sea coastline in the period 1992-2014. Urban expansion towards and along the coast mainly adjusted to big cities is of 4 % coastal area in Georgia and up to 12 % in Turkey[2], urbanization becoming an important pressure on the coastal zone.

The social and economic conditions of the riparian states are not homogeneous: Bulgaria and Romania are EU member states, Turkey is negotiating its accession to the EU, the Russian Federation is implementing its social-economic policy, Georgia and Ukraine have declared an intention to the accession to the EU. However, all the riparian states make a significant investment in the enhancement of economic growth rates to improve the quality of life of their population (Papava V., 2010). Economic and other kinds of human activities in the coastal region kept pressure during 2009-2014 on the marine and coastal environment ongoing. Natural features of the region have increased and the effect of this pressure.

The Black Sea is practically landlocked because has a very narrow connection with the ocean and restricted opportunity to exchange marine waters with the World Ocean. These circumstances make the region especially vulnerable and sensitive to influence different natural and economic pressures. The state of the natural component of the coastal zone of the Black Sea indicates that both terrestrial and marine ecosystems are suffering from massive anthropogenic influence (UNDOC) caused by different sectors of economic activities. In this regard, the shelf area of the North-Western part of the Sea is an area of significant impact.

In general, the quality of coastal water is far away from the natural level due to the bad management and bays, golfs and harbour area of large cities in particular (e.g., Constanta, Odesa, Sebastopol, Novorossiysk, Poti, Batumi, Trabzon, Istanbul, Varna, etc.) are the most polluted areas in the Black Sea (UNDOC).

Severe degradation of the marine ecosystem has started in the ’80s and still ongoing despite undertaken efforts of the Black Sea countries and the international community. Basic critical factors affecting the marine environment in the region, which were typical for the late decades of the 20th century are still in place. They comprise but not restricted to extensive use of terrestrial and marine resources. In the Black Sea catchment, land and water are used for intensive agriculture, forests for the paper industry, and construction, rivers and the sea for navigation and commercial fishing, coastal resources for tourism, energy generation, transport infrastructure, construction and other industries. To meet increasing demands for oil and gas, coastal and marine areas used for pipelines construction. As a result, natural landscapes are deteriorated and gradually replacing by anthropogenic landscapes.

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[1] https://www.eea.europa.eu/themes/water/europes-seas-and-coasts/europes-seas-and-coasts/#environmental-challenges

[2] http://www.blacksea-commission.org/The%20Black%20Sea/Socio-Economy/

Another problem is the water quality. River's run-offs, oil and gas extraction activities, atmospheric deposition, intentional and accidental discharge from vessels are the main sources of pollution. Rivers flows are polluted by agriculture, industries, communal wastewaters, transport and other sectors located in the Sea basin. Over 300 rivers running into the BS drain almost half of Europe and significant parts of Eurasia. The main rivers are the Danube, Dnieper, and Don, which are the second, the third and the fourth major European rivers.

The estimated maximum annual river discharge entering the Black Sea and Azov Sea is of 480 km^3. Polluted rivers run-off causes sufficient deterioration of the marine ecosystem. Sources of pollution locate both at the coastal zone and the overall catchment area. Management of the impact requires consolidated efforts of the catchment area states.

Pollution causes a direct and indirect impact on the marine ecosystem. In particularly, pollutions represented by heavy metals, oil and other harmful substances are causing a toxic effect on biota directly. Suspended solid particles decrease sun ray's penetration through the water layer and thus depress the development of benthic biocenoses and pelagic algae and other organisms. Mineral and organic fertilizers originated from agricultural fields stimulate microflora bloom (eutrophication) and in such a way cause destructive effect and damage coastal water biocoenosis.

In general, the quality of coastal water is far away from the natural level due to the bad management and bays, golfs and harbour area of large cities (e.g., Constanta, Odesa, Sebastopol, Novorossiysk, Poti, Batumi, Trabzon, Istanbul, Varna, etc.) are the most polluted areas in the Black Sea (UNDOC).

Other factors of effects on the marine environment related to the harbour and coastal activities. Dredging, coastal and offshore construction (e.g., construction of oil/gas facilities, pipelines, coastal protection installations, wave breakers, etc.) are harmful to benthic communities, and directly and indirectly deteriorate bottom landscapes and depress phytoplankton and benthic macrophytes because of dumping huge amount of silty mud. Dredges and some fishing practices damage bottom landscapes biocenoses and have a significant impact on the ecosystem. Unsustainable fisheries and extraction of other living resources (e.g., the biomass of Phyllophora algae) are destroying the fish stock and macrophytes fields. Decreasing of the population of fish species is provoking further negative processes in the marine ecosystem and unpredictably push ecosystem evolution.

Depressing biota of the marine ecosystem and decreasing its productivity due to pollution of the coastal water, coastal and bottom landscapes transformation activities, and unsustainable exploitation of living resources still constitute one of the most problems of the Black Sea's environment.

The aim of the deliverable is included in the name of *the ANEMONE project - Assessing the vulnerability of the Black Sea's marine ecosystem to human pressures*. The deliverable responds to the specific objectives 2. Provide new environmental monitoring data and information needed for the assessments of the Black Sea state of the environment, including pressures and impacts, focusing on filling the knowledge gaps identified at the national and regional level. Pilot studies on the various pressures impact upon the coastal ecosystems in selected study areas were conducted - two hot spots in Odessa region (WWTP South and WWTP city and port Chernomorsk); Constanta area: three harbours (Midia, Constanța and Mangalia) and one WWTP (Eforie) and Samsun port and WWTP area in Turkey.

1 Short description of the hot spots

1.1 Ukraine

In the Ukrainian part of the Black Sea North western Shelf, the main load on the marine ecosystems is determined by the flow of the main rivers: Danube, Dniester, and Dnieper, together with the Southern Bug and other land-based sources of pollution. Among such sources, there are two, which are considered "Hot Spots" – the wastewater treatment plants WWTP Odessa "South" and WWTP city and port Chernomorsk.

The WWTP of the city Odessa "South"

This station receives household wastewater from the southern part of Odessa (Kievsky district, Tairov residential area, Chernomorka and the left bank of the Sukhoi Liman). According to statistical reports, the population of this region is about 200 thousand people. The incoming water is purified by passing a treatment plant and discharged into the Black Sea through a 2 km long deep-water outlet. According to the data from the management of "Infoxvodokanal", the annual volume of discharge into the Black Sea is 26367729 m^3 of standardly treated wastewater.

The qualitative composition of wastewater and the average annual concentration of the analyzed parameters are shown in Table 1.1. The table shows for comparison the concentrations of the same hydrochemical parameters in the bottom layer of seawater at the discharge site, which were 2019 monitoring's results.

Table 1.1 - Average annual concentrations of hydrochemical parameters and volume of discharge into the Black Sea (tons/year) from WWTP of the city Odessa "South"

Parameters	Bottom layer concentration at discharge point	Average annual Concentration in wastewater, mg/L	Discharge, tons/year
NO_2	0.48 μM	2.20	58.009
NO_3	1.52 μM	37.84	997.755
NH_4	0.04 μM	7.99	210.678
PO4	0.50 μM	9.15	241.265
Sulphates		116.80	3079.751
TSS	7.26 mg/L	11.75	309.820
BOD-5		9.48	249.175
COD		72.00	1898.476
Fe total	0.05 mg/L	0.10	2.637

Figure 1.1 shows diagrams of the annual discharge of hydrochemical indicators into the Black Sea from the WWTP Odessa "South".

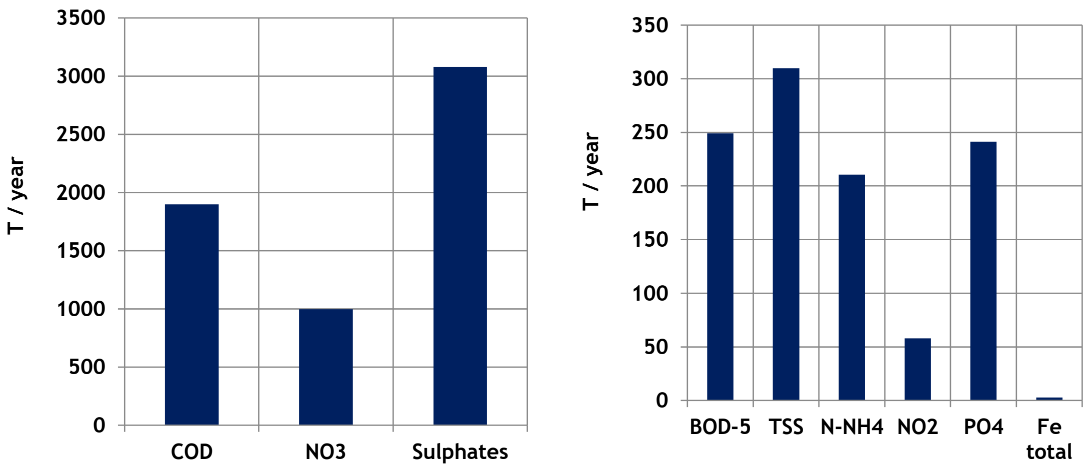


Figure 1.1 - Annual volume of discharges from the WWTP of the city Odessa - "South", WWTP of the city and port Chernomorsk

This station provides services for centralized water supply and centralized drainage to consumers of Chernomorsk and nearby settlements (Oleksandrivka, Malodolynske, Burlacha Balka, Molodizhne, Velykodolynske and other consumers of Ovidiopol district). A centralized water supply is provided to 100 % of the city's population. According to statistical reports, the population of this region is 71 472 inhabitants.

According to the data from the management of "Chernomorskvodokanal", the annual volume of discharge into the Black Sea is 3095439 m^3 of standardly treated wastewater.

The qualitative composition of wastewater and the average annual concentration of the analyzed parameters are shown in Table 1.2. The table shows for comparison the concentrations of the same hydrochemical parameters in the bottom layer of seawater at the discharge site, as for 2019 monitoring's results.

Table 1.2 - Average annual concentrations of hydrochemical parameters and volume of discharge into the Black Sea from WWTP of the city and port Chernomorsk

Parameters	Bottom layer concentration at discharge point	Average annual Concentration in wastewater, mg/L	Discharge, tons/year
NO_2	0.05 μM	0.13	0.415
NO_3	0.14 μM	8.17	25.289
NH_4	<0.04 μM	1.57	4.859
PO_4	0.14 μM	6.13	18.975
Sulphates		92.56	286.507
Chlorides		191.88	593.952
Total mineralization		606.26	1876.647
TSS	7.43 mg/L	8.05	24.918
BOD-20		6.90	21.370
COD		33.36	103.263
Fe total	0.023 mg/L	0.04	0.124
TPHs		0.023	0.070

Figure 1.2 shows diagrams of the annual discharge of hydrochemical indicators into the Black Sea from the WWTP of the city and port Chernomorsk.

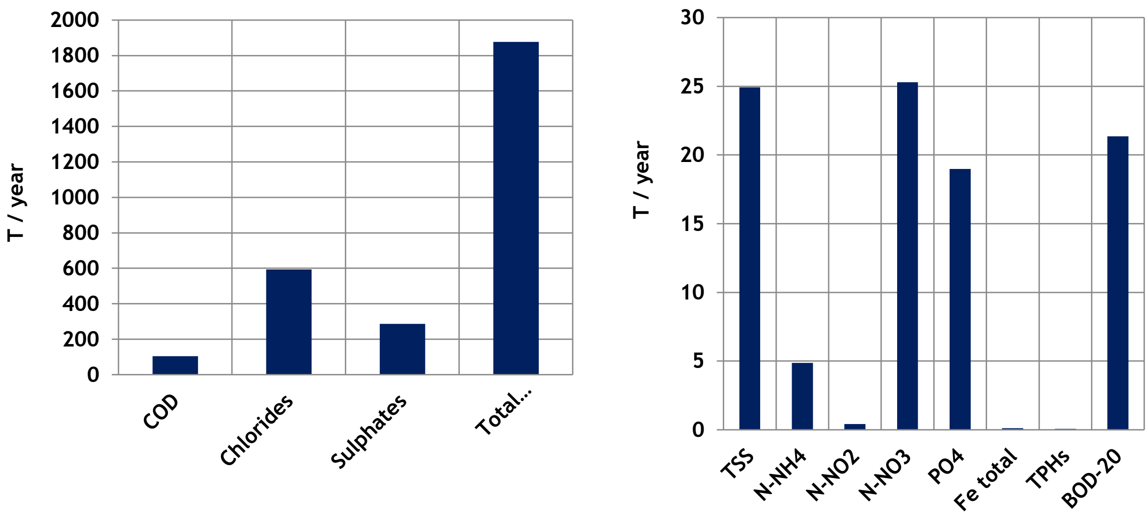


Figure 1.2- Annual volume of discharges from the WWTP of the city and port Chernomorsk

Conclusions

The volume of wastewater discharge from the WWTP “South” into the Black Sea is 8.5 times higher than from the WWTP city and port of Chernomorsk. Accordingly, the amount of chemicals entering the marine environment is higher at the place of discharge from WWTP “South”.

However, this proportion is observed only for some parameters. Table 1.3 shows how many times the WWTP “South” load is greater than that from WWTP city and port of Chernomorsk. WWTP “South” significantly contributes to the marine environment's pollution and especially by nutrients (Table 1.3).

Table 1.3 - Comparison of loads on the marine environment from 2 "Hot spots"

Parameters	Ratio=Load WWTP "South"/ WWTP Chernomorsk
N-NO_2	140.0
N-NO_3	40.0
N-NH_4	42.0
PO_4	12.6
SO_4	10.6
TSS	12.9
BOD	12.0
COD	18.0
Fe total	21.0

1.2 Romania

Ports – Midia, Constanta, Mangalia, and Eforie wastewater treatment plant

The Port of Constanta is located at the crossroad of the trade routes linking the markets of the landlocked countries from Central and Eastern Europe with the Trans-Caucasus, Central Asia, and the Far East. It is the main Romanian port on the Black Sea, playing the role as the transit node for the landlocked countries in Central and South-East Europe, located on the west coast of the Black Sea about 179 nautical miles from the Bosphorus and 85 nautical miles from the mouth of the Sulina waterway, through which the Danube flows into the Black Sea.

Port of Constanta has a total area of 3926 ha (Figure 1.3). It is divided into three subdivisions:

- Seaport with an annual handling capacity of 100 million tons, 140 berths served by allowing access functional vessels with a capacity of 220000 dwt to,

- River port allows access to any type of river vessel having an annual handling capacity of 10 million tons,

- Touristic port, a major milestone for passenger ships sailing along the Black Sea

The port complex consists of the old part to the North and the new part to the South. The North part is entirely operational and consists of 12 basins, water depth between 7 m and 14 m, 15.5 km of the quay and 82 berths. It has specialized terminals for ores, coal, crude oil and oil products, cereals, chemical products, rolled metals, containers, general cargo, platforms, and warehouses.

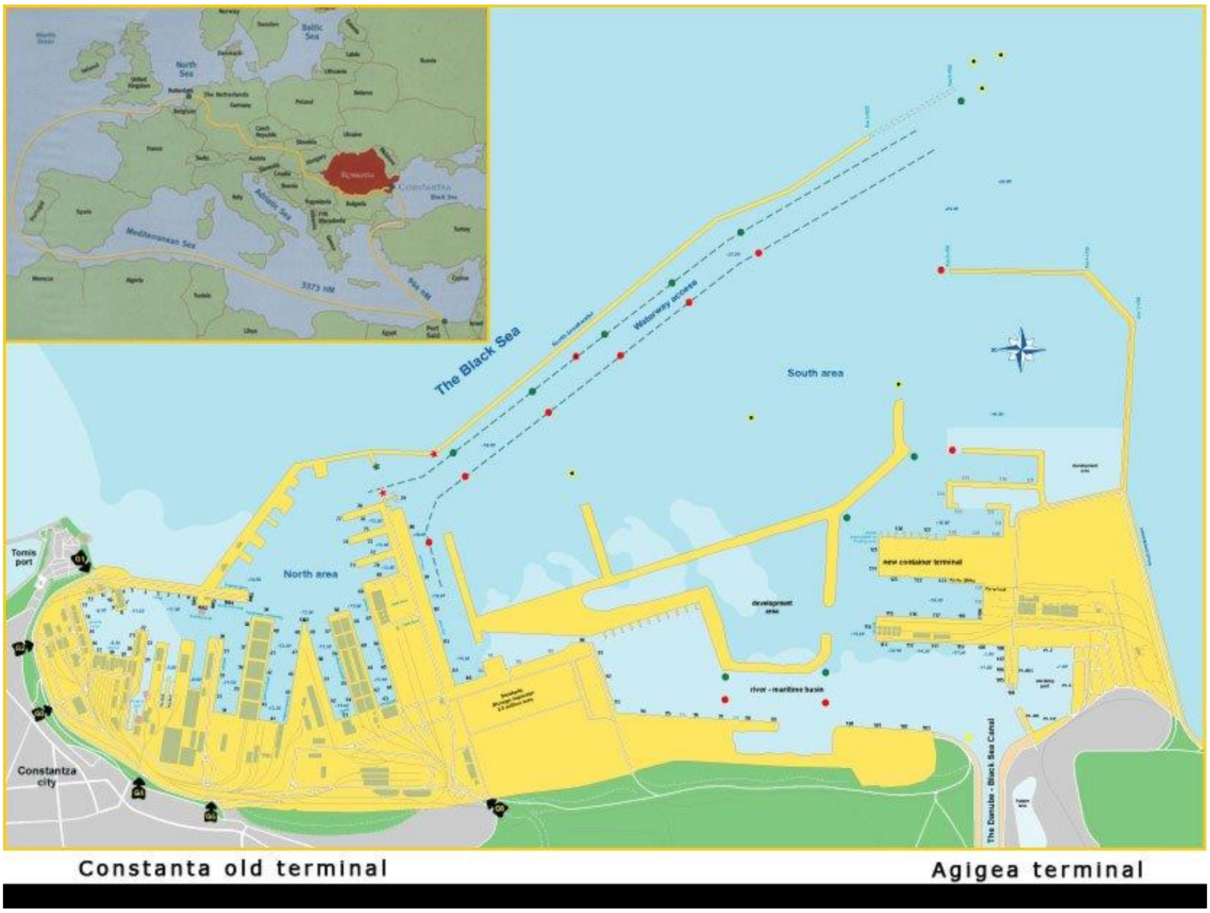


Figure 1.3 – Port of Constanta (https://allaboutromania.wgz.ro/paneltop/constanta-ports)

The South Port is partly operational. It has 14.6 km of quays, 74 operational berths and handling capacity for containers, ores, coal, phosphate, crude oil, and oil products, rolled metals, general goods for platforms and warehouses. Part of the traffic is handled as ro-ro and ferry cargo. The South Port encompasses the entrance to the Danube- Black Sea Canal, which is part of Europe's most important waterway, the Rin-Main-Danube corridor.

The South Port has a dedicated river/maritime basin for the transhipment of cargo into river barges. Of the cargo handled by Constanta, 80 % is bulk cargo. Of that, half is liquid bulk, manly crude oil and derivative products, and the other half is dry bulk, mainly iron, ore and nonferrous ores, coal, coke, phosphate, apatite, and cereal. The general cargo consists of imports of industrial equipment, foods, fertilizers and chemical products, clothes and electrical appliance and exports of furniture and wood products, metal products, fertilizers, and chemical products, foodstuff, textiles, glass products and cars.

The two satellite ports of Constanta are Midia, located 25 km north of the Constanta and Mangalia, 38 km to the south. Both perform a vital function in the plan to increase the efficiency of the main port's facilities - and both are facing continuous upgrading to meet the growing demands of cargo owners. In 2008 the traffic achieved by the two satellite ports was 4 % from the general traffic, 96 % being achieved by the Port of Constanta.

The two satellite ports, Midia and Mangalia, are part of the Romanian maritime port system under the coordination of Maritime Ports Administration SA Constanta.

Midia International Port (Năvodari), is one of the Romanian maritime and river ports, located in south-western Romania, approx. 13.5 nm north of Constanta, with direct access to the Black Sea and the Danube to the Black Sea (Figure 1.4). It is one of the satellite ports of Constanta and was designed and built to serve the adjacent industrial and petrochemical facilities. The terminal has a good geographical position, being one output port to Europe and import-export basis only live animals in Romania. The Danube is one of the best modes, representing an effective alternative to congested road and rail transport in Europe. Since the '80s, has become the establishment of a livestock loading terminal, the ship and cargo, the Port Basic Special unique animals. Due to heavy traffic and commercial demands of countries in eastern, western, and central Europe, it was necessary to smooth traffic of goods from the port of Constanta, this determining design and execution of a livestock export bases in Midia port.

Figure 1.4 – Port of Midia (https://www.portofconstantza.com/pn/page/np_prezentare_port)

The north and south breakwaters have a total length of 6.97 m. The port covers 834 ha, of which 234 ha represents land and 600 ha, water. There are 14 berths (11 operational berths, 3 berths belong to Constanta Shipyard) with a total length of 2.24 km. Further to dredging operations performed the port depths are increased to 9 m at crude oil discharging berths 1-4, allowing access to tankers having an 8 m maximum draught and 20000 dwt.

Midia International Port has an annual operating capacity of about 60000 tons, being served by four berths, all operational. The total length of the piers is 350 m and 8.5 m deep, being able to perform the loading operation of four ships simultaneously. Main cargoes operated: crude oil and derivatives, agribulk, LPG, and metallic products.

The Port of Mangalia is located on the Black Sea, close to the southern border with Bulgaria. It has an area of 142.19 ha, of which 27.47 ha is land and 114.72 ha is water (Figure 1.5). The north and south breakwaters have a total length of 2.74 km. There are 4 berths (2 operational) with a total length of 540 m. The maximum depth is 9 m. The main cargo: chemicals, fertilizers, bitumen, general cargo.

Figure 1.5 – Port of Mangalia (https://www.portofconstantza.com/pn/page/np_prezentare_port)

All three ports have also WWTPs and industrial sources discharging into their waters – Rompetrol Rafinare, WWTP Constanta Sud, WWTP Constanta Port, and WWTP Mangalia.

WWTP Eforie

WWTP was completely rebuilt and equipped with the tertiary stage including the biological removal of nitrogen and phosphorus and is one of the most modern from Romania. The wastewater is discharged into the Black Sea through a 2 km pipeline.

Benefits – compliance of waste water quality with EU rules & directives; both superior level of construction technologies and supplementary measures for treated Waste water discharge into the Black Sea at approx. 2 km from shore; assurance of protection conditions for Black Sea continental shelf's fauna and flora and bathing waters from southern Romanian littoral; collect and treat sewage from Eforie Nord, Eforie Sud, Agigea, Techirghiol, Costinesti and Schitu being integrated into the sewage system (140000 equivalent people). Now, due to the tertiary stage, WWTP Eforie Sud is one of the most modern from Romania with the flow within 0.518 – 0.745 m^3/s, with a significant decrease of TSS, BOD_5, ammonium and total nitrogen loads.

1.3 Turkey

1.3.1 Samsun harbour area

In the Black Sea region of Turkey, pollutants including contaminants arise from numerous anthropogenic sources such as land-based industrial and agricultural activities, pollution by ship, atmospheric deposition and mineral exploration and riverine inputs. They include synthetic compounds, such as pesticides, and non-synthetic compounds, such as metals, dispersed by industrial processes, and polycyclic aromatic hydrocarbons, dispersed by combustion and oil spills. Nutrient and organic matter enrichment is very high in Turkish Black Sea coastal areas. Insufficient wastewater treatment, marine outfall discharges and river inputs are the principal sources of input. In addition, solid wastes (storage areas by the coast) are causing problems in the coastal areas. High sedimentation rates at several fishing ports mean that dredging is a frequent activity, causing the release of sediment-trapped nutrients back into the water column. Some localized activities, such as agriculture (with associated erosion), sand/gravel extraction, industry and aquaculture also contribute to eutrophication along the Black Sea coast.

Samsun is one of the major cities bordering the Turkish Black Sea coast. The city has an approximate population density of 220 capita/km^2 (TUIK 2018), the average amount of wastewater per capita was 1.4 kg/day and the amount of municipal waste collected was 57592 tonnes/year. Since the landscapes of the Black Sea region are not suitable to construct wastewater treatment facilities, some of the cities use the sewerage system directly disposing of deep marine outfalls but most of the small settlement areas used septic tanks or package biological treatment. Samsun has both combined and separate systems draining the city (Bakan *et al.*, 1996). Besides this, solid wastes deposited in coastal areas may cause pollution problems.

Generally, industrial facilities are low in number in the Black Sea region of Turkey. Copper and iron/steel production are important industrial sectors in Samsun and its surroundings. Other industries are food manufacturing, manufacture of fertilizers, pesticides, resins, plastics, tobacco, and textile. The Samsun harbour with the 14 million gross tones capacity (MoT&C, 2019) is an important transportation centre for these industries, as well as for the fertilizer industry in Samsun. The port was assessed as “highly dense” in terms of ship traffic and cargo handled.

Eutrophication based pressure-impact analysis in the Black Sea was undertaken in the DEKOS Project. The water bodies under the impact of Yeşilırmak river and also Samsun province was identified as the highest-pressure area. The city with point sources on the BS coast has been specified as one of the “**Hot spot**” areas among other coastal cities[3] (EU HotBlackSea Project). These coastal waters (water bodies) are also designated as “sensitive” areas (under the UWWTD) in 2015. These coastal areas are defined as mesotrophic/eutrophic according to their average DIN, TP, bottom water oxygen saturation and chlorophyll *a* concentrations. They have a relatively limited exchange/mixing with waters further offshore, with phytobenthos and zoobenthos results suggesting moderate levels of impact. Marine benthic macrophytes are used as indicators for the assessment of ecological status. The ecological status of stations along the Black Sea coast was assessed (MoEU & TUBITAK-MRC, 2015) using the Ecological Evaluation Index. According to the ecological status levels of the Black Sea coasts, the lowest values were usually observed at the stations including Samsun.

Dredging of the bottom sediments for the deepening of the ports/harbours and dumping of dredged material in coastal waters has been a common practice, especially concerning fishing ports and industrial harbours such as Samsun. Release of the harmful substances from the contaminated dredged material is considerable pressure on the marine environment (Tolun et al., 2015, Tan et al., 2015).

Contamination from thermal power plant wastes such as ashes and slag is another important issue. The nitrogen plant at Samsun, use lignite at Çatalağzı Thermal Power Plant cause deposition in the environmental matrices such as sediment, soil and water (Bat. et al., 2018). Maritime activities including port and harbour facilities are another source of pollution for the Samsun area. Contaminants such as Petroleum Hydrocarbons and other chemicals transported represent a risk to the aquatic environment when they released accidentally or during handling operations (Bat et al. 2018,). A furthermore significant amount of pesticide usage in agricultural activities was reported for Samsun province in 2015 (MoEU, 2016). Studies have shown that the concentrations of the OCs and PCBs in mussels were higher in coastal areas close to the largest city of the region, the Samsun harbour area (Kurt & Ozkoc, 2004).

[3] http://bs-hotspots.eu

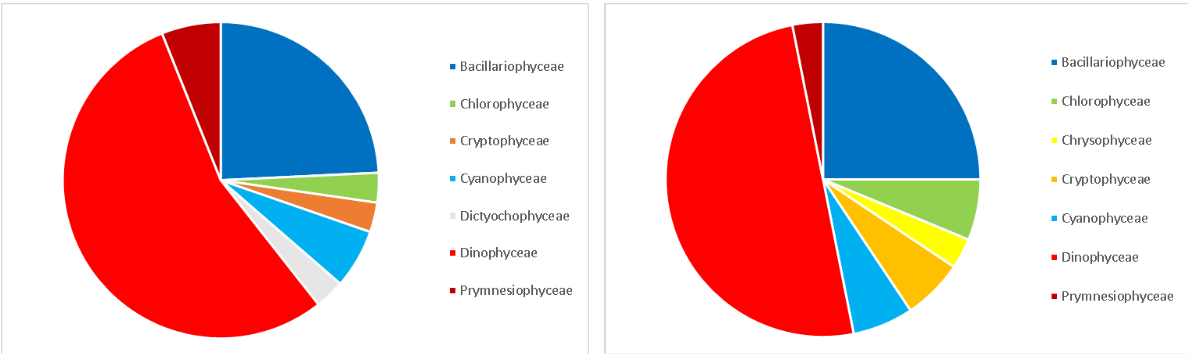
2 Pelagic habitats

2.1 Phytoplankton

2.1.1 Ukraine

For the analysis of “hot spots” of Odessa surroundings, we studied the seawater in the place of discharge from WWTP city and port Chornomorsk (ShW_UA_2) and in the place of discharge from WWTP Odessa "South" (ShW_UA_3).

In the place of discharge from WWTP city and port Chornomorsk, were found 33 species belonging to 7 classes and in the place of discharge from WWTP Odessa "South" 32 species of 7 classes (Annex C). The taxonomic structure of the phytoplankton community of Odessa region “hot spots” is shown in Figure 2.1. The values of the Shannon index were relatively high. In the place of discharge and port Chornomorsk, the index was 1.42-1.60, lower than the area under the WWTP Odessa "South" influence– where the index value was 2.37-2.47.



a ***b***

Figure 2.1 - Taxonomic structure of phytoplankton community in the place of discharge from WWTP city and port Chornomorsk (a) and the place of discharge from WWTP Odessa "South" (b), September 2019

The phytoplankton abundance and biomass in the area under the WWTP and Chornomorsk harbour influence were rather low. In the place of discharge and port Chornomorsk, the abundance was $103 \cdot 10^3$ -$165 \cdot 10^3$ cells/L, the biomass 404-1 302 mg/m^3, in the place of discharge from WWTP Odessa "South" it was $60 \cdot 10^3$ -$151 \cdot 10^3$ cells/L, and 34-171 mg/m^3, respectively.

According to the indicator of phytoplankton biomass, the ecological state of the environment in the place of discharge from WWTP Odessa "South" may be assessed as “high”; in the place of discharge and port Chornomorsk, as “high” at near-bottom layer and “moderate” in the surface layer, average assessment is “good”.

The index of Menhinick in the place of discharge from WWTP Odessa "South" was 0.067-0.069, in the place of discharge and port Chornomorsk 0.060-0.069, which corresponds to “moderate” ecological status class (Moncheva S., 2016).

In the autumn, in the “hot spots” of the Odessa region, the poly-dominant complex of phytoplankton with high Shannon biodiversity index and rather low biomass of microalgae developed. The state of the marine environment there may be assessed as “high” and “good”.

However, for a more complete picture, it is necessary to conduct year-round monitoring and assessment of the water area based on long-term observations, especially in the summer, when the load on wastewaters treatment stations increases significantly due to the hot weather and a large number of tourists.

2.1.2 Romania

Port of Midia

A total of 73 species, varieties and forms were identified inside and outside Midia harbour belonging to 10 taxonomic classes (Annex C). The phytoplankton community was mainly composed of dinoflagellates – 38 species (45 % of the total) and diatoms – 21 species (27 %). The classes Clorophyceae and Cyanophyceae contributed with 8 % and 5 %, respectively. The other classes (Chlorodendrophyceae, Cryptophyceae, Dictyochophyceae, Ebriophyceae, Euglenoidea and Prymnesiophyceae) were represented only by 1-3 species. Among dinoflagellates species, genera Protoperidinium (4), Gymnodinium (3), Prorocentrum (3), Glenodinium (3), Tripos (3) were the most diverse species. Among diatoms species, genera Nitzschia (4) and Thalassiosira (3) reached the highest species diversity (Figure 2.2).

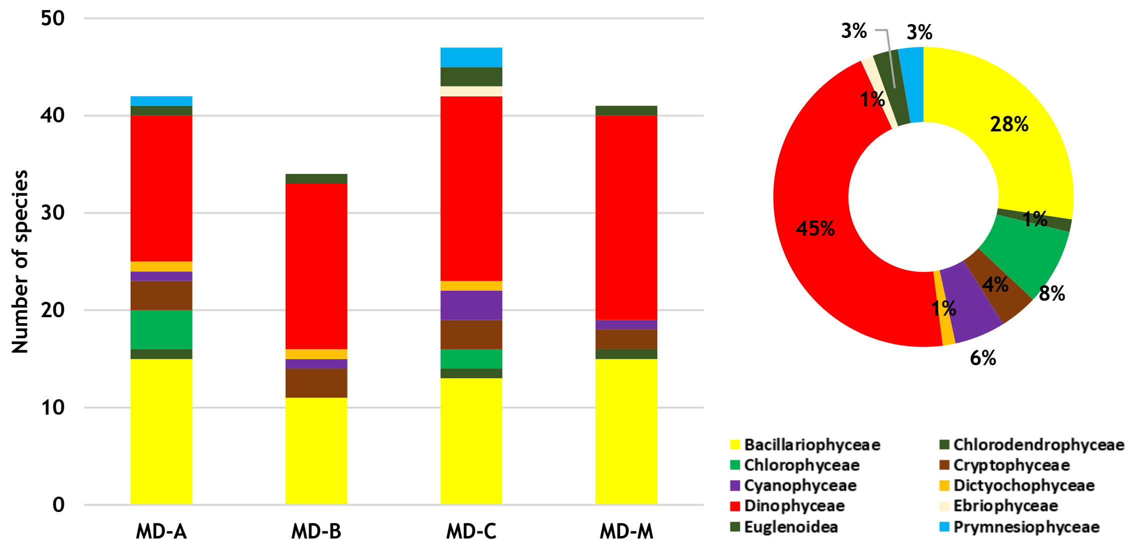


Figure 2.2- Phytoplankton taxonomic composition - Port of Midia, September 2019

The number of species varied between 34 (MD-B) and 47 (MD-C). Even though the diversity in MD-B was slightly lower than in the other stations, there was no significant difference between the diversity inside harbour (MD-A) and the control station, MD-M.

The average abundance of phytoplankton varied between 65.20 $\cdot 10^3$ cells/L and 258.20 $\cdot 10^3$ cells/L and the average biomass, between 149 mg/m^3 and 468 mg/m^3 (Figure 2.3).

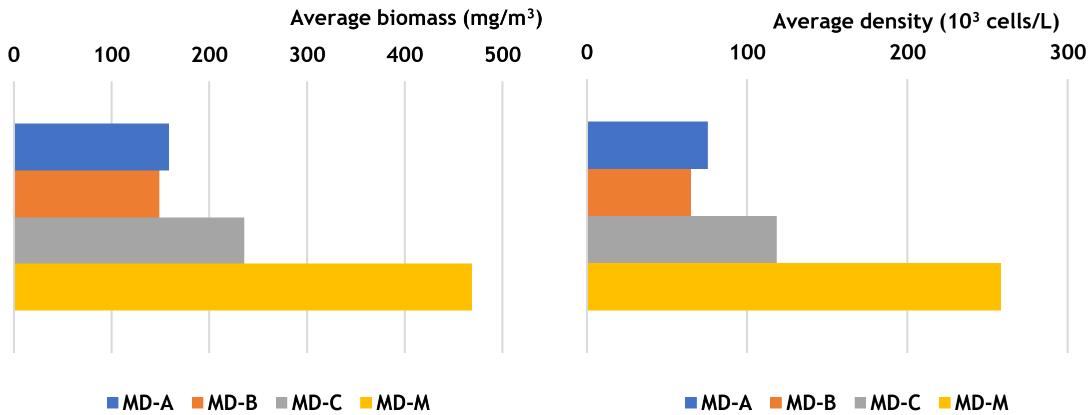


Figure 2.3 - Phytoplankton average abundance and biomass variation - Port Midia, September 2019

Phytoplankton average abundance recorded in the control station (MD-M, 258.20·10^3 cells/L) was approx. 2-4 times higher than in the outer stations, MD-B and MD-C (65.20·10^3 cells/L and 118.50 cells/L, respectively) and 3 times higher than in the inner station, MD-A (75.20·10^3 cells/L). The values of average biomass (Figure 2.3), in the inner and outer harbour stations, were 2-3 times lower (between 149 mg/m^3 and 236 mg/m^3) than in the control station (468 mg/m^3).

Phytoplankton communities' taxonomic structure (Figure 2.4) was featured by the dominance of diatoms (Bacillariophyceae) in the abundance (contributing up to 84 %) while in the **biomass,** dinoflagellates represented most of the assembly (~77 %). Even though the contribution of the "Other classes" was lower in the average biomass (2-15 %), in the average density they accounted together a higher contribution than the dinoflagellates (between 24-39 %) in the inner and outer stations (MD-A, B and C). In the control, they represented only 5 %.

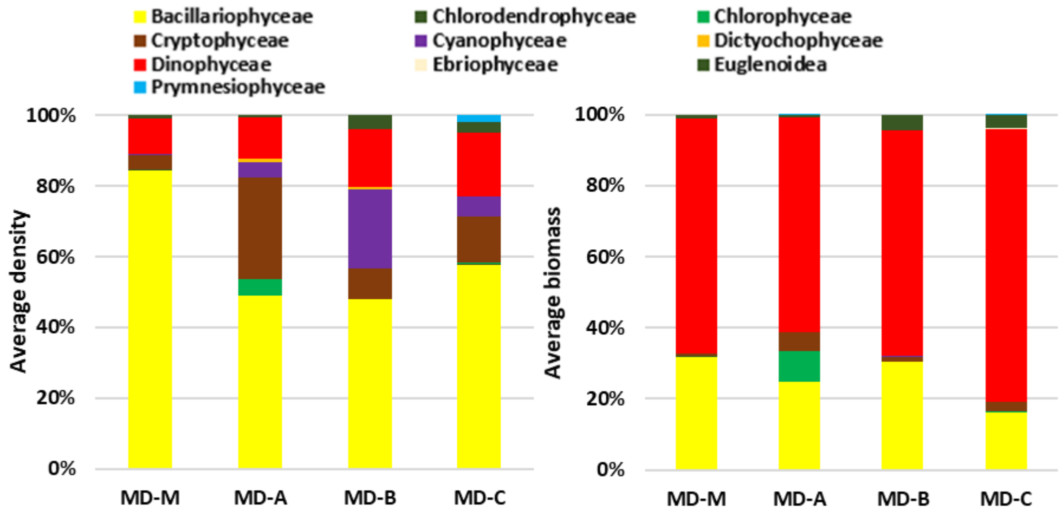


Figure 2.4 - Phytoplankton taxonomic structure based on average abundance and biomass - Port of Midia, September 2019

The bulk of phytoplankton abundance was mainly represented by the development of a common group of diatoms (*N. delicatissima, Leptocylindrus minimus, N. tenuirostris, Synedra nitzschioides* f. *nitzschioides, Lennoxia faveolata*) and dinoflagellates (*Prorocentrum cordatum, P. micans, Gymnodinium* sp.), found in similar proportions in the outer harbour stations, MD-M and MD-C. The exception of the species distribution in the outer stations was the presence of the freshwater cyanobacteria, *Pseudanabaena limnetica*, a potentially toxic species (Preece *et al.*, 2017). *P. limnetica* represented up to 23 % and it was present only in MD-B. In the inner station, MD-A, the species proportion was distinct, the community is mainly formed by the diatom, *Nitzschia tenuirostris* and the cryptophyte *Hillea fusiformis* (Figure 2.5).

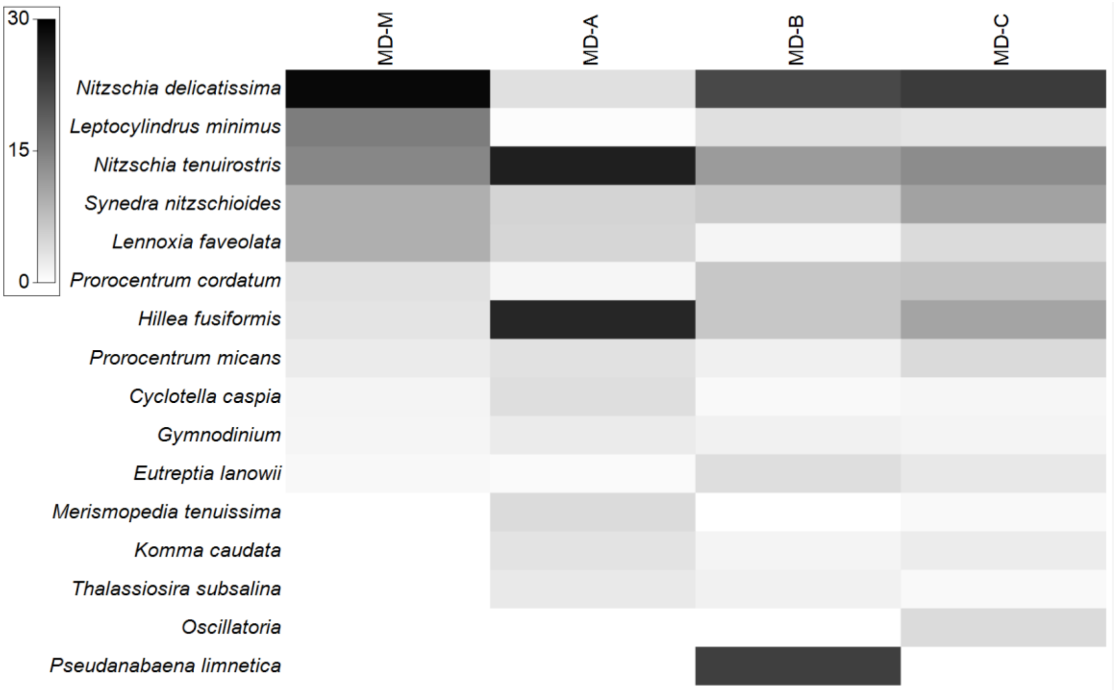


Figure 2.5 - Species average abundance matrix (%) and sampling stations (white spaces indicate the absence of the species at that site; the intensity of the grey scale is linearly proportional to the percentage of the total average abundance per station)

The phytoplankton community biomass (Figure 2.6) was mainly composed of *P. micans* (up to 44 % on MD-C), a dinoflagellate considered an indicator of eutrophication (Dorgham et al., 1987). Other important dinoflagellates were *Protoperidinium granii* (up to 16 % on MD-B), *P. depressum, P. steinii, Tripos fusus, T. muelleri*. The species of Tripos genus were found only in the outer stations.

The diatoms biomass contributed with the highest share (up to 14 %) were *Thallassiosira subsalina* (on MD-A) and *Coscinodiscus radiatus* (on MD-B). The cryptophyte, *H. fusiformis* and the chlorophyte, *Pseudopediastrum boryanum* were present with 4 %, respectively, 8 % of the total biomass, only in MD-A.

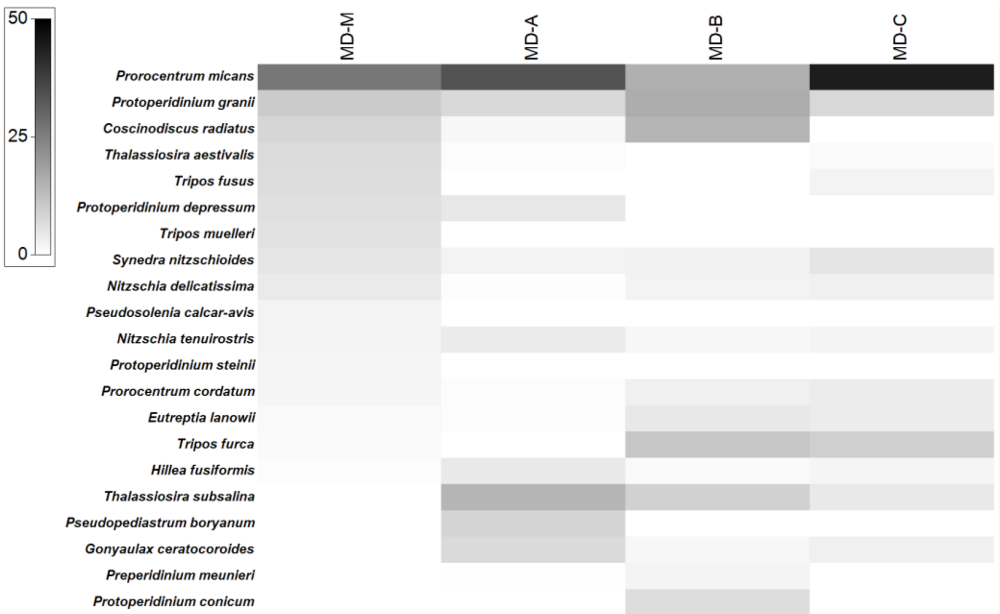


Figure 2.6 - Species average biomass matrix (%) and sampling stations (white spaces indicate the absence of the species at that site; the intensity of the grey scale is linearly proportional to the percentage of the total average biomass per station)

Port of Constanta

A total of 68 species, varieties and forms were identified inside and outside Constanta harbour belonging to 11 taxonomic classes (Annex C). The phytoplankton community was mainly composed of dinoflagellates – 36 species (53 % of the total) and diatoms – 18 species (26 %). The classes Clorophyceae and Cyanophyceae contributed with 3 % and 4 %, respectively. The other classes (Chlorodendrophyceae, Cryptophyceae, Dictyochophyceae, Ebriophyceae, Euglenoidea and Prymnesiophyceae) were represented only by 1-2 species. Among dinoflagellates species, genera Protoperidinium (5), Gymnodinium (3), Prorocentrum (3), Glenodinium (3), Tripos (3) were the most diverse. Among diatoms species, genera Nitzschia (3) and Thalassiosira (3) reached the highest diversity (Figure 2.7).

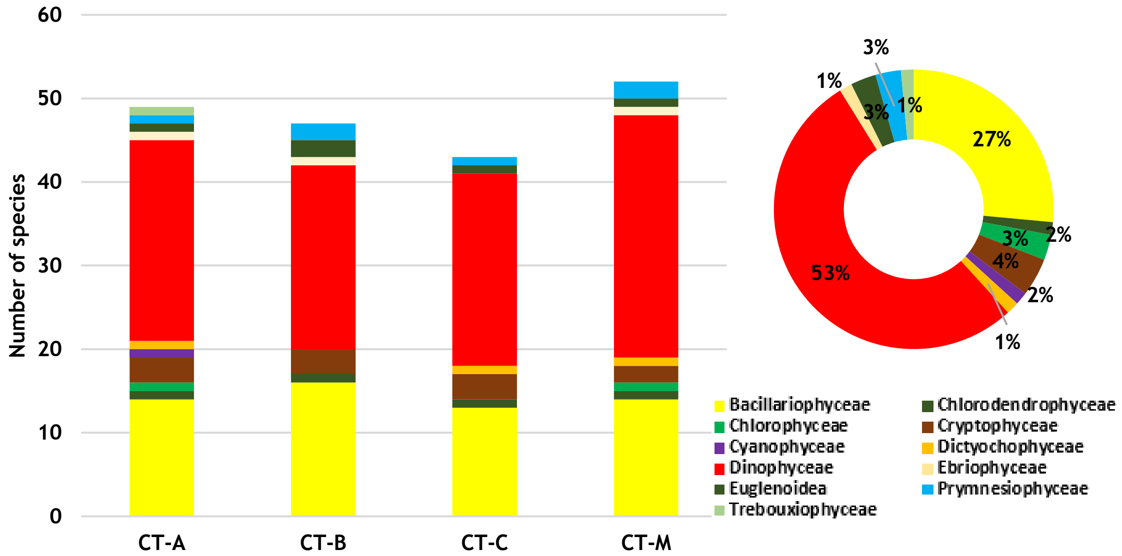


Figure 2.7- Phytoplankton taxonomic composition – Port of Constanta, September 2019

The number of species identified varied between 43 (CT-C) and 52 (CT-M). There were no significant differences between the diversity inside the harbour (CT-A, 49 species) and the control station, CT- M.

The average abundance of phytoplankton varied between $54.28 \cdot 10^3$ cells/L and $126.30 \cdot 10^3$ cells/L and the average biomass, between 130 mg/m³ and 468 mg/m³ (Figure 2.8), the highest values being found in the inner harbour station (CT-A) and the lowest in the outer station (CT-C).

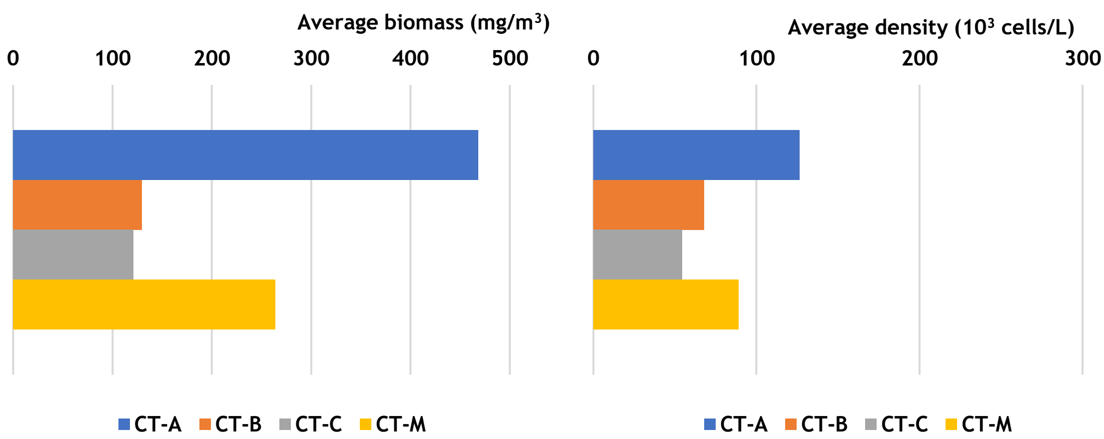


Figure 2.8 - Phytoplankton average abundance and biomass variation - Port of Constanta, September 2019

Phytoplankton communities' taxonomic structure around Constanta harbour (Figure 2.9) was featured by the dominance of diatoms (Bacillariophyceae) in the abundance (contributing up to 74 %) while in the **biomass,** dinoflagellates represented the majority of the assembly (~80 %). Even though the contribution of the other classes was lower in the average biomass (1-7 %), in the average density they accounted together a higher contribution (19 %) than the dinoflagellates in the outer stations (CT-B and C). In the control and the inner station, they represented 9 % and 7 %, respectively.

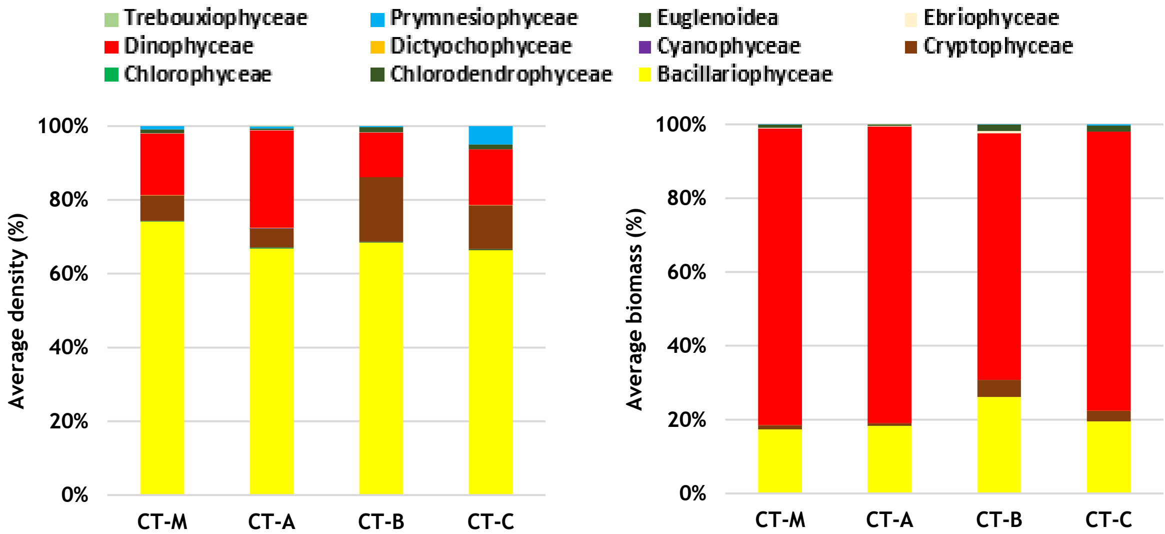


Figure 2.9 - Phytoplankton taxonomic structure based on average abundance and biomass - Port Constanta, September 2019

The bulk of phytoplankton abundance (Figure 2.10) was mainly represented by the development of a common group of diatoms (*N. delicatissima, Synedra nitzschioides, N. tenuirostris, Lennoxia faveolata, Thalassiosira parva*) associated with dinoflagellates (*Prorocentrum cordatum, P. micans, Gymnodinium* sp., *Gonyaulax ceratocoroides*), found in similar percentages in the outer harbour stations, CT-M, CT-B and CT-C. The exception of the species distribution in Constanta harbour stations was the presence of the marine centric diatom, *Thalassiosira parva* which represented between 1-3 % in the outer stations and up to 24 % in the inner station (CT-A). Iron concentrations, temperature and macronutrient availability have been identified as important factors for the composition of Thalassiosira species communities in marine waters (Dreux et al., 2013).

In the inner station, CT-A, the species proportion was distinct, the community was mainly formed by the diatom, *Nitzschia tenuirostris* and the cryptophyte *Hillea fusiformis*.

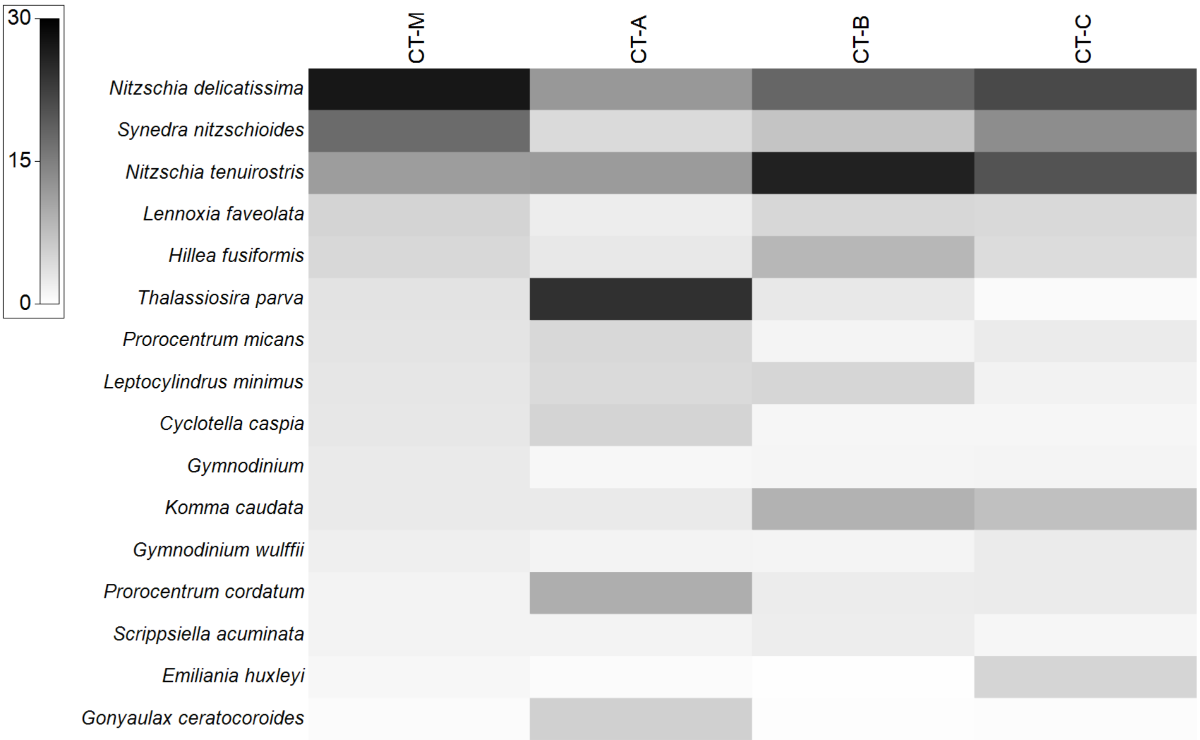


Figure 2.10 - Species average abundance matrix (%) and sampling stations (white spaces indicate the absence of the species at that site; the intensity of the grey scale is linearly proportional to the percentage of the total average abundance per station)

In terms of biomass (Figure 2.11), the phytoplankton community inside the harbour was mainly composed of *Gonyaulax ceratocoroides* (34 %) and *P. micans* (25 %). Other important dinoflagellates were *Protoperidinium depressum* (4 %), *P. cordatum* (3 %) and Gyrodinium pingue (2 %) along with the diatoms *Thalassiosira parva* (9 %) and *Gailonella sulcata* (2 %).

These dinoflagellates were present also in the outer and control stations, but with lower contributions, being replaced mainly by *Protoperidinium granii* (10-14 %), *Tripos furca* (7-11 %), *Diplopsalis lenticula* (12 %, present only in CT-M), *Scrippsiella acuminata* (1-3 %) and the diatoms, *Synedra nitzschioides* (3-6 %), *N. tenuirostris* (1-4 %), *N. delicatissima* (2 %), *Thalassiosira subsalina* (3-6 %) and *T. aestivalis* (present only in CT-C with 4 %).

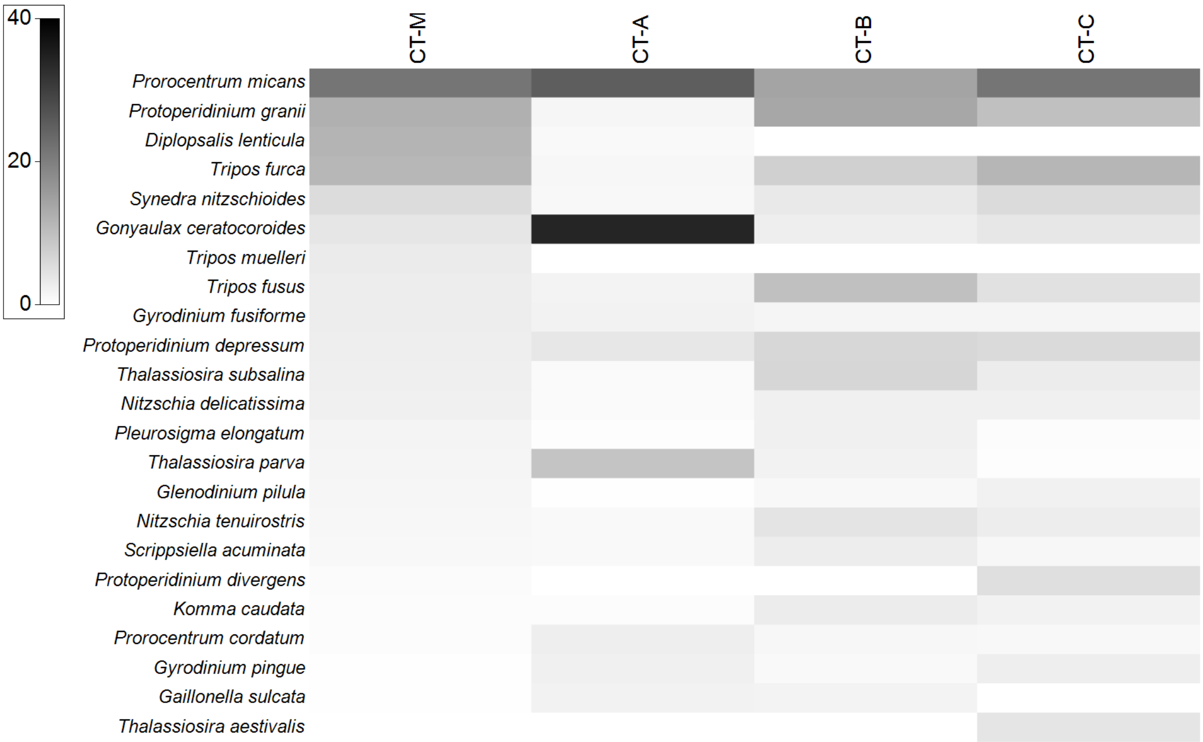


Figure 2.11 - Species average biomass matrix (%) and sampling stations (white spaces indicate the absence of the species at that site; the intensity of the grey scale is linearly proportional to the percentage of the total average biomass per station)

Eforie wastewater treatment plant

A total of 52 species, varieties and forms were identified in the study area belonging to 7 taxonomic classes (Annex C). The phytoplankton community was mainly composed of dinoflagellates – 29 species (56 % of the total number of species) and diatoms – 15 species (29 %). The classes Cryptophyceae and Prymnesiophyceae contributed with 6 % and 4 %, respectively. The other classes (Clorodendrophyceae, Dictyochophyceae and Euglenoidea) were represented only by 1 species each. Among dinoflagellates species, genera Protoperidinium (4), Gymnodinium (3), Gyrodinium (2), Prorocentrum (2), Tripos (3) were the most diverse. Among diatoms, genera Thalassiosira (3) and Nitzschia (3) reached the highest diversity (Figure 2.12).

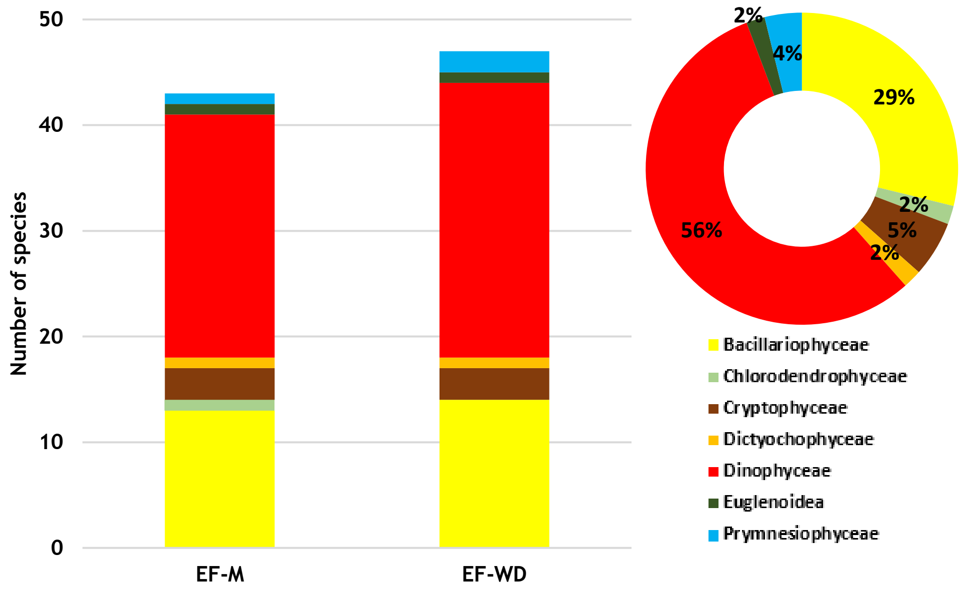


Figure 2.12 - Phytoplankton taxonomic composition - Eforie WWTP discharge, September 2019

The phytoplankton diversity along the Eforie wastewater discharge pipeline did not vary significantly. A slightly higher number of species was recorded in EF-WD (47) compared with the control station, EF-M (43).

The average abundance of phytoplankton varied between $54.28 \cdot 10^3$ cells/L and $65.54 \cdot 10^3$ cells/L and the average biomass, between 121 mg/m^3 and 158 mg/m^3 (Figure 2.13), maximum being found in the wastewater discharge estimated point (EF-WD) and the lowest in the control station (EF-M).

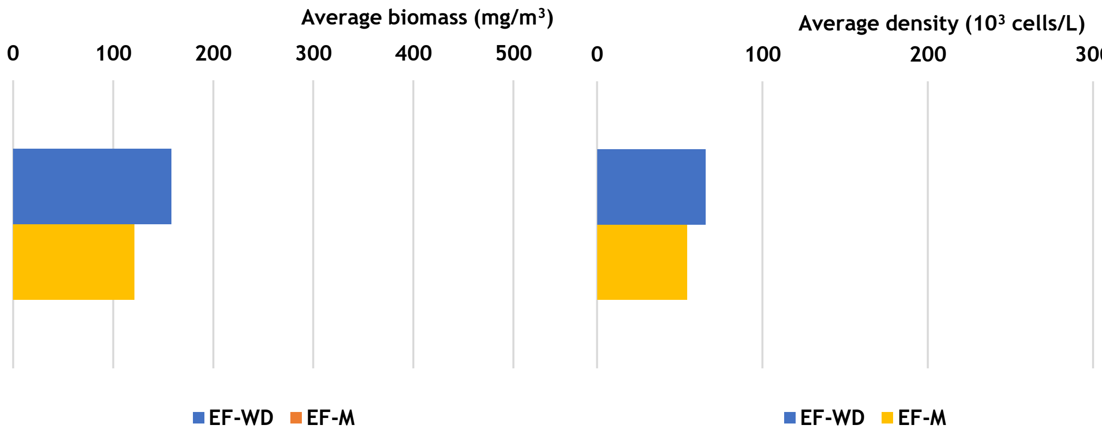


Figure 2.13 - Phytoplankton average abundance and biomass variation - Eforie WWTP discharge, September 2019

Phytoplankton communities' taxonomic structure near Eforie wastewater discharge was featured by the dominance of diatoms (Bacillariophyceae) in the abundance (contributing up to 71 %) and the dominance of dinoflagellates in biomass (up to 76 %), in both stations (Figure 2.14). Even though the contribution of the other classes was lower in the average biomass (4-5 %), in the average density, compared to the dinoflagellates, they accounted together a slightly higher contribution in EF-M (19 %) and a lower contribution (13 %) in EF-WD.

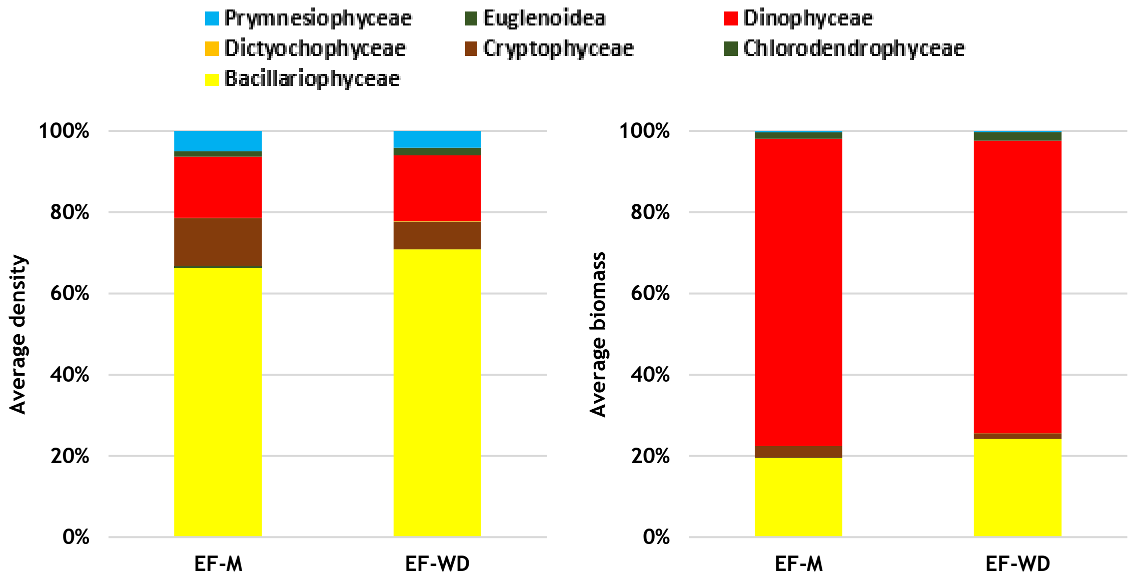


Figure 2.14 - Phytoplankton taxonomic structure based on average abundance and biomass - Eforie WWTP discharge, September 2019

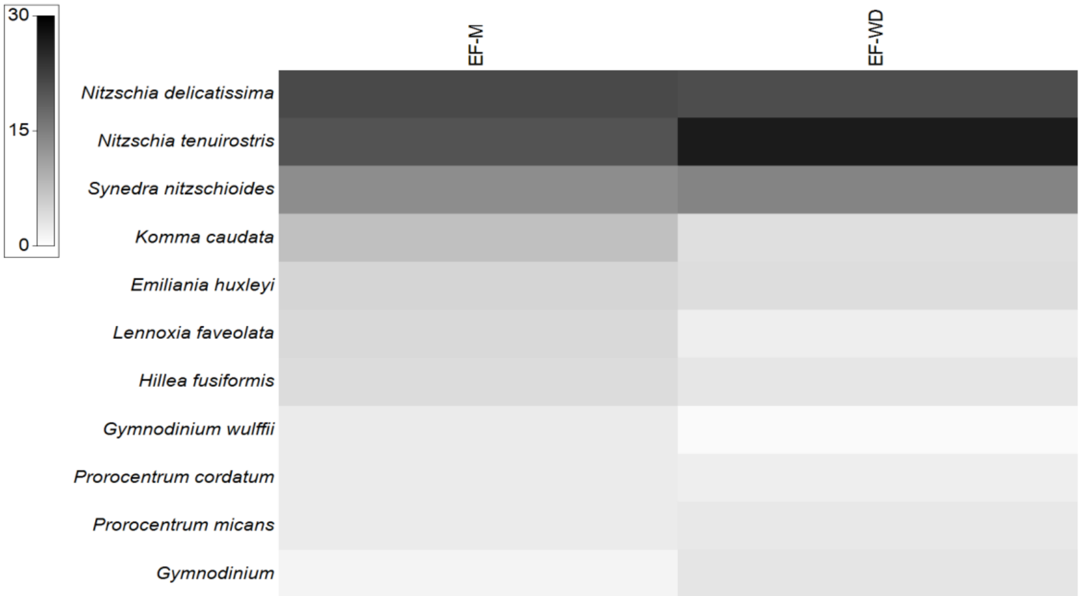


Figure 2.15 - Species average abundance matrix (%) and sampling stations (white spaces indicate the absence of the species at that site; the intensity of the grey scale is linearly proportional to the percentage of the total average abundance per station)

The bulk of phytoplankton abundance was mainly represented by the development of a common group of diatoms (*N. delicatissima, N. tenuirostris and Synedra nitzschioides* f. *nitzschioides*) associated with the cryptophytes, *Komma caudata* and *Hillea fusiformis* and the dinoflagellates, *Gymnodinium wulfii*, *Prorocentrum cordatum*, *P. micans*, found in both stations, in similar percentages (Figure 2.15).

In terms of biomass (Figure 2.16), the phytoplankton community in the control station (EF-M) was mainly composed of the dinoflagellates, *Prorocentrum micans* (22 %), Tripos furca (11 %), *Protoperidinium granii* (10 %), *P. depressum* (6 %), *P. divergens* (5 %), followed by the diatoms *Synedra nitzschioides* f. *nitzschioides* (6 %), Thalassiosira aestivalis (4 %), T. subsalina (3 %). In the wastewater discharge station, the phytoplankton structure was similar to control, with the majority represented by dinoflagellates and diatoms. *P. micans* (23 %), one of the most important dinoflagellates maintained its dominance, being followed in this station, by *T. muelleri* (18 %).

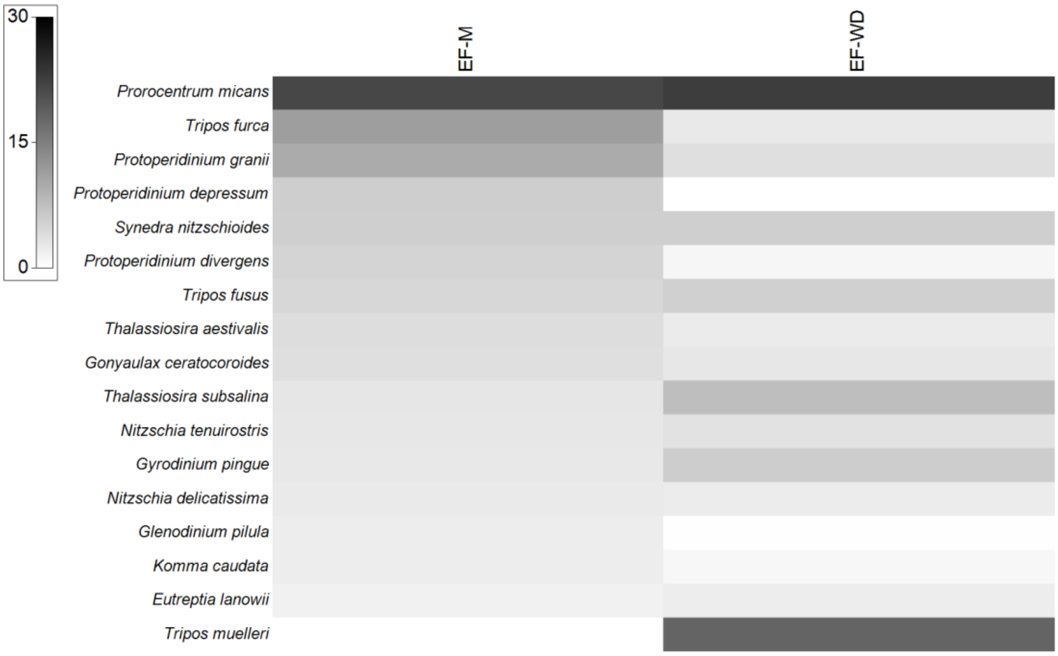


Figure 2.16 - Species average biomass matrix (%) and sampling stations (white spaces indicate the absence of the species at that site; the intensity of the grey scale is linearly proportional to the percentage of the total average biomass per station)

Port of Mangalia

A total of 80 species, varieties and forms were identified inside and outside Mangalia harbour belonging to 11 taxonomic classes (Annex C). The phytoplankton community was mainly composed of dinoflagellates – 33 species (41 % of the total number of species) and diatoms – 22 species (28 %). The classes Clorophyceae and Cyanophyceae contributed with 9 % each and Cryptophyceae with 5 %. The other classes (Dictyochophyceae, Ebriophyceae, Euglenoidea, Prasinophyceae, Prymnesiophyceae and Trebouxiophyceae) were represented only by 1-2 species. Among dinoflagellates species, genera Protoperidinium (5), Gymnodinium (4), Gyrodinium (4), Prorocentrum (2), Glenodinium (2), Tripos (3) were the most diverse. Among diatoms species, genera Thalassiosira (4) and Nitzschia (3) reached the highest diversity (Figure 2.17).

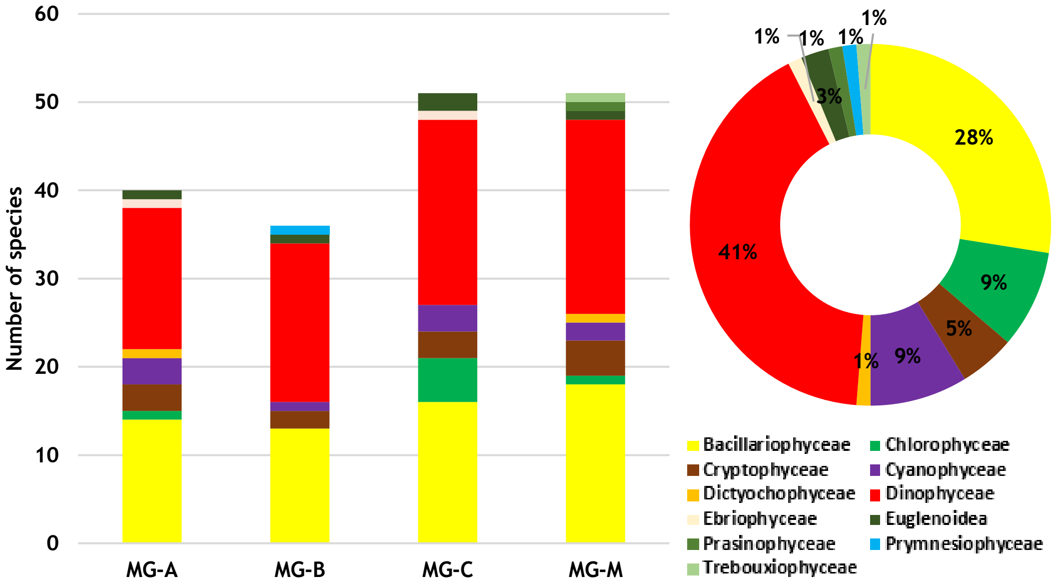


Figure 2.17 - Phytoplankton taxonomic composition - Port Mangalia, September 2019

The number of species varied between 36-40 inside and near the harbour basin (MG-B and MG-A, respectively) and 51 in the outer stations (MG-C and MG-M). This difference in diversity was due to the bloom of two diatoms, *Nitzschia delicatissima* and *N. tenuirostris* in the inner station, MG-A.

The average abundance of phytoplankton in the study area varied between 90.20·10^3 cells/L and 4 868·10^3 cells/L and the average biomass, between 168 mg/m^3 and 3 417 mg/m^3 (Figure 2.18), the highest values being found in the inner harbour station (MG-A) and the lowest in the outer one (MG- B).

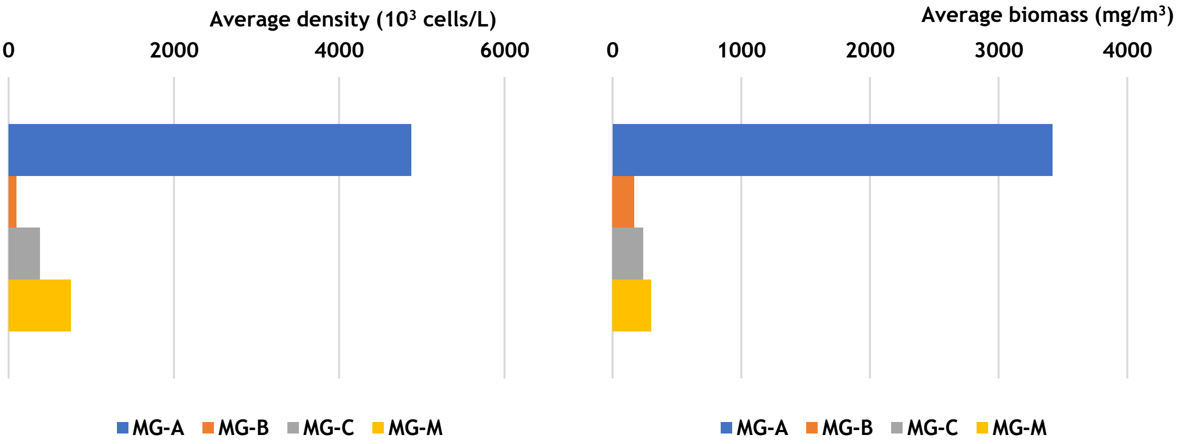


Figure 2.18 - Phytoplankton average abundance and biomass variation - Port Mangalia, September 2019

Phytoplankton communities' taxonomic structure around Mangalia harbour was featured by the dominance of diatoms (Bacillariophyceae) in the abundance (contributing up to 94 %) in all the stations and biomass, in the outside stations MG-M and MG-C (54 % and 58 %, respectively). The dinoflagellates represented most of the assembly biomass (60-75 %), in the stations inside (MG-A) and near the harbour (MG-B). Even though the contribution of the other classes was lower (1-7 % average biomass), in the average density, compared to the dinoflagellates they accounted together a similar contribution in MG-A and MG-B and a higher contribution (6 %) only in the outer station, MG-C. In the control, the other classes represented only 2 % (average density) (Figure 2.19).

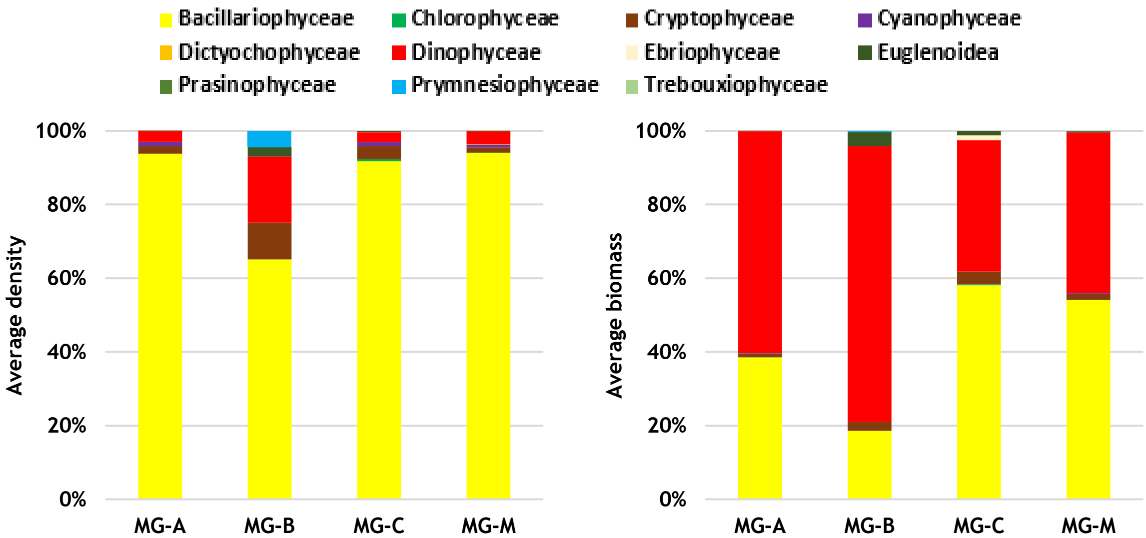


Figure 2.19 - Phytoplankton taxonomic structure based on average abundance and biomass - Port Mangalia, September 2019

The bulk of phytoplankton abundance was mainly represented by the development of a common group of diatoms (N. delicatissima, N. tenuirostris and Lennoxia faveolata) associated with dinoflagellates (*Prorocentrum cordatum, P. micans, Scrippsiella acuminata*) and the cryptophytes, *Komma caudata and Hillea fusiformis,* found in all the stations, in different percentages (Figure 2.20). Thereby, *N. tenuirostris* reached the highest contribution to density outside harbour (MG-C, 59 %), being followed by *L. faveolata* (18 %) and *N. delicatissima* (9 %). However, inside the harbour (MG-A), *N. tenuirostris* (56 %), along with *N. delicatissima* (34 %), formed a bloom of $4.37 \cdot 10^6$ cells/L. In the outer harbour station, MG-B, *N. tenuirostris* and *N. delicatissima* maintained their dominance in density even though their proportions were lower (34 % and 12 %, respectively). In the control station MG-M, the dominance was taken over by *L. faveolata* (39 %), being followed by *N. delicatissima* (29 %) and *N. tenuirostris* (23 %).

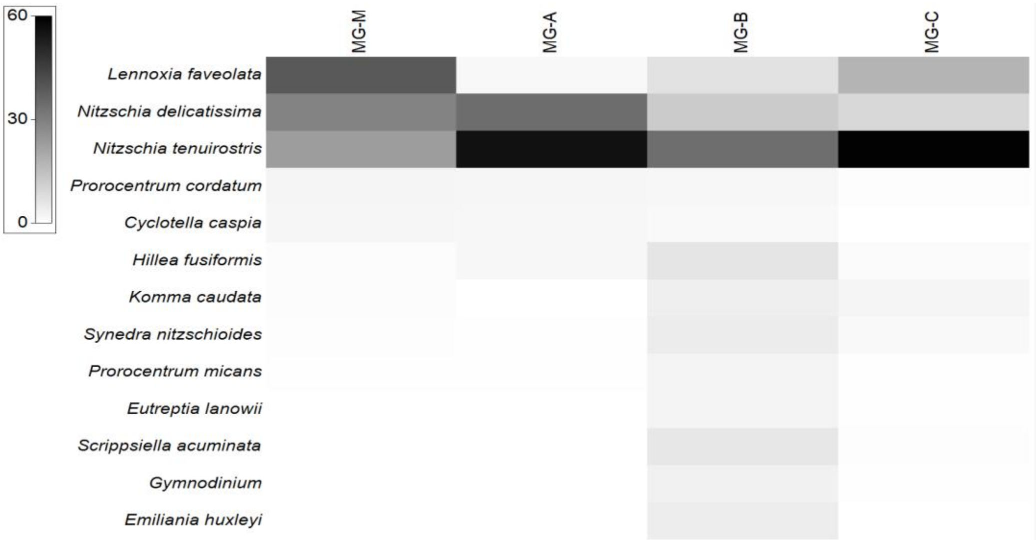


Figure 2.20 - Species average abundance matrix (%) and sampling stations (white spaces indicate the absence of the species at that site; the intensity of the grey scale is linearly proportional to the percentage of the total average abundance per station)

The phytoplankton community biomass in the control station (MG-M) was mainly composed of the diatoms *N. delicatissima* (18 %), *N. tenuirostris* (18 %) and *Lennoxia faveolata* (10 %) associated with the dinoflagellates, *Prorocentrum micans* (16 %), *P. cordatum* (6 %), *Tripos muelleri* (5 %) and *Protoperidinium granii* (4 %). Inside harbour (MG-A), the community was mainly represented by the dinoflagellate *Protoperidinium depressum* (48 %) along with *N. tenuirostris* (24 %) and *N. delicatissima* (12 %). In the outer station, MG-B, it was maintained the dominance of the dinoflagellates, but there were other species involved, such as *P. micans* (29 %), *Protoperidinium granii* (18 %), *Scrippsiella acuminata* (8 %) and *Tripos furca* (6 %), being followed by diatoms, of which the most important were *Thalassiosira aestivalis* (6 %), *N. tenuirostris* (6 %) and *Synedra nitzschioides* f. *nitzschioides* (2 %). The situation met in the outer station, MG-C, might be comparable with MG-M, where the diatoms represented over 50 % of the total biomass, even though the proportions of the species was slightly different (Figure 2.21).

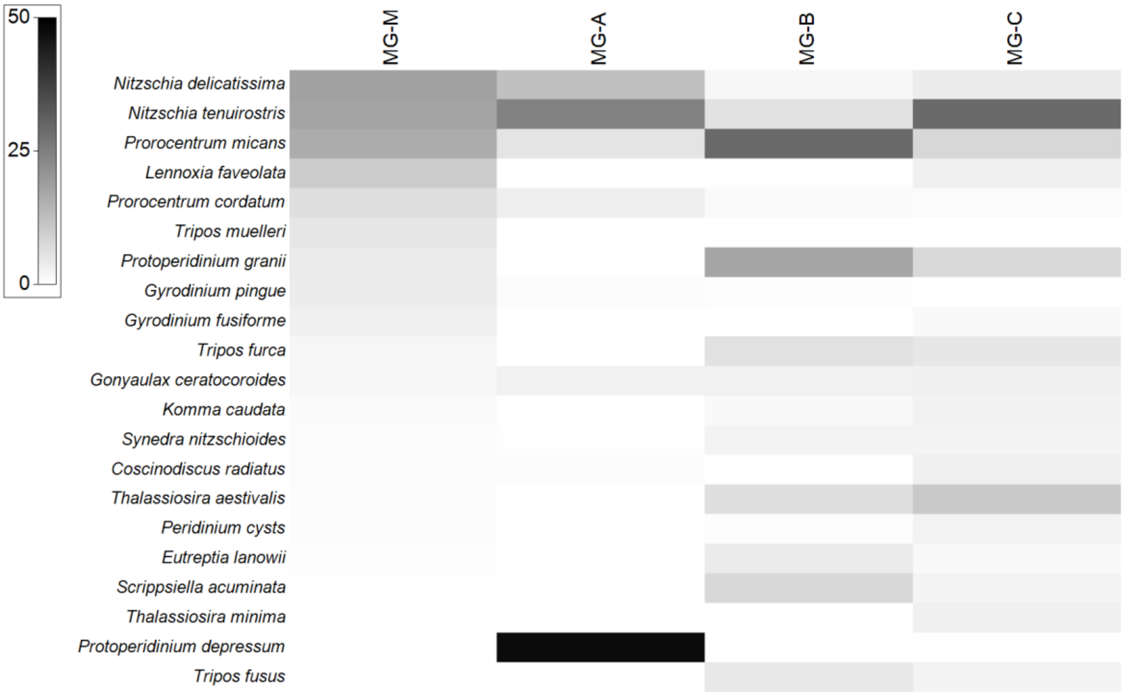


Figure 2.21 - Species average biomass matrix (%) and sampling stations (white spaces indicate the absence of the species at that site; the intensity of the grey scale is linearly proportional to the percentage of the total average biomass per station)

Conclusions

The analysis of the phytoplankton community in ports of Midia, Constanta and Mangalia and the Eforie wastewater discharge pipeline stations pointed out that:

The highest diversity was found in the less polluted areas/in the furthest stations from the port, both in the northern (control stations from Constanta and Mangalia) and southern areas (stations C from Midia and Mangalia) and in the Eforie wastewater discharge station.

A bloom event was noticed in the inside Mangalia harbour, caused by the development of the diatoms *Nitzschia tenuirostris* ($3.72 \cdot 10^6$ cells/L and 1 142 mg/m^3) and *N. delicatissima* ($2.75 \cdot 10^6$ cells/L and 695 mg/m^3) which recorded the highest values in the surface layer (0 m). Even though these diatoms were dominant in density, the dinoflagellate *Protoperidinium depressum* (3 260 mg/m^3) represented 57 % of the total biomass in the surface layer (0 m). In Midia, Constanta and Eforie stations the average density and biomass values were lower (up to $258 \cdot 10^3$ cells/L and 468 mg/m^3).

Some of the dominant species (*N. delicatissima*, *Prorocentrum cordatum* and *Gonyaulax ceratocoroides*) are listed as harmful in IOC-UNESCO Taxonomic Reference List of Harmful Micro Algae (Moestrup *et al.*, 2009) and *Prorocentrum micans* is recorded as an eutrophication indicator (Dorgham et al., 1987). These species were distributed along the entire study area, but they reached their maximum development inside harbours.

2.1.3 Turkey

In July 2019, a total of 53 species were identified in the study area, from 6 taxonomic classes (Annex C). The bulk of the species pool was composed of Dinoflagellates (37), 16 genera (70 % of the total) among which the genus *Protoperidinium* (12), *Prorocentrum* (5) and *Dinophysis* (4) were the most diverse species. Among diatoms (14 species, 8 genera), the genus *Chaetoceros* (4 species) along with genus *Coscinodiscus* showed the highest species richness. Also, a few species belonging to the classes Prymnesiophyceae and Dictyochophyceae have been identified in the study area (Figure 2.22).

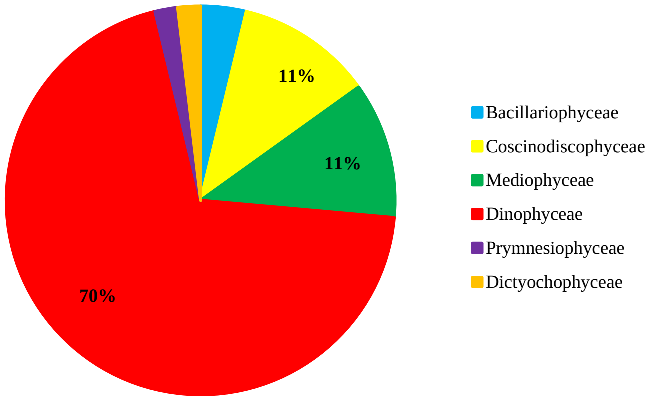


Figure 2.22 - Proportional distribution of phytoplankton classes, July 2019

Species belonging to 11 classes have been recorded in January 2020. A total of 52 species were determined 43 % was represented by dinoflagellates, 40 % by diatoms and 17 % by the other classes. From dinoflagellates, the genus *Protoperidinium* (7), *Tripos* (4), *Dinophysis* (3) and *Prorocentrum* (3) were the most diverse. Among diatoms, the genus *Chaetoceros* (7) showed the highest species richness. Also, a few species belonging to the classes Prymnesiophyceae, Cyanophyceae, Cryptophyceae, Dictyochophyceae, Noctilucophyceae, Trebouxiophyceae and Thecofilosea have been identified in the study area (Figure 2.23).

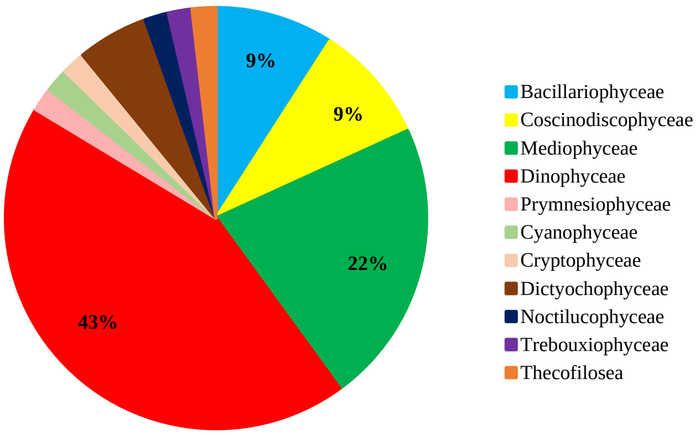


Figure 2.23 - Proportional distribution of phytoplankton classes, January 2020

In July 2019, the average total abundance of phytoplankton for the entire area varied between $5.1 \cdot 10^3$ cells/L and $2.7 \cdot 10^4$ cells/L and the average biomass between 127.26 mg/m^3 and 435.01 mg/m^3. Dinoflagellates dominated 71 % of the total phytoplankton biomass sampled from all depths. 35 % of the total phytoplankton abundance obtained from all depths was dominated by dinoflagellates. The highest abundance value was registered at the station SN01 (located at eastern nearshore). It was observed that *Emiliania huxleyi* was dominant in this sampling station. Also, this species was shown to be dominant in all other sampling stations. However, it was found that the diatom abundance values in this sampling period are low (Figure 2.24).

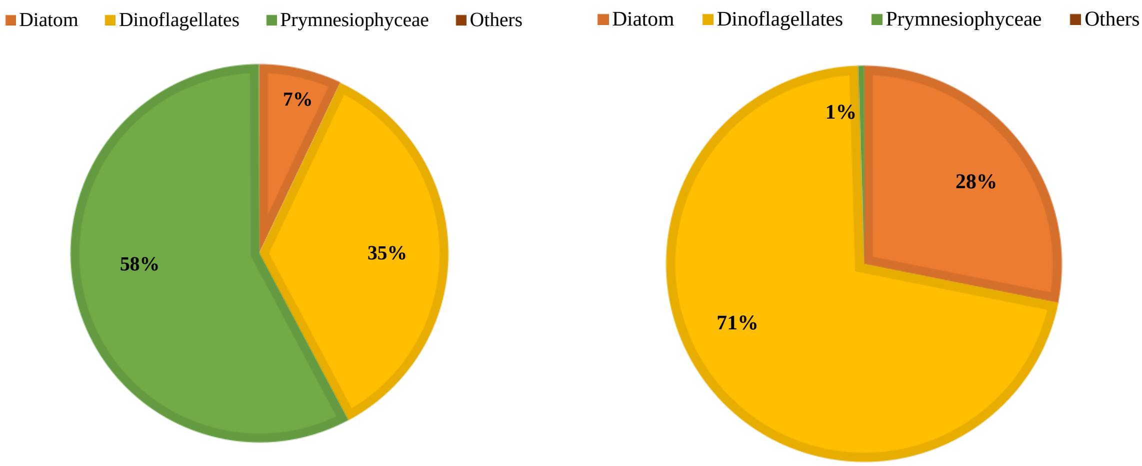


Figure 2.24 - Phytoplankton taxonomic structure based on average abundance (Left) and biomass (Right), July 2019

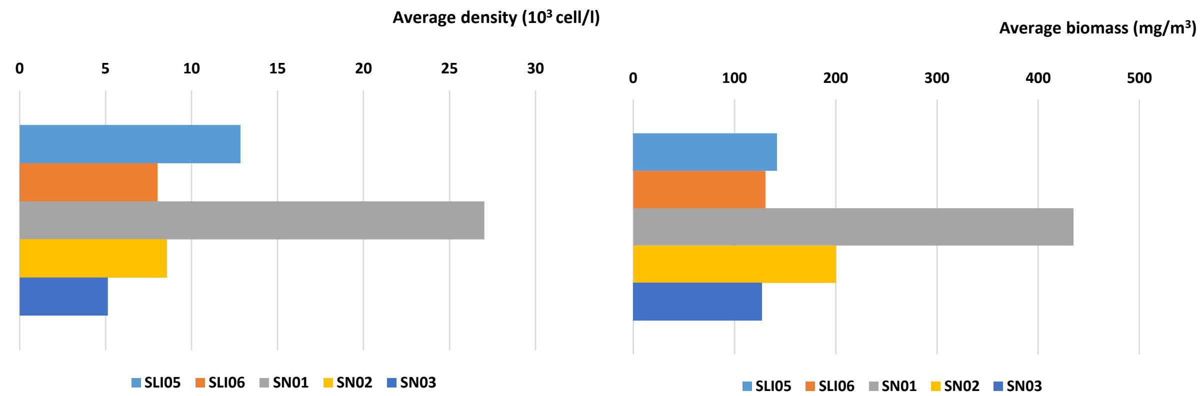


Figure 2.25 - Phytoplankton average abundance and biomass variation - July 2019

In January 2020, the average total abundance of phytoplankton for the entire area varied between $8.5 \cdot 10^3$ cells/L and $1.4 \cdot 10^4$ cells/L and the average biomass between 34.09 mg/m^3 and 96.11 mg/m^3. The highest phytoplankton abundance was at the station SN03. Also, *Prorocentrum cordatum* was observed to be dominant in stations SN03. However, *Emiliania huxleyi* were found to be dominant in other stations. *E. huxleyi* were found to be dominating 34 % of the total phytoplankton abundance of all depths of the sampling stations (Figure 2.26). When biomass was considered, it was found that the highest value of phytoplankton biomass was at the station SN01 (Figure 2.27). *Prorocentrum micans* was dominant in station SN01. Also, this species was shown to be dominant in stations SLI06, SN02 and SN03. Dinoflagellates dominated 67 % of the total phytoplankton biomass sampled from all depths of the stations (Figure 2.26).

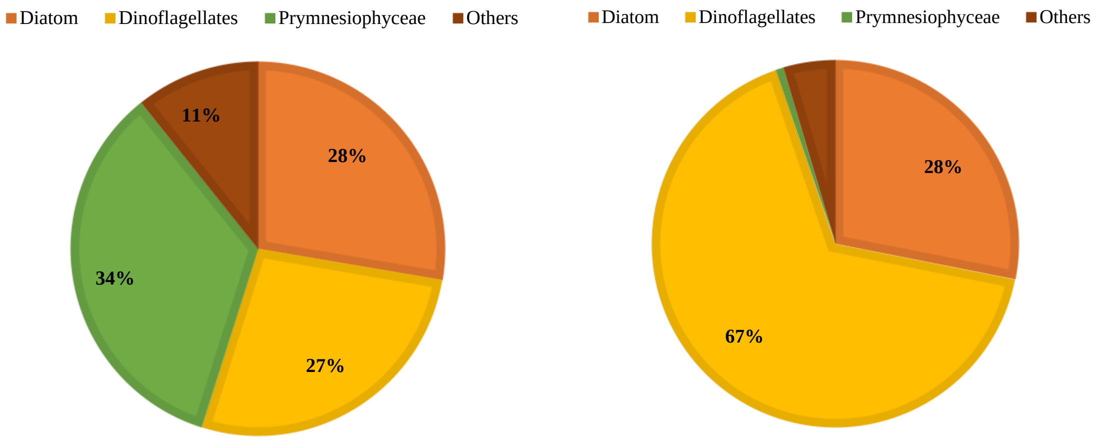


Figure 2.26 - Distribution (%) of average total abundance and total biomass of phytoplankton groups, January 2020

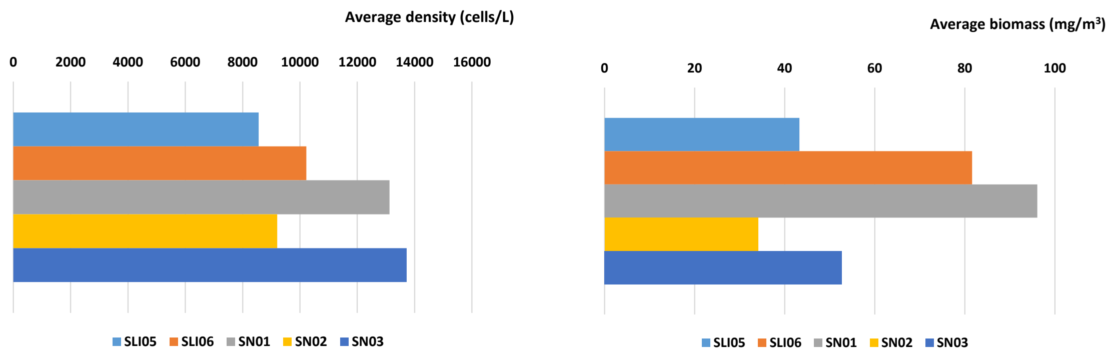


Figure 2.27 - Phytoplankton average abundance and biomass variation, January 2020

Environmental disturbance generated by human pressure may cause structural changes in communities and influence species biodiversity. SL stations, outside the port, are not affected by pollution inside the port and these stations represented by lower phytoplankton abundance and biomass values (compared to SN stations). This difference between the stations overlaps with the physicochemical results of the water, too.

2.2 Zooplankton

Zooplankton is an important part of marine ecosystems. It is an essential link in the food chain. In addition, due to the sensitivity of zooplankton organisms to environmental changes, the state and structure of the zooplankton community may indicate the state of the ecosystem. The Marine Strategy Framework Directive (Directive 2008/56/EU) of the European Union defines zooplankton as an essential component of the assessment of the ecological state of water bodies. Various indicators of marine zooplankton can provide valuable information on ecological processes that are important for the quality of life and economies of coastal countries. The state of zooplankton and its structural characteristics are of particular interest, because, in contrast to short-cycle phytoplankton, which reflects mainly momentary changes, and long-cycle macrozoobenthos, which has a large inertia, zooplankton is the only one that reflects the state of the environment in the medium term.

Port environments are one of the vital habitats in the coastal ecosystem. They serve as gateways for the introduction of marine organisms and their larval forms. An estimate of the zooplankton standing stock can provide useful information on the biological production potential of the area and any changes in the water quality parameters will directly affect the abundance and composition of the zooplankton population (Gaonkar et al., 2010).

2.2.1 Ukraine

We identified 25 taxa belonging to the marine and freshwater complex (Annex C). Species diversity was based on copepods (7) and cladocerans (5). Meroplankton organisms were represented by 7 taxa. Non-forage zooplankton was represented by jellyfish (2). The rest of the taxa (4) did not significantly contribute to the diversity. The taxonomic structure of the zooplankton community of Odessa region "hot spots" is shown in Figure 2.28. The Shannon-Weaver index was 2.29 bit/ind. near the port of Chornomorsk and 1.75 bit/ind. near the WWTP Odessa "South".

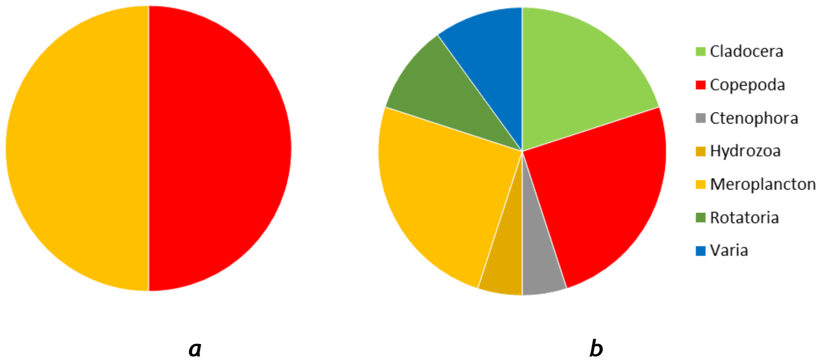


Figure 2.28 - Taxonomic structure of zooplankton community in the place of discharge from WWTP Odessa "South" (a) and the place of discharge from WWTP city and port Chornomorsk (b), September 2019

The zooplankton abundance and biomass in the port of Chornomorsk (22616 ind./m^3 and 402.476 mg/m^3) were medium and on WWTP Odessa "South" were rather low (540 ind./m^3 and 5.202 mg/m^3). According to the indicator of zooplankton biomass, the ecological state of the environment may be assessed as "Bad". According to the indicator of the Shannon-Weaver index, the ecological state of the environment may be assessed as "High". We did not find *N. scintillans* in samples from both "hot spots", which corresponds to the "High" ecological status class. The contribution of Copepods in total biomass in the place of discharge from WWTP Odessa "South" was 94.06 %, in the place of discharge and port Chornomorsk 50.55 %, which corresponds to "High" ecological status class, on both stations.

Generally, the ecological state of the environment on both "hot spots" may be assessed as "Good". So, we may conclude that in the autumn, in the "hot spots" of the Odessa region, the poly-dominant complex of zooplankton with high Shannon biodiversity index and rather low biomass developed. The state of the marine environment there may be assessed as "Good". However, for a more complete picture, it is necessary to carry out year-round monitoring and assessment of the water area based on long-term observations, especially in the summer, when the load on wastewaters treatment stations increases significantly due to the hot weather and many tourists.

2.2.2 Romania

2.2.2.1 Microzooplankton

A total number of 13 species of tintinnids (6 indigenes and 7 non-indigenes), belonging to five families, were identified in Romanian coastal waters (Annex C). The highest biodiversity (13) was recorded in the Constanta profile, while in the WWTP Eforie area was recorded the lowest diversity (Figure 2.29). Variations of the number of species between the two analysed layers, 0 m and 10 m, were recorded only in the WWTP Eforie and Mangalia areas where a decrease from surface to depth was registered.

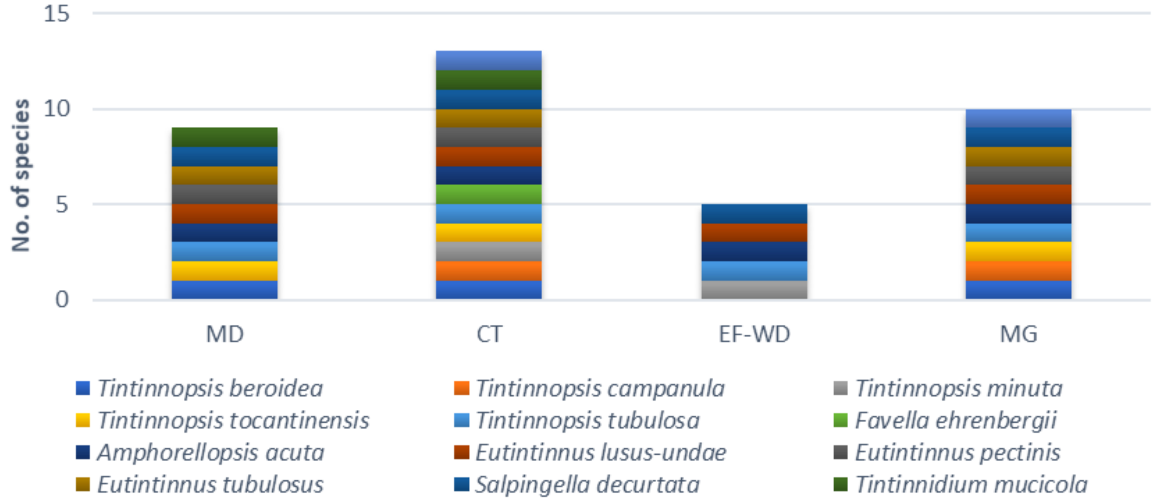


Figure 2.29 - The diversity of tintinnids from investigated area

10 species of tintinnids have been identified in the Midia area of which 6 are non-indigenous (Annex C). The species that dominated the community of tintinnids, both in surface and 10 m layers, is a non-indigene one - *Amphorellopsis acuta* . *A. acuta* recorded density and biomass means of 55 ind/L and 0.45 µgC/L in the 0 m layer and 38 ind/L and 0.31 µgC/L in the 10 m layer, respectively. The highest diversity and abundance of tintinnids is recorded in the MD-C station and it is a positively correlated with transparency (Figure 2.30).

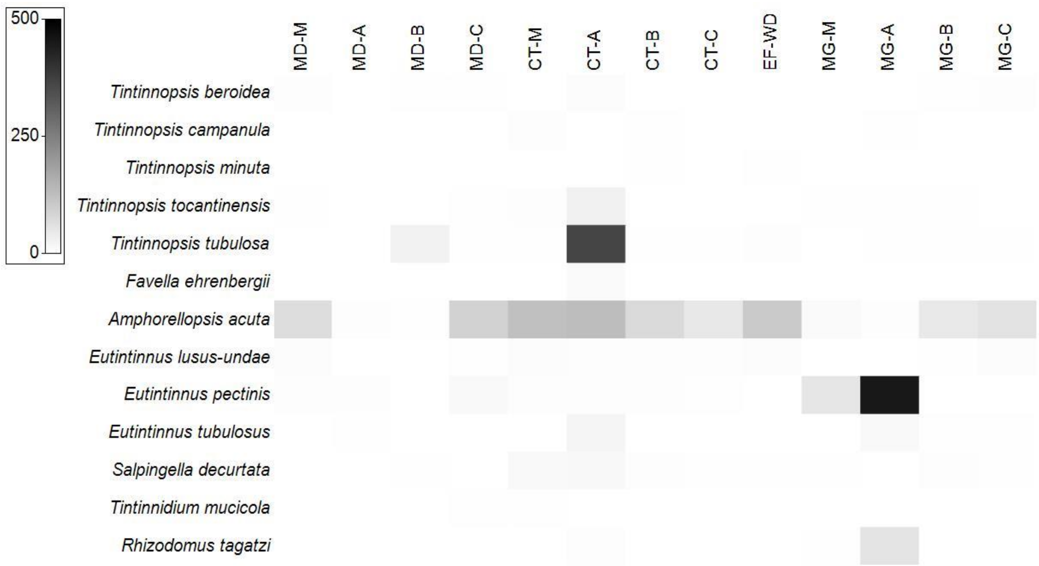


Figure 2.30 - Shade plot (Primer 7) showing quantitative (ind/L) structure of tintinnids community from the Romanian Black Sea

Inside the Midia harbour (MD-A) was recorded the lowest abundance and diversity from the entire investigated area. The situation is correlated with lower oxygen values, respectively with higher biochemical oxygen consumption, and higher concentrations of heavy metals and hydrocarbons (Figure 2.31).

Constanta area is characterized by a total of 13 species of tintinnids of which seven are non-indigenous. The species with higher abundance in this area are the *Tintinnopsis tubulosa* and *Amphorellopsis acuta* (Figure 2.31). The highest diversity and abundance of tintinnids was recorded in the CT-A station (inside the harbour). The situation from the CT-A station was correlated positively with higher transparency and large nutrients concentrations (nitrates, silicates, and phosphates) and chlorophyll *a*.

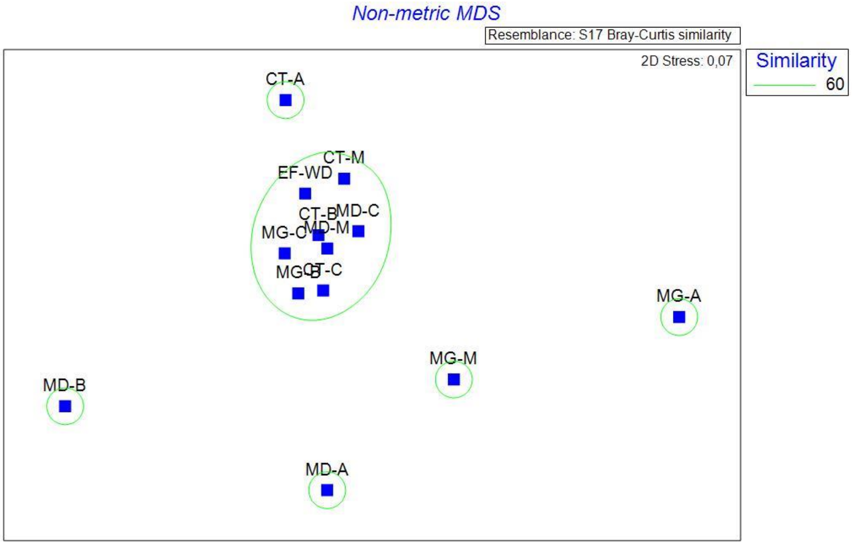


Figure 2.31 - Non-metric multidimensional scaling ordination based on the similarity between stations

The WWTP Eforie area is characterized by a total of five species of tintinnids (Annex C) being the area with lower diversity. The species that dominated the community of tintinnids is *Amphorellopsis acuta* in both, surface, and 10 m layer. *A. acuta* recorded mean densities and biomasses of 106 ind/L and 0.87 µgC/L (0 m) and 100 ind/L and 0.83 µgC/L (10 m), respectively (Figure 2.30).

The Mangalia profile is characterized by a total of 11 species of tintinnids, including all 7 non-indigenous (Annex C). The species which dominated quantitatively the community of tintinnids was the non-indigenous one *Eutintinnus pectinis* in both analysed layer. *E. pectinis* recorded density and biomass mean values of 359 ind/L and 1.25 µgC/L in 0m layer and 141 ind/L and 0.49 µgC/L in the 10 m layer, respectively. The highest mean density and biomass of tintinnids is recorded in the MG-A station (Figure 2.31) and was correlated positively with large quantities of nitrates, silicates, phosphates, and chlorophyll *a*.

Conclusions

In September 2019, in the Romanian Black Sea, 13 species of tintinnids (6 indigenes and 7 non-indigenes) were identified (Annex C).

The highest biodiversity (13 species) was recorded in the Constanta area, while the WWTP Eforie area recorded the lowest diversity (5 species) with the mention that there only one station was tested compared to 4 stations, for each other analysed area. Regarding the number of species from the analysed layers, there is registered a vertically decrease in the WWTP Eforie and Mangalia areas.

The lowest abundance of the microzooplankton tintinnids was recorded inside of Midia harbour and was correlated with lower oxygen values, respectively with a higher level of heavy metals and hydrocarbons in the area. The highest abundance was recorded inside the Constanta and Mangalia harbours and was correlated positively with large quantities of nitrates, silicates, phosphates, and chlorophyll *a*.

The tintinnids community are dominated by three species - *Amphorellopsis acuta (*Midia and Eforie Waste Discharge area*)*, *Eutintinnus pectinis* (Mangalia area) and *Tintinnopsis tubulosa* (Constanta area). Also, *Amphorellopsis acuta* recorded the highest frequency in the sample from all Romanian area this fact being in agreement with the ecology of the species.

The mean density of the tintinnids community, varied between 5-106 ind/L in the surface layer and 2-72 ind/L in the 10 m layer. The mean biomass of the tintinnids community, varied between 0.03-0.42 µgC/L in the surface layer and 0.01-0.51 µgC /L in the 10 m layer.

The presence of 7 species of tintinnids newly introduced in the Black Sea basin (*Tintinnopsis tocantinensis, Amphorellopsis acuta, Eutintinnus lusus-undae, E. pectinis, E. tubulosus, Salpingella decurtata* and *Rhizodomus tagatzi*) but also the tendency to enrich the microzooplankton component from the last decades with new non-indigene species (Gavrilova & Dolan, 2007, Gavrilova & Dovgal, 2016, Gavrilova, 2017, Selifonova & Makarevich, 2018, Tabarcea, 2019), can make this component an indicator of the assessment of the marine good environmental status, that corresponds to the descriptor D2 (D2C1 criteria).

2.2.2.2 Mesozooplankton

Port environments are one of the vital habitats in the coastal ecosystem. They serve as gateways for the introduction of marine organisms and their larval forms. An estimate of the zooplankton standing stock can provide helpful information on the area's biological production potential, and any changes in the water quality parameters will directly affect the abundance and composition of the zooplankton population (Gaonkar et al.,2010).

Regarding the mesozooplankton's qualitative structure, we identified a total number of 19 species (Annex C); Copepoda represented seven species, followed by the meroplanktonic component with five species. The nonfodder component, represented by *Noctiluca scintillans,* appeared in all the analysed samples, reaching higher density values in MG-A and MD-C in the other stations recording lower densities. *Oithona similis* recorded the highest densities from the Copepoda group, with the peak in stations MD-A and MD-C. The cyclopoid *Oithona spp*. has been described as being eurythermal, euryhaline and omnivorous, being adapted to a wide range of habitats (Hansen et al., 2004), maintaining their populations even under adverse conditions (Drira et al., 2018).
Another copepod with high densities was *Acartia clausi*, showing high densities in stations MD-A and MD-M. Cladocerans represented four species, from which *Penilia avirostris* and *Pleopis polyphemoides* recorded the highest abundances.
Temporal distribution of marine cladocerans is discontinuous, recording high abundances from early spring to late summer, in winter recording a rapid decline and even absence from the mesozooplankton component (Pestoric et al., 2010). They are sensitive to disturbance, like eutrophication due to anthropogenic pressures such as urbanization, domestic and industrial pollutants, sewage disposal (Buyukates et al., 2007).
The meroplanktonic component reached high densities, Bivalvia and Balanus being dominant in the area. Other groups, represented by two species, recorded the lowest density values (Figure 2.32).

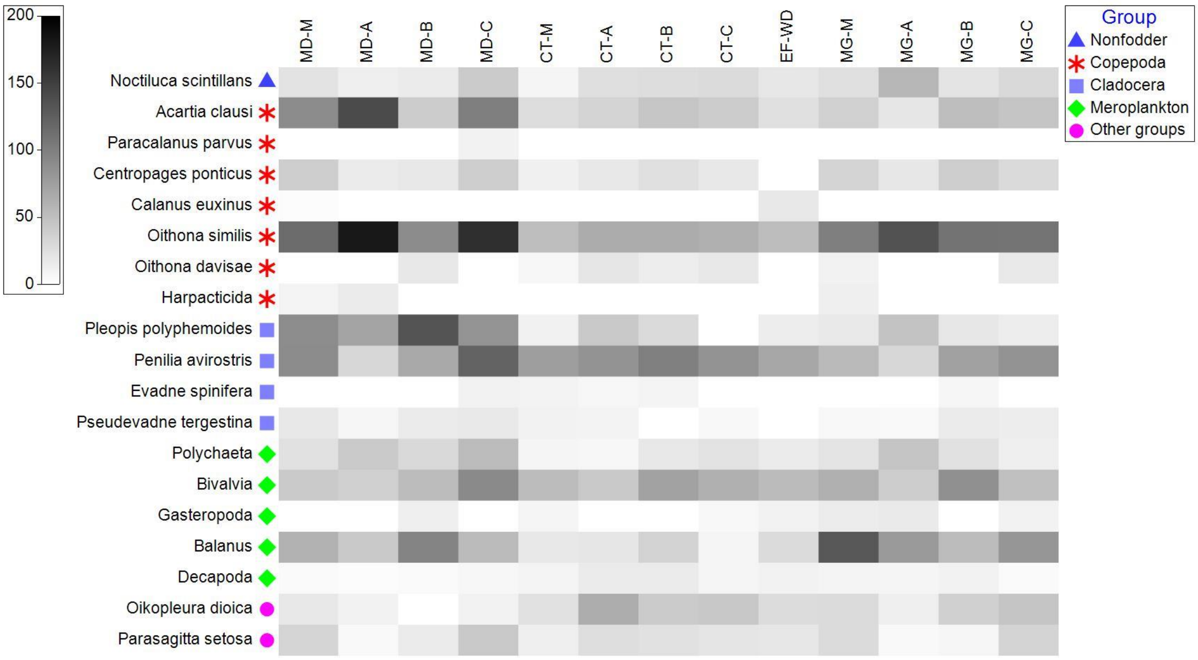


Figure 2.32 - Mesozooplankton's densities

The Shannon diversity index (H') is used to characterize species diversity, richness, and evenness of the community's species. In biological communities, the Shannon-Wiener diversity index varies from 0 to 5; values less than 1 indicating "heavily polluted" condition, values in the range of 1 to 2 being characteristics of "moderate" polluted condition, values above 3 showing "stable" environmental conditions (Shah et al., 2013).

Considering the Shannon index calculated for samples collected from the harbour areas of the Romanian Black Sea coast, values ranged from 1.3 to 2, which indicate "moderate" pollution; the highest value occurred in MD-C while the lowest in MD-A, where HCB had the highest concentrations. None of the values showed a stable environment (Figure 2.33).

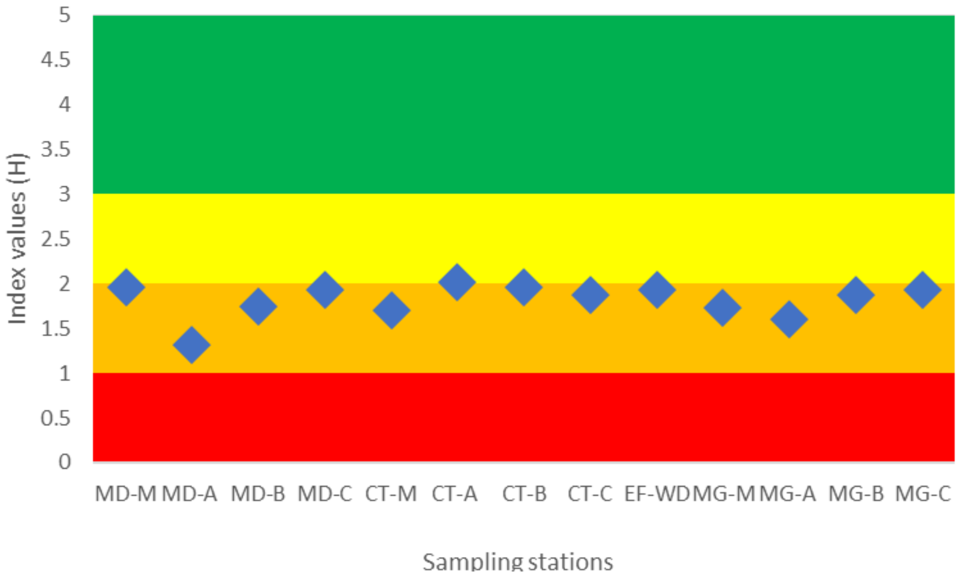


Figure 2.33 - Shannon diversity index

The fodder component was dominant in the mesozooplankton's community structure, the highest densities occurring in MD-C and the lowest in CT-M. The nonfodder component represented by *Noctiluca scintillans* recorded low densities, with an outburst in MG-A, where ammonium concentrations were the highest. High concentrations of ammonium may have been due to nutrient generation by *Noctiluca scintillans*, generated by the high levels of ammonia contained in their vacuoles (Mohamed et al., 2007) (Figure 2.34).

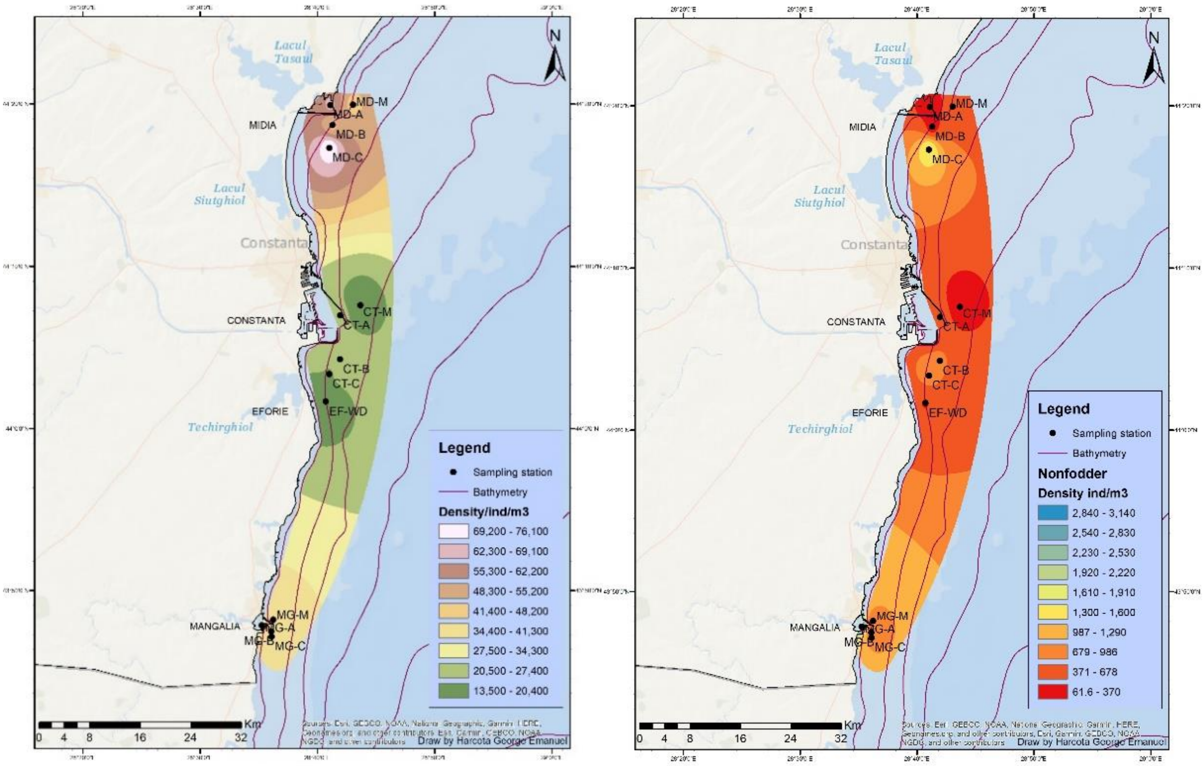


Figure 2.34 - Distribution of fodder (right) and nonfodder (left) zooplankton densities

Analysing the nonmetric multidimensional scaling (nMDS) for the fodder and nonfodder densities, similarities of 80 % were observed between the stations. An outlier arose in the stations CT-M and EF-WD, driven by the lowest mesozooplankton densities (Figure 2.35).

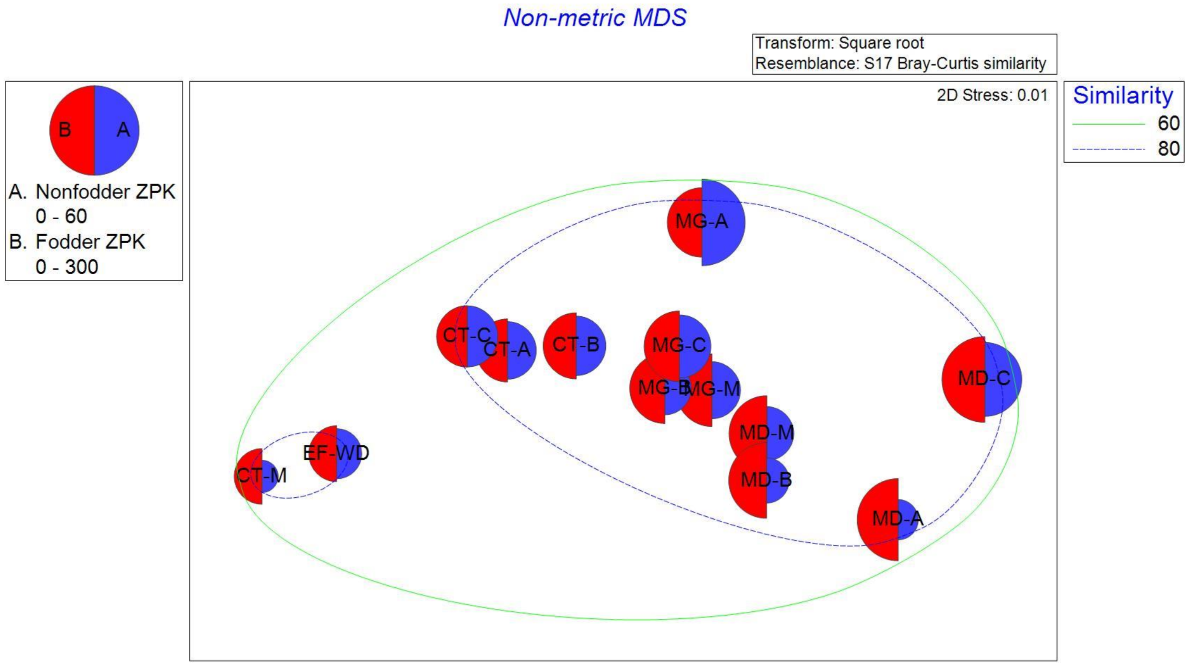


Figure 2.35 - Non-metric multidimensional scaling (NMDS) ordination based on fodder and nonfodder densities

As far as the fodder component is concerned, Copepoda represented the community's bulk, contributing 33.25 % to the mesozooplankton community with the maximum densities in MD-A and MD-C. Cladocera contributed with 29.06 % with maximum values in MD-B, being followed by the meroplanktonic component (27.29 %) (Table 2.1) with the peak recorded in MG-M (Figure 2.36).

Table 2.1 SIMPER -Group contribution based on mesozooplankton densities

Group	Av. Abund.	Av. Sim	Sim/SD	Contrib. (%)	Cum. (%)
Copepoda	118.04	26.03	4.43	33.25	33.25
Cladocera	93.31	22.75	4.59	29.06	62.31
Meroplankton	88.29	21.36	4.99	27.29	89.59

Similarities (80 %) in the fodder component structure were recorded for the stations, samples from Constanta and Eforie forming a cluster, while samples from Midia and Mangalia formed another one (Figure 2.36). The outlier was inside Midia harbour (station MD_A), where the copepods were the most abundant and HCB recorded the highest value.

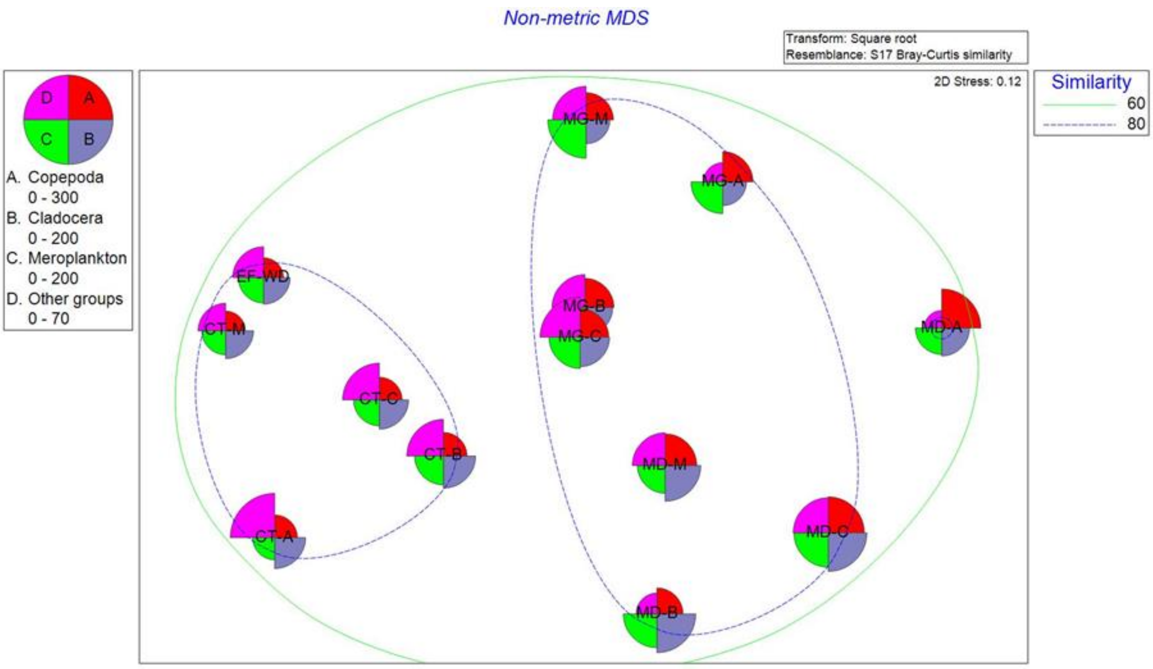


Figure 2.36 - Non-metric multidimensional scaling (NMDS) ordination based - fodder densities

Conclusions

Oithona similis, a cyclopoid species that can maintain its population even under anthropogenic pressures, were the most abundant.

Copepoda, followed by Cladocera and meroplanktonic components, were the significant contributors to the mesozooplankton community.

Shannon-Wiener diversity index recorded variations, indicating “moderate” pollution in the area under study.

Noctiluca scintillans was dominant, the fodder component recording low densities. High concentrations of ammonium also occurred in the station with *N. scintillans* higher proliferation, which might become a pressure for eutrophication (D5).

Samples inside Midia harbour represented an outlier driven by the persistent organic pollutants (HCB high concentration). Thus, in this station, the Shannon index recorded the lowest value, and Copepoda recorded an outburst.

2.2.3 Turkey

In total, 22 mesozooplankton taxa were identified in Samsun port-WWTP sampling stations. Eight species of the subclass Copepoda (*Acartia (Acartiura) clausi* (Giesbrecht, 1889), *Acartia (Acanthacartia) tonsa* Dana, 1849, *Acartia* sp. Dana, 1846 *Calanus euxinus* (Hulsemann, 1991), *Centropages ponticus* (Karavaev, 1895), *Oithona davisae* (Ferrari F.D. & Orsi, 1984), Oithona similis (Claus, 1866), *Paracalanus parvus* (Claus, 1863) and *Pseudocalanus elongatus* (Boeck, 1865), three species of the superorder Cladocera (*Penilia avirostris* (Dana, 1849), *Pleopis polyphemoides* (Leuckart, 1859) and *Pseudevadne tergestina* (Claus, 1877)), one species of the phylum Chaetognatha *(Parasagitta setosa* (Müller, 1847)), one species of the class Appendicularia (*Oikopleura (Vexillaria) dioica* Fol, 1872)), and seven groups belonging to meroplankton were found.

Mesozooplankton average abundance and biomass values were higher in July 2019 (5386 ind/m^3 and 128 mg/m^3) than in January 2020 (1891 ind/m^3 and 29 mg/m^3). The mean abundance was approximately 3 times and the mean biomass more than 4 times higher in summer compared to winter.

The mesozooplankton abundance and biomass values varied between 3652 ind/m^3 (Station SLI06) and 7020 ind/m^3 and 72 mg/m^3 (Station SLI06) and 198 mg/m^3 (Station SLI05) in July 2019, 1156 ind/m^3 (Station SN02) and 4036 ind/m^3 (Station SLI05) and 15 mg/m^3 (Station SN03) and 66 mg/m^3 (Station SLI05) in January 2020, respectively (Figure 2.37). The abundance was 4 times and biomass more than 6-10 times higher in summer compared to winter in Station SN. The abundance was 2 times and biomass 3 times higher in summer compared to winter in Station SLI.

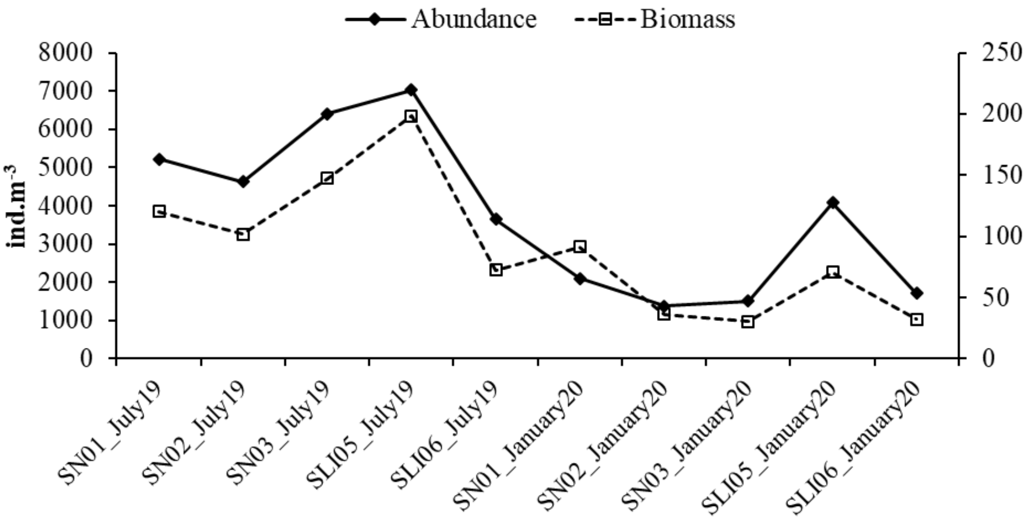


Figure 2.37 - The abundance (ind/m^3) and biomass (mg/m^3) values of mesozooplankton at sampling stations in Samsun port-WWTP sampling stations

In terms of relative mesozooplankton abundance and biomass, Copepoda had high percentages in all stations (abundance – 79 %, SN01, July 2019 – 92 %, SLI05, January 2020 and biomass – 66 %, SN01, January 2020 – 93 %, SLI05, January 2020) (Figure 2.38). *Acartia clausi*, *Acartia* sp. and *Centropages ponticus* made a high contribution to the Copepod biomass in July 2019, while *A. clausi* and *Paracalanus parvus* made a high contribution in January 2020.

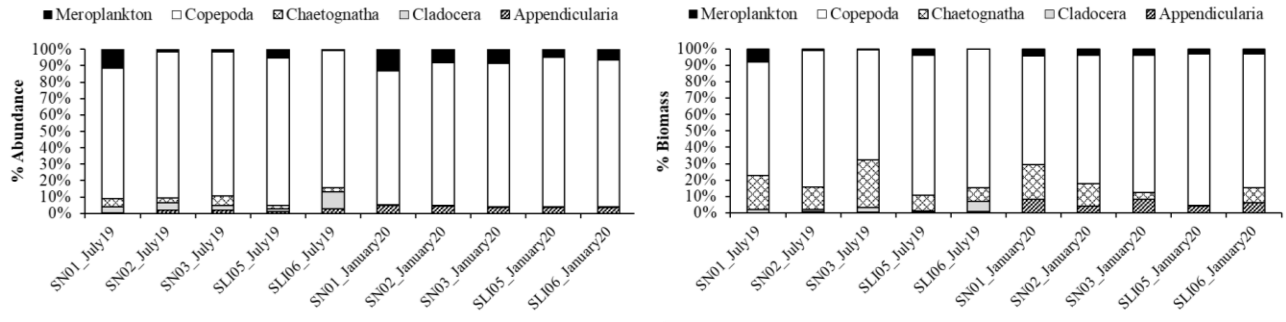


Figure 2.38 - The relative abundance and biomass of the mesozooplankton groups in Samsun port-WWTP sampling stations

The lowest number of taxa was recorded in January 2020 at SN01 and SN03 (10 taxa or groups) and the highest was recorded in July 2019 at the SN02 (18 taxa or groups). The maximum Shannon diversity index was found in July 2019 SLI05 (2.51). The minimum Shannon diversity index was determined in January 2020 (SLI05) (1.73). This decrease in diversity was due to the numerical dominance of *A. clausi* and *P. parvus* (Figure 2.39).

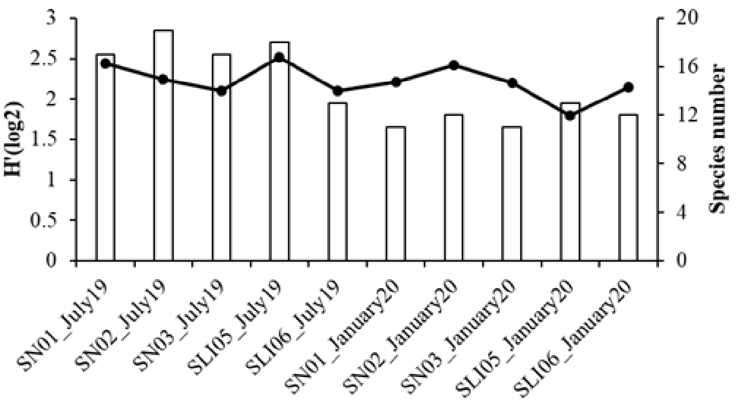


Figure 2.39 - The Shannon diversity index (H') for mesozooplankton for each month and sampling station (absent Noctiluca)

Noctiluca scintillans

The abundance and biomass values of *N. scintillans* varied between 2 ind/m^3 (SN02) and 10 ind/m^3 (SLI05) in and 0.2 mg/m^3 (SN02) and 1 mg/m^3 (SLI05) in July 2019; 46 ind./m^3 (SLI05) and 784 ind/m^3 (SN01) and 4 mg/m^3 (SLI05) and 69 mg/m^3 (SN01) in January 2020. This species was not present in samples from July 2019 in Station SN01, SN03 and SLI06. Abundance and biomass values of *N. scintillans* were higher in winter than in summer (Figure 2.40).

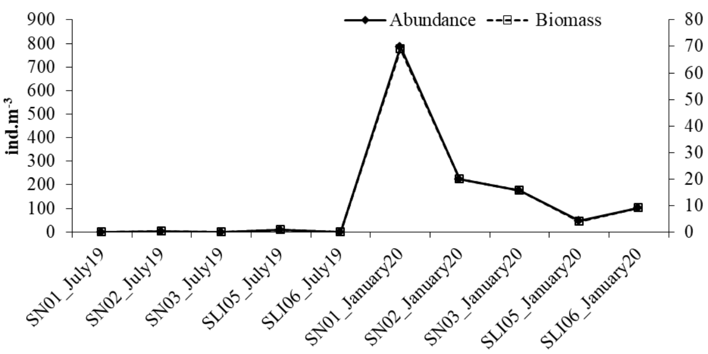


Figure 2.40 - The abundance (ind/ m^3) and biomass (mg/m^3) values of Noctiluca scintillans at sampling stations in Samsun port-WWTP sampling stations

Although zooplankton biomass values were low in the study period, July 2019 values were considerably higher than January 2020. Zooplankton biomass values of station SLI05 were higher than other stations values both in July 2019 and January 2020. The zooplankton biomass values at stations SLI06, SN01, SN02 and SN03 were very close to each other in both summer and winter. Since the zooplankton biomass values varied between 15 mg/m^3 and 198 mg/m^3, the ecological state of the environment may be assessed as "Bad".

The contribution of Copepoda biomass to total zooplankton biomass varied between 82-93 % in station SLI and between 66-84 % in station SN. The ecological state of the environment may be assessed as "High", on both stations and seasons.

The Shannon diversity index values were very close to each other. The summer values were slightly higher than the winter. Since the Shannon diversity index values varied between 1.7 and 2.5, the ecological state of the environment may be evaluated as "Moderate".

Although *Noctiluca scintillans* biomass values were low in the study period, July 2019 values were considerably lower than January 2020 values. *N. scintillans* biomass values were higher at SN stations than SLI stations in January 2020. According to *N. scintillans* values, the ecological state of the environment may be assessed as "High", on both stations and seasons.

2.3 Chemistry - water column

Nutrients

Inputs of nutrients to transitional, coastal, and marine waters from upstream catchments, atmospheric deposition and neighbouring waters may result in elevated nutrient concentrations or nutrient enrichment. The nutrient concentrations in seas vary considerably, both in time and in space. Over the year, the concentrations often build up over the winter period, then decline because of the spring bloom and are low for most parts of the summer and autumn periods. High nutrient concentrations are often found near large cities and where rivers discharge into the sea. Land-sea gradients are pronounced in some regions (EEA, 2019), like the Black Sea. The direct effects of nutrient enrichment are well documented and include accelerated growth of either phytoplankton in the upper part of the water column or perennial macroalgae in shallow coastal waters. The outcome of accelerated growth of phytoplankton is elevated phytoplankton biomass, usually measured as an elevated concentration of chlorophyll *a* in surface waters or as harmful algal blooms and subsequently the reduction in water clarity and light penetration. The indirect effects are reduced depth distribution of submerged aquatic vegetation, changes in the structure and functioning of benthic invertebrate communities, and oxygen depletion. Overall, the nutrients excessive input and their effects are defined as eutrophication which needs an integrated assessment essential in the process of pressures assessment and targets designation.

Contaminants

Contaminants are defined in the EU legislation as, "substances (e.g., chemical elements and compounds) or group of substances that are toxic, persistent and liable to bio-accumulate and other substances or group of substances which give rise to an equivalent level of concern" (Water Framework Directive, Article 2-29). This definition is like the hazardous substances defined in OSPAR and HELCOM and Barcelona Conventions. Safe chemical contaminant concentrations are an essential aspect of achieving healthy, biologically diverse, and productive seas in the MSFD context (Law et al. 2010). MSFD considers synthetic and non-synthetic contaminants. The non-synthetic contaminants are naturally occurring chemicals such as: trace metals found in the earth's crust, or polyaromatic hydrocarbons (PAH) which predominantly result from the combustion of fossil fuels and organic materials. Synthetic contaminants are man-made products such as polychlorinated biphenyls (PCBs), pesticides, brominated flame retardants, dioxins and organotins (e.g., tributyltin - TBT) and introduced into the marine environment through human activities. Contaminants adsorbed to particulate matter are deposited in the water column and stored in the sediment.

Metals fall into the category of non-degradable pollutants and, by this persistent character, can sometimes quite strongly alter the natural biogeochemical balance in contaminated environments. Processes that remove metals from seawater primarily include active biological absorption processes, but also passive deposition processes, i.e., the combined process of superficial adsorption on a wide variety of high-affinity surfaces associated with the particulate material, followed by particle deposition. Much of this particulate material (along with associated metals) is recycled either in the water column or in the superficial sediments. Weakly bound metals may be released from the surface of the depositing particles, replenishing the stock of dissolved metals. Marine sediments can also act as a source of metals by releasing them back into the water column. Primary flow processes between sediments and 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 can be substantial and long-lasting, even in the case of restoration efforts (Richir & Gobert, 2016).

Most of the persistent organic pollutants (POPs) do not occur in nature but are synthetic chemicals released because of anthropogenic activities. Despite their ban or restricted use, polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are among the most prevalent environmental pollutants and can be found in various environmental compartments. Vast amounts of POPs have been released into the environment and due to long-distance transport on air currents, POPs have become widespread pollutants and now represent a global contamination problem (Allsopp et al., 2001). They have different intrinsic physical-chemical properties, which dictate their environmental behaviour (Lohmann et al., 2007).

The input sources of PCBs and OCPs into aquatic environments include discharge of domestic sewage and industrial wastewater and runoff from nonpoint sources. Coastal areas are highly relevant in terms of POP cycling since they are highly populated and at the interface between open oceans and continents. It has been suggested that continental shelves are important global sinks of PCBs (Jonsson et al., 2003). Sediment resuspension has been identified as a key process capable of reintroducing POPs to the water column (Jurado et al., 2007) and this process could thus prevent POPs deposited to continental shelves from being considered permanent sinks.

The presence of PAH in the marine environment is largely attributed to oil spills, discharge and natural river infiltration, or atmospheric deposition. PAHs sorbet to atmospheric particles can settle on the surface of oceans by dry or wet deposition and there they are dispersed by currents (Hussein I. Abdel-Shafy & Mona S.M. Mansour, 2015). PAHs are mainly derived from the incomplete combustion of coal and oil, and wastewater discharge is one of the main channels for PAHs to enter the environment. Therefore, global increased human activity has increased risks to the marine environment (Latimer & Zheng, 2003). More than 100 different PAHs have been identified in environmental samples and 16 PAHs are generally measured in most exposure and environmental pollution studies.

2.3.1 Ukraine

2.3.1.1 Physical-chemical parameters

Salinity in the surface layer varied in the range 17.14 – 17.22 ‰, and in the bottom layer from 17.16 ‰ to 18.01 ‰ (Figure 2.41), which is typical for transitional waters (mesohaline marine type). The salinity increased with depth reaching its maximum in the bottom layer (18.5 m) at station 5.

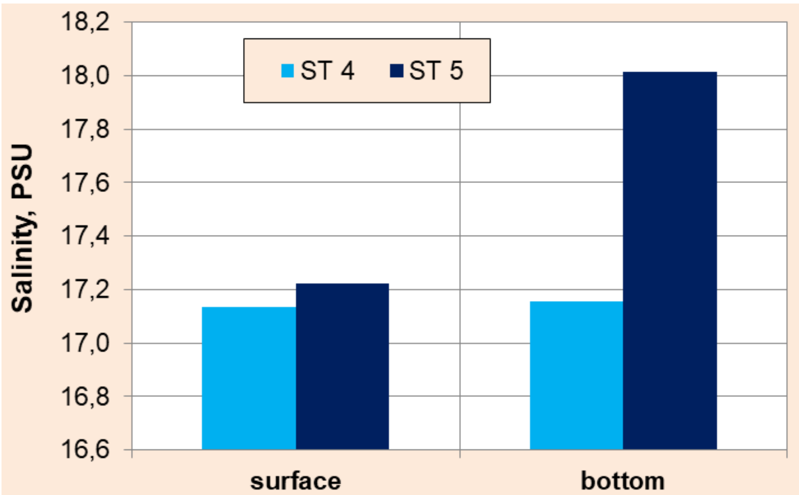


Figure 2.41 – Seawater salinity in the place of discharge from "Hot spots", September 2019

The content of **total suspended solids** (TSS) in seawater was maximum in the bottom layers on both stations 1 (St. 4 – 7.43 mg/L, St. 5 – 7.26 mg/L), while in the surface layer concentrations of TSS did not exceed 0.63 mg/L (Figure 2.42).

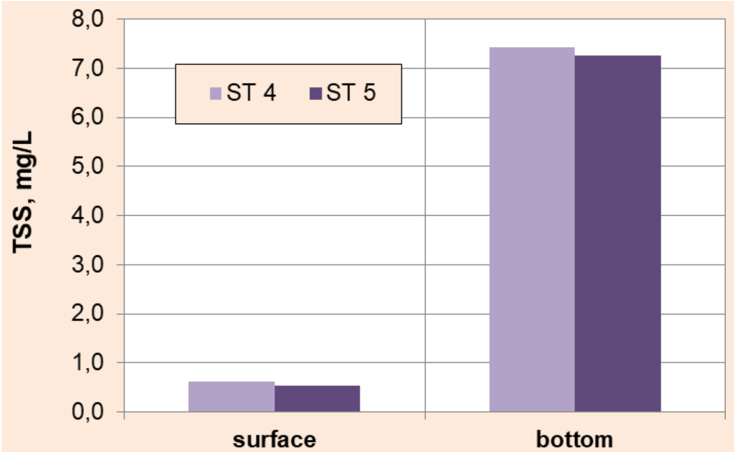
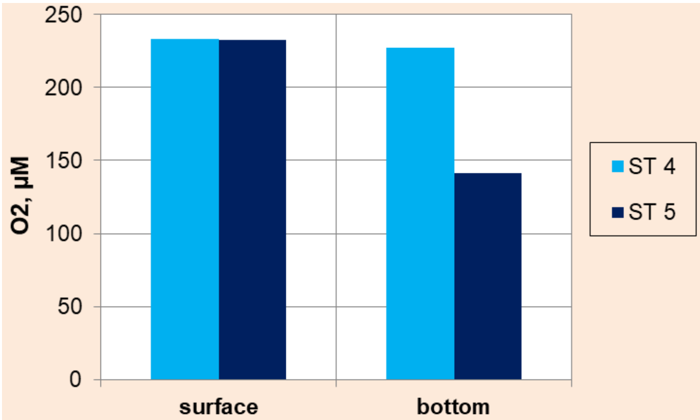
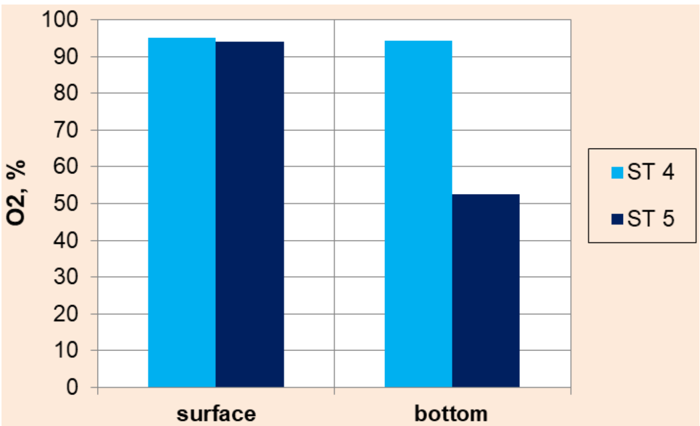


Figure 2.42 - Total Suspended Solids (TSS) content of the seawater in the place of discharge from "Hot spots", September 2019

The concentration of **dissolved oxygen** in the surface layer was similar (Figure 2.43a, Figure 2.43b), 233.1 µM (95.1 % saturation, St. 4) and 232.8 µM (95.1 % saturation, St. 5). In the bottom layer, the content of dissolved oxygen in station 4 decreased slightly and amounted to 227.2 µM (94.4 % saturation), while in the area of station 5 dropped to 141.6 µM (52.5 % saturation), which indicates the ongoing process of hypoxia at the place of wastewater discharge from the city of Odessa.



(a)



(b)

Figure 2.43 - Concentrations of oxygen dissolved (a) and saturation (b) in seawater in the place of discharge from "Hot spots", September 2019

2.3.1.2 Nutrients

Mineral forms of phosphorus in the surface layer are characterized by low concentrations from 0.10 μM (St. 5) to 0.13 μM (St. 4). In the bottom layer, the concentration of dissolved inorganic phosphorus in the area of discharge from the wastewater treatment plant "South" (St. 5) was 0.50 μM, which is 5 times higher than in the area of discharge from the WWTP of the city and port "Chornomorsk".
Concentrations of total phosphorus in the study areas were approximately the same in the surface layer and amounted to 0.68 μM (St. 5) and 0.71 μM (St. 4). In the bottom layer, the total phosphorus content was higher in station 5 (0.65 μM).
The predominant form of phosphorus in the surface layer at both stations is its organic component, while in the bottom layer at station 5, the mineral one predominates (Figure 2.44).

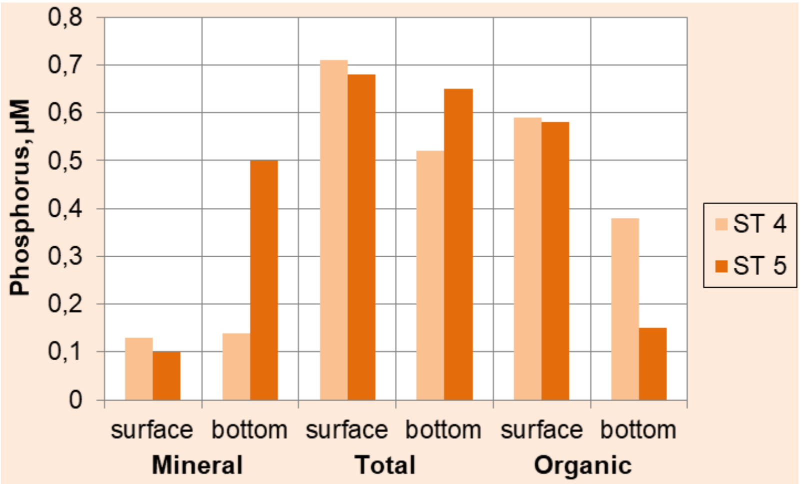
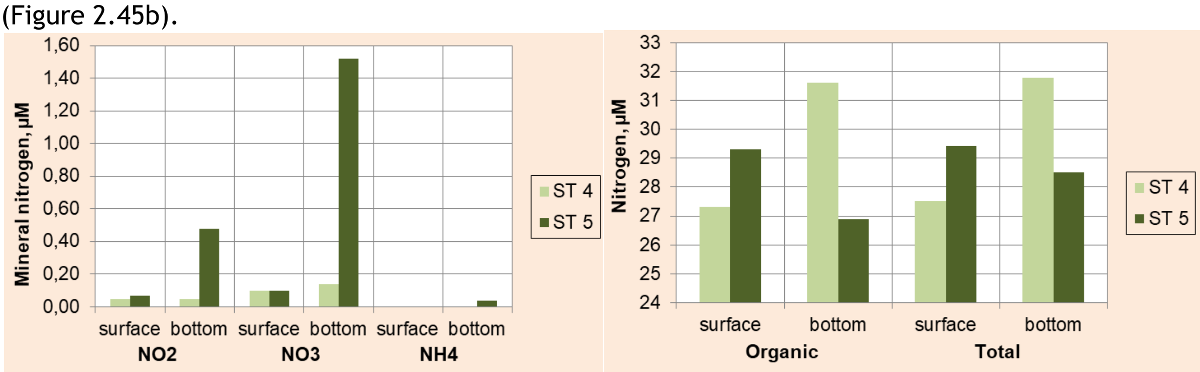


Figure 2.44 - Forms of phosphorus in seawater in the place of discharge from "Hot spots", September 2019

Concentrations of nitrites in the surface layer were insignificant and did not exceed 0.07 μM in both stations. In the bottom layer, the content of nitrites was maximum in the area of discharge from the WWTP "South" (St. 5) and amounted to 0.48 μM but did not exceed the environmental standard (ES) for the quality of the marine environment (ES = 0.714 μM).
Concentrations of nitrates were also insignificant in the surface layer being in the range of 0.10-0.14 μM. In the bottom layer, the content of nitrates was maximum in the area of discharge from the WWTP "South" (1.52 μM, St. 5), but did not exceed the environmental standard (ES) for the quality of the marine environment (ES = 7.14 μM).
The concentration of ammonium did not exceed the detection limit (Figure 2.45a).
Concentrations of total nitrogen (TN) varied within the range of 27.6-31.8 μM. The contribution of organic nitrogen to the TN at both stations in the surface and bottom horizons was more than 94 % (Figure 2.45b).



(a) (b)

Figure 2.45 - Mineral forms of nitrogen (a), total and organic nitrogen (b) in seawater in the place of discharge from "Hot spots", September 2019

2.3.1.3 Heavy Metals and Organic Pollutants

In Ukraine, the national methodology to assess the ecological state is by calculation of a pollution factor, Kz, developed by UkrSCES. Kz reflects the concentration of all pollutants of the same type in a certain period, in a given area. This factor represents the sum of the ratios of the concentration of each pollutant to its maximum available concentration, under EU Directive 2013/39/EU (MAC-EQS) for water, to the number of measurements performed in a given time. There are five quality classes ("very good", "good", "satisfactory", "bad" and "very bad") and the overall assessment of the ecological condition of water or bottom sediments in the study area is determined by the worst assessment of the group of pollutants.

The formula for calculating the pollution factor Kz is:

Kz

$$CR = \frac{C_{mon}}{C_{Treshold}}$$

$$\mathrm{Kz} = \frac{1}{n}\sum_{i=0}^{n} CR_i$$

Where: CR is the contamination ratio

The ecological condition assessed with Kz is estimated as:

Kz < 0.5	Very Good
Kz = 0.5 - 1.0	Good
Kz = 1.0 - 2.5	Satisfactory
Kz = 2.5 - 5.0	Bad
Kz >5.0	Very Bad

Water pollution by polyaromatic hydrocarbons (PAHs) and groups of Polychlorinated biphenyls (PCBs sum - Ar1254 and Ar1260) are at a low level and correspond to a "very good" ecological status, pollution with organochlorine pesticides (OCPs) and trace metals (TM) also at a low level, except for the bottom water layer at station 4, where Kz OCPs corresponds to a "very bad" ecological status, and Kz TM corresponds to a "satisfactory" ecological status. However, the level of pollution by individual PCBs at these stations is very high and corresponds to a "very bad" ecological status, as a result, the overall assessment of the ecological state of water in the areas of influence of "Hot Spots" corresponds to a "very bad" ecological status.

Table 2.2 - Kz groups of pollutants in seawater in the areas of influence of "Hot Spots"

Station	Depth[m]	Kz PCBs individual	Kz TM	Kz OCPs	Kz PCBs (Ar1254 and Ar1260)	Kz PAHs
ST4	0	15.00	0.13	0.12	0.05	0.40
ST4	9.5	12.26	2.08	64722	0.04	0.08
ST5	0	12.76	0.18	0.12	0.04	0.26
ST5	18	15.61	0.23	0.12	0.08	0.09

The main pollutants in the places of influence of "Hot Spots" are individual PCBs, and for station 4 also OCPs and TM (Figure 2.46).

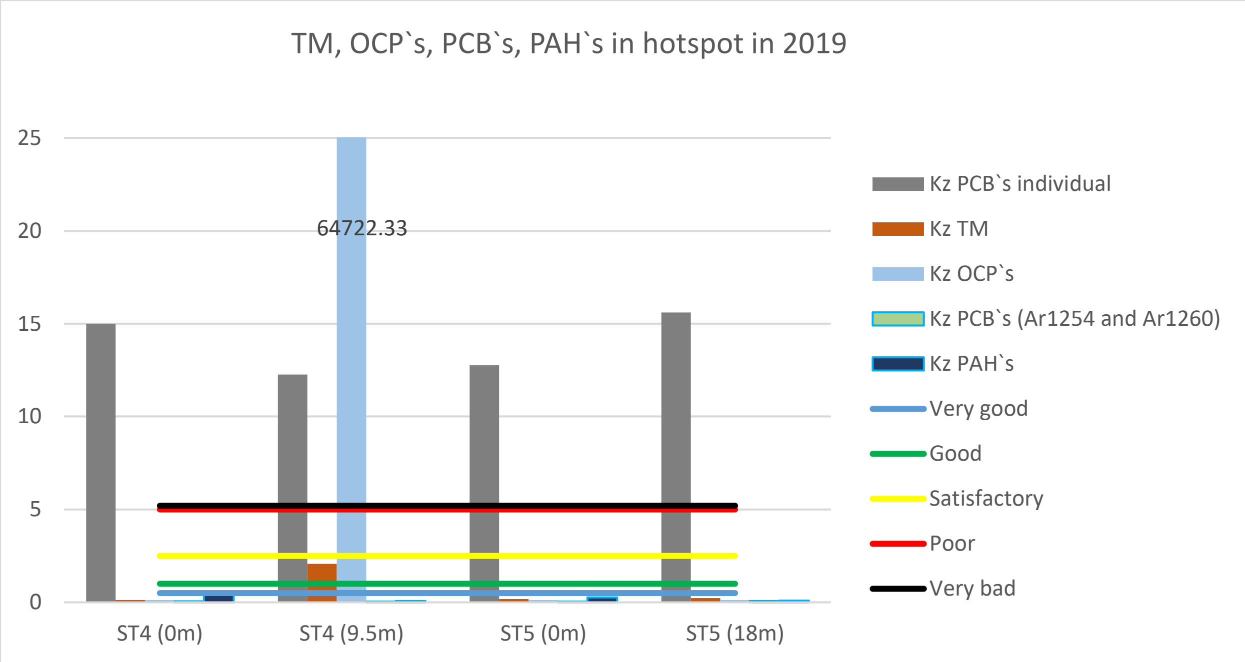


Figure 2.46 - Kz groups pollutants in seawater hotspot

Among the pollutants, the concentrations of mercury, benzo(g,h,i)perylene, heptachlor, PCB101, PCB118 reduce the ecological assessment of the quality of sea waters to the greatest extent and are classified as bad (Table 2.3).

Table 2.3 - Kz individual pollutants in seawater in the areas of influence of "Hot Spots"

Station	Depth[m]	Kz Cd	Kz Pb	Kz Ni	Kz Hg
ST4	0	0.04	0.16	0	0.30
ST4	9.5	0.12	0.00	0	8.21
ST5	0	0.49	0.08	0	0.16
ST5	18	0.46	0.11	0	0.36

Station	Depth[m]	Kz Naphthalene	Kz Anthracene	Kz Fluoranthene	Kz Benzo[b]fluoranthene	Kz Benzo[k]fluoranthene	Kz Benzo[a]pyrene	Kz Benzo(g,h,i)perylene
ST4	0.0	0	0	0.01	0.24	0.19	0	2.39
ST4	9.5	0	0	0.00	0.05	0.04	0	0.48
ST5	0.0	0	0	0.01	0.16	0.13	0	1.52
ST5	18.0	0	0	0.00	0.05	0.04	0	0.57

Station	Depth[m]	Kz HCB	Kz HCH total	Kz Heptachlor	Kz ciclodiene total	Kz DDT	Kz DDT total	Kz AR-1254	Kz AR-1260
ST4	0.0	0	0.09	0	0	0.46	0.18	0.10	0
ST4	9.5	0	0.08	388333	0	0.40	0.16	0.08	0
ST5	0.0	0	0.05	0	0	0.48	0.19	0.08	0
ST5	18.0	0	0.11	0	0	0.43	0.17	0.15	0

Station	Depth[m]	Kz PCB-101	Kz PCB-118	Kz PCB-153	Kz PCB-138	Kz PCB-180
ST4	0.0	21.5	30.00	0.00	23.5	0.00
ST4	9.5	17.5	24.23	0.08	19.5	0.00
ST5	0.0	19.0	23.85	0.11	20.5	0.35
ST5	18.0	18.0	33.08	0.17	26.5	0.30

From the trace metals group, mercury is present at all stations and has the greatest contribution to the pollution at station 4, and at station 5, cadmium has the greatest contribution to pollution (Figure 2.47). In the OCPs group, heptachlor is present only in the bottom layer of water at station 4 and has the greatest contribution to the OCPs pollution, DDT and DDT total are present at all stations and make the greatest contribution to the pollution of the OCPs group at station 5 and in surface water layer at station 4 (Figure 2.47). Benzo(g,h,i)perylene (PAH`s group) at all stations has the greatest contribution to the group's pollution (Figure 2.47). In the PCBs group, Ar1254 at all stations has the greatest contribution to the group's pollution (Figure 2.47).

Figure 2.47 - Contribution of individual pollutants to the overall Kz of groups in seawater

Black Sea waters quality in the areas of influence of "Hot Spots" (WWTP of the city of Odessa "South" and WWTP of the city and port of Chernomorsk), corresponds to a "very bad" ecological state.

There are high concentrations of individual PCBs, among which PCB-101 and PCB-118 are the largest. Mercury is present at all stations, and at station 4 it has the greatest contribution to overall pollution, Kz Hg corresponds to a very bad ecological state. DDT and DDT total are present at all stations. Benzo(g,h,i)perylene at all stations has the greatest contribution to the PAHs group of pollution.

2.3.2 Romania

2.3.2.1 Physical-chemical parameters

Seawater **temperature** recorded, in the water column, homogenous, typical values for the end of the warm season (Annex D and Figure 2.48). Maximum, 22.49 ºC, was measured near the bottom, Port Midia (control), 7m. Minimum, 20.96 ºC, was measured at the bottom depth, 26m (WWTP Eforie).

Overall, at the surface, **salinity** did not show a particular gradient. The lowest values are associated with the stations' A, the most influenced by ports activities. Minimum occurred in Port Midia (A, 0 m) (Figure 2.48). Increased salinities were significantly higher (r=0.59) near-bottom.

The **dissolved oxygen** content was highest at the surface (221.5 – 293.9 µM). The maximum was in the Port Mangalia influence area (A); the minimum was measured for Port Constanta (A), water column, 10m. The coastal sources' impact was outlined by the lowest median measured in the stations' A, while the highest is from control samples (M) (Figure 2.49). Dissolved oxygen saturation was significantly correlated with chlorophyll *a* concentration (r=0.45).

pH was normal overall**.** The lowest values and the highest variability are related to stations type A (Figure 2.49) due to the inorganic phosphate input (r=-0.72).

The biological oxygen demand (BOD_5) recorded its maximum inside Port Midia (A). The median is highest in the immediate impact area (Figure 2.50).

2.3.2.2 Nutrients

Phosphate and silicate concentrations followed almost the same pattern at the surface is significantly correlated with salinity (r=-0.68 and r=-0.70). Phosphate highest concentrations were recorded inside Port Midia (A) while silicate maximum in Port Mangalia (A)(Figure 2.51).

The inorganic nitrogen species had different behaviour. Thus, nitrate revealed a coastal input explained by the significant correlation with salinity (r=-0.78). Maximum occurred at the surface, Port Midia (A). Although relatively high, no significant correlations were found between salinity, nitrite, and ammonium concentrations. However, again, in station Port Midia (A), a maximum occurred for nitrite level. Ammonium reached its highest concentrations in Port Mangalia (A) area (Figure 2.52).

The total suspended solids content (TSS) reached the maximum at distance from the interior port (station Constanta C) (Figure 2.53).

Conclusions

The influence of the coastal sources is mainly observed for the nutrients input. Thus, high levels and significant correlations with salinity were found for phosphate, silicate, nitrate, total nitrogen, and total phosphorus.

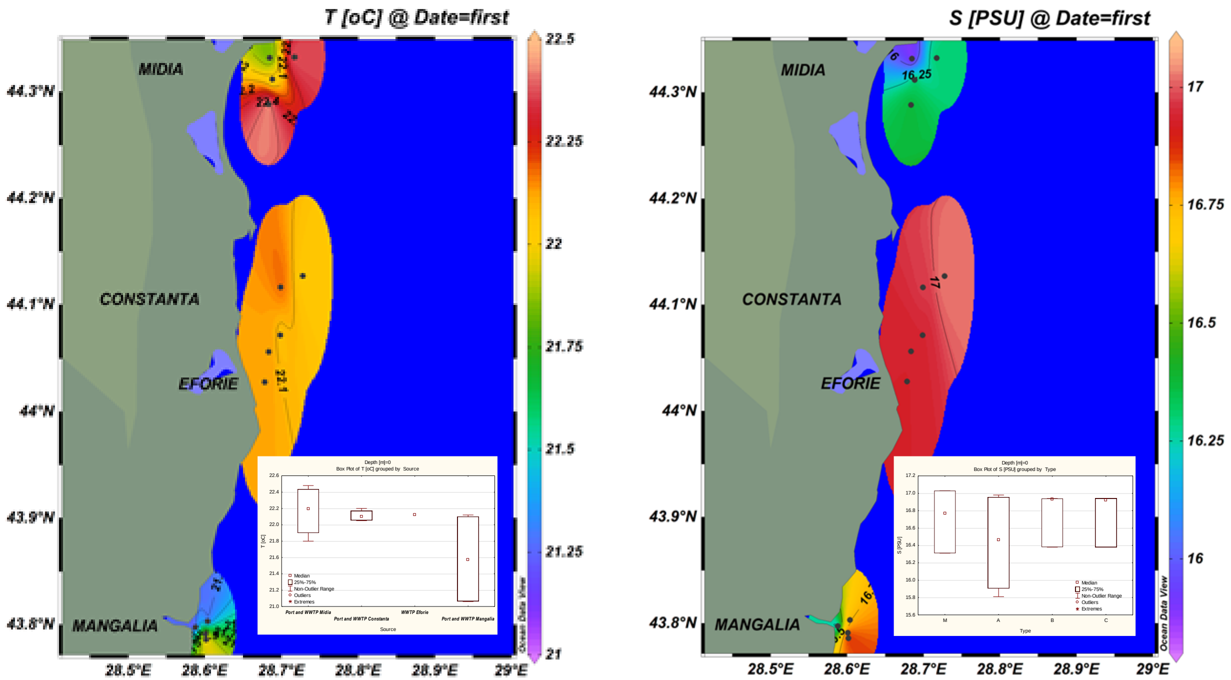


Figure 2.48 - Surface seawater temperature and salinity, September 2019

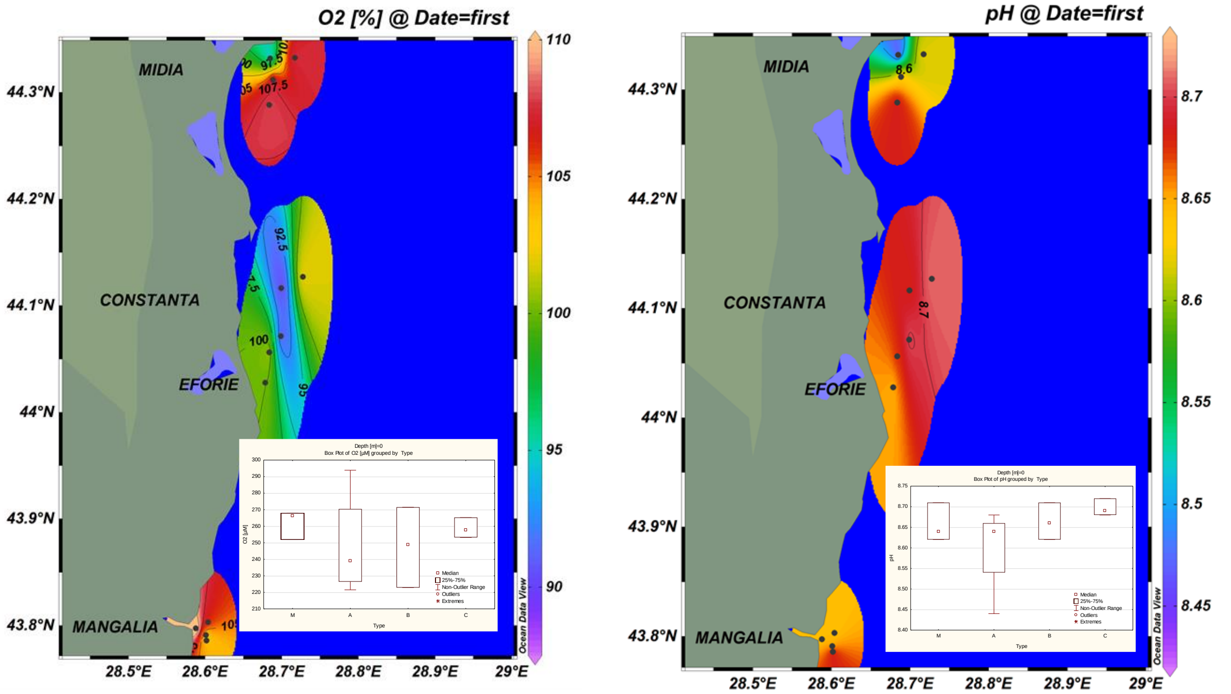


Figure 2.49 - Surface oxygen saturation and pH, September 2019

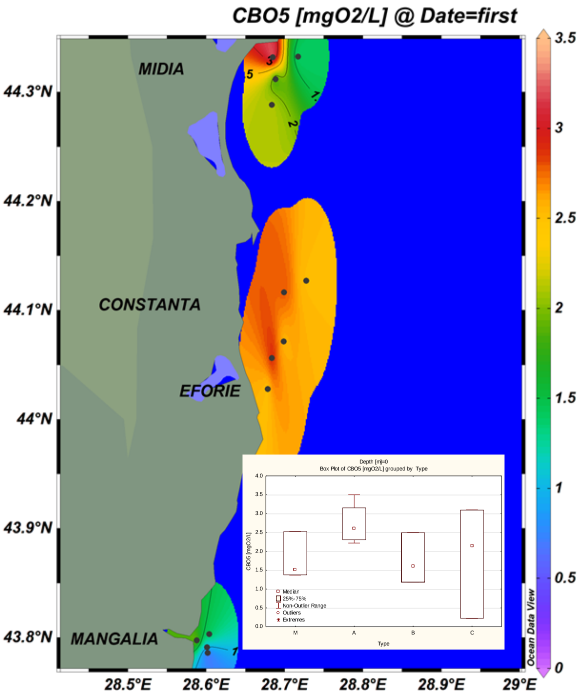


Figure 2.50 - Biological Oxygen Demand (BOD5), September 2019

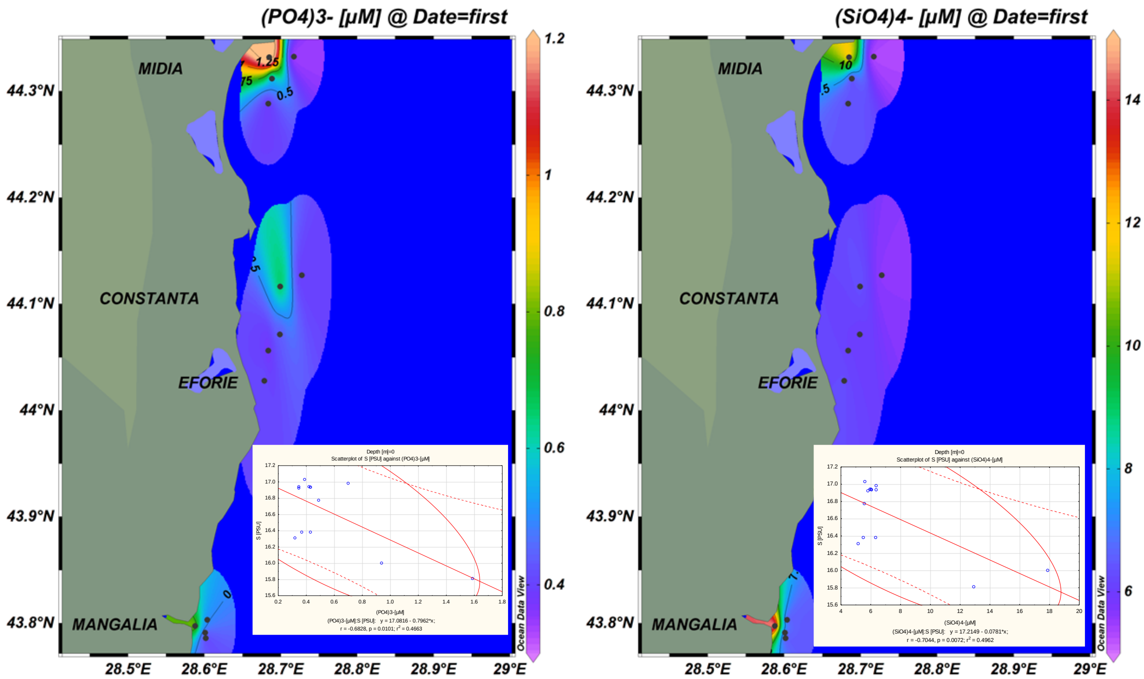


Figure 2.51 - Phosphate and Silicate concentrations spatial distribution (0 m) and correlation with salinity (0 m), September 2019

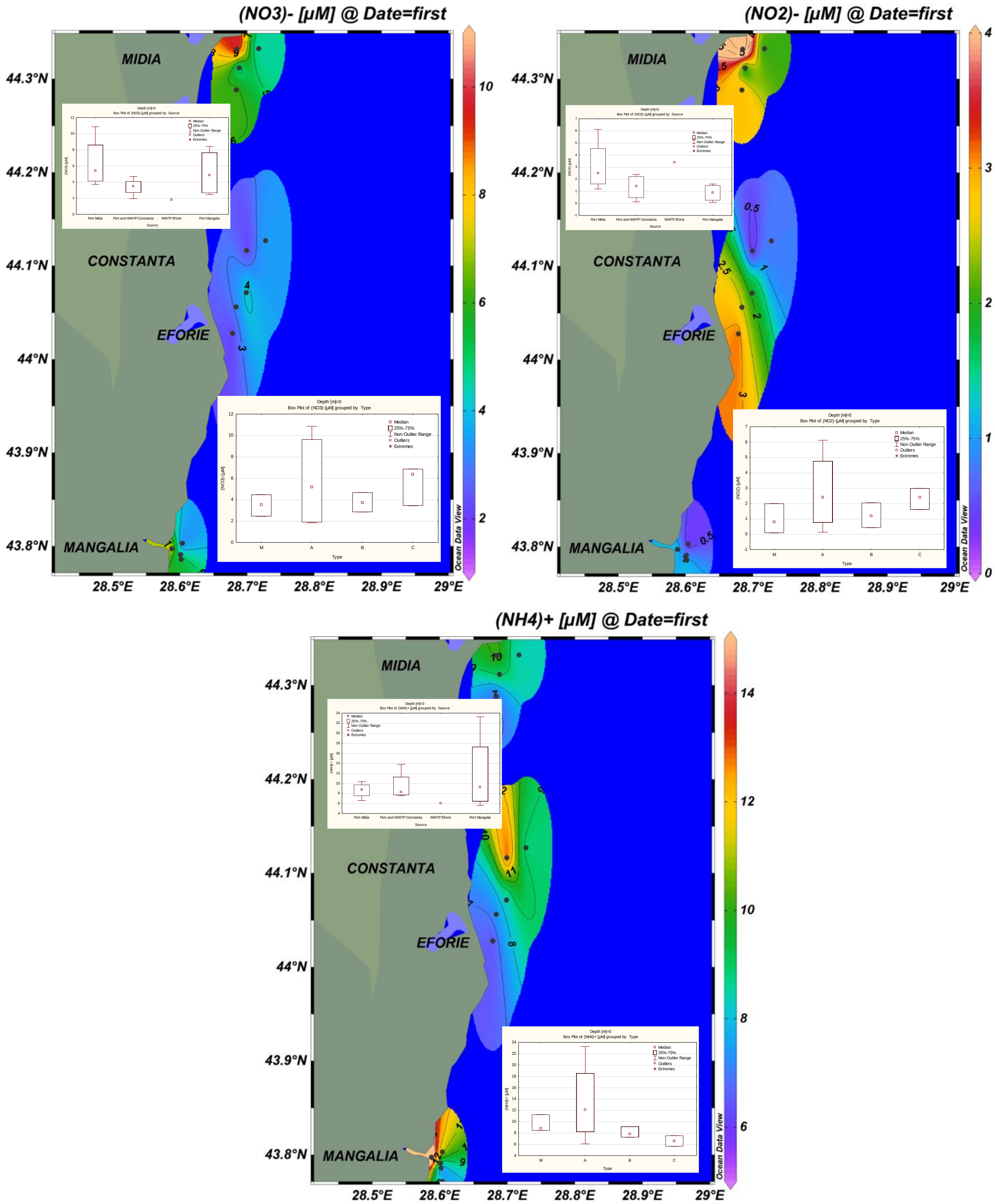


Figure 2.52 - Dissolved Inorganic Nitrogen (Nitrate, Nitrite and Ammonium) concentrations spatial distribution (0 m) by type and source, September 2019

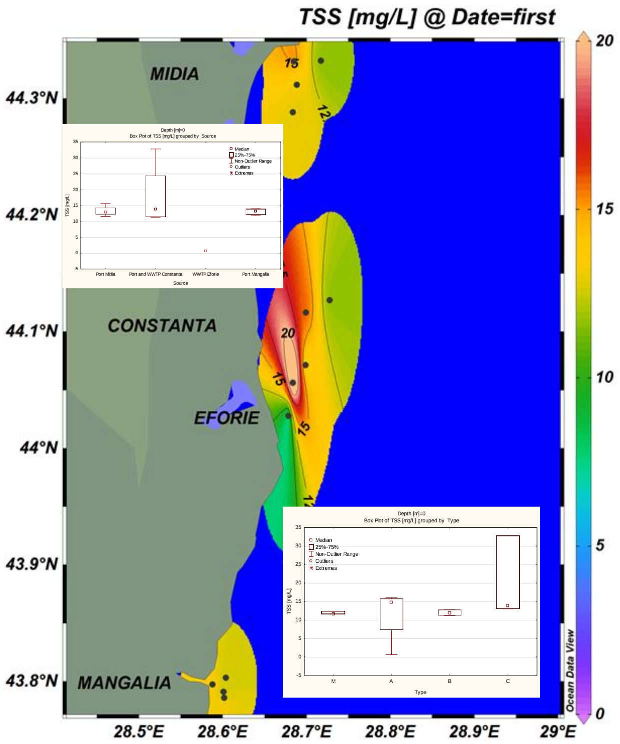


Figure 2.53 - Total Suspended Solids spatial distribution (0 m), September 2019

2.3.2.3 Heavy Metals

Major activity related to sea navigation, shipbuilding and repairs, and loading/unloading cargo is concentrated in three main ports: Constanta, Mangalia and Midia.

The physical and chemical parameters and their dynamics in the harbour area in every case depend on human economic activity. The Midia and Constanta ports also received freshwater through Danube channels. Thus, contaminants collected from a broad catchment area are carried into the port basin, and pollution also enters from sources in the port itself. Sources include shipping activities (including anti-fouling paints, dry dock, loading and bunkering operations, and ship repair and building), industry (e.g., pyrogenic processes, spills, and leaks), urbanisation (e.g., sewage outfall, urban run-off, stormwater inputs) and agricultural waste. The waters of the Black Sea could play a positive role in diluting the polluted harbour water, thereby reducing its contamination level. A certain percentage of the contaminants that enter the water, including heavy metals, could leave the harbour basin before settling to the bottom. Another percentage reaches the bottom in the harbours and becomes lodged in the bottom sediments (Galkus et al., 2012).

Metals concentrations in surface seawater from all four study areas were characterized by high variability, within the following ranges: 4.95 – 16.08 µg/L Cu; 0.03 – 1.35 µg/L Cd; 0.09 – 11.14 µg/L Pb; 1.56 – 6.36 µg/L Ni; 0.85 – 6.87 µg/L Cr. Data obtained during this cruise for the hot-spots areas (average values 8.97 µg/L Cu; 0.27 µg/L Cd; 2.52 µg/L Pb; 3.27 µg/L Ni; 2.38 µg/L Cr) are not significantly different in comparison with typical ranges reported for Black Sea marine waters, for instance, the limit of predominant values (75th percentile of 2012 – 2017 monitoring data) being as follows: 6.31 µg/L Cu; 1.14 µg/L Cd; 7.43 µg/L Pb; 3.78 µg/L Ni; 3.21 µg/L Cr (Oros A., 2019).

The specific port morphology and hydrodynamic conditions occurring both inside and offshore port area represent factors influencing the transport of sediments, especially the finest ones, which are the main vehicles for contaminant dispersion. Thus, hydrodynamic features inside the port have an important role in facilitating the settling down of fine particles (Mali et al., 2018). It should be noted that the maximum concentrations were measured inside Constanta Port basin (16.08 µg/L Cu, 1.35 µg/L Cd, 11.14 µg/L Pb and 6.87 µg/L Cr) and Midia Port basin (6.36 µg/L Ni). In comparison, most metals presented decreased concentrations in the surrounding areas of Midia (Cu, Pb, and Ni) and Constanta Port (Cu, Cd, Pb, Cr). Slightly higher concentrations were measured in front of Eforie South

WWTP discharge for Cd (1.26 µg/L) and Pb (5.57 µg/L). In Mangalia Port, there were no significant differences between the inside and offshore port area. (Table 7.9, Figure 2.54).

Once entered the marine system, trace metals are removed from the surface water body by internal fluxes like sedimentation on biogenic or terrigenous particles, by diffusive exchange of dissolved species across interfaces or by advective vertical transport. Consequently, heavy metals that are particle reactive, like Pb, have very low residence time, vertical sedimentation (sinking associated with particles) and lateral transport, as much as atmospheric input are in the same order of magnitude, while the metals (Cd, Cu, Zn) with "nutrient-like" behaviour have longer residence time primarily due to their coupling to biological processes, in their case the lateral transport being more important than vertical sedimentation (Pohl et al. 2006). This demonstrates that the system reacts very fast for particle reactive elements like Pb, while for Cu and Cd sedimentation processes are not the preferential sink and can be neglected (Pohl et al., 2006).

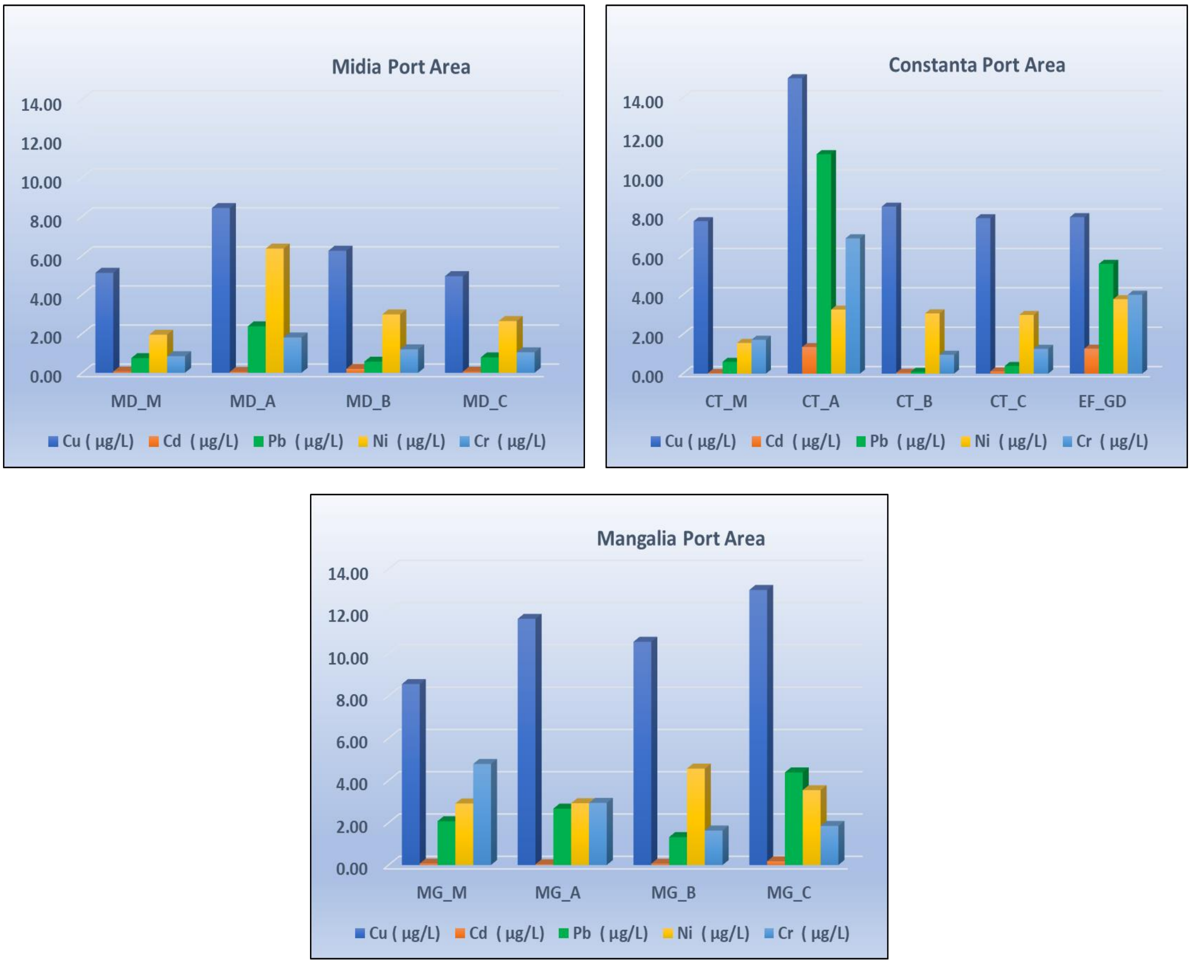


Figure 2.54 - Spatial distribution of heavy metals concentrations in surface waters, September 2019

These measurements indicated a low level of trace metal pollution since concentrations of all elements in surface waters did not surpass recommended environment quality standards (EQS) (Directive 2013/39/EU: 1.5 µg/L Cd, 14 µg/L Pb, 34 µg/L Ni; national legislation: 30 µg/L Cu).

In comparison with available monitoring data (2015 – 2018) from the same areas, the results in 2019were generally maintained between similar variability ranges, with no significant increasing or decreasing trends. Midia and Mangalia Port basins, and surrounding areas, were characterized by lower concentrations in 2019 for all elements. Higher concentrations were although measured in 2019 in Constanta Port for Cu and Cr, and Eforie WWTP discharge for Cd, Pb, and Cr (Figure 2.55- Figure 2.58).

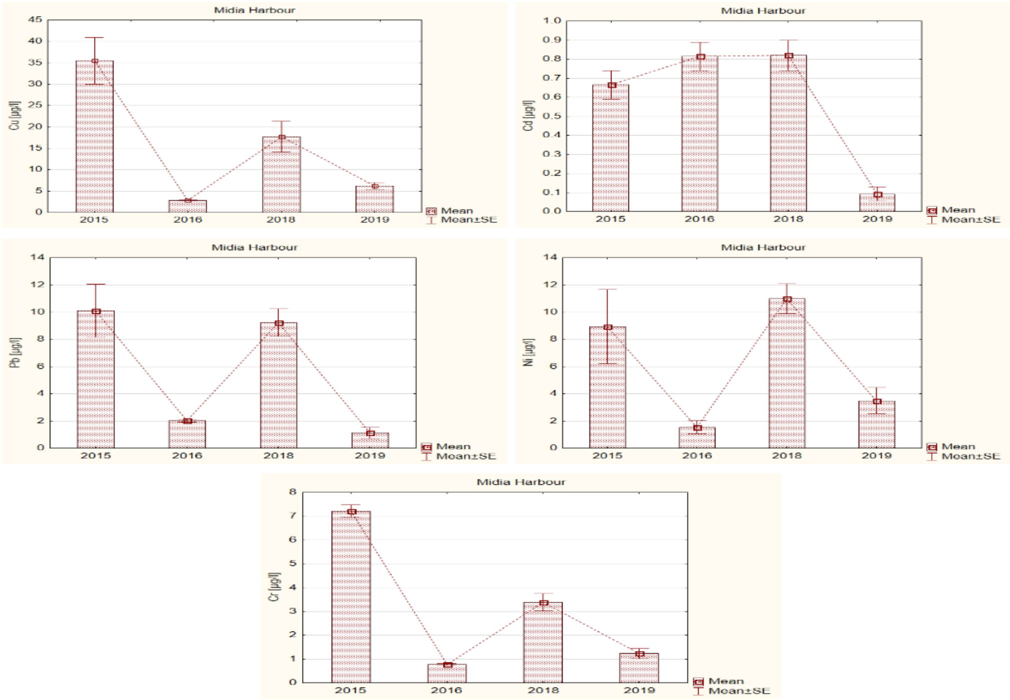


Figure 2.55 - Trends of heavy metals concentrations in surface waters - Midia Port area, 2015 – 2019

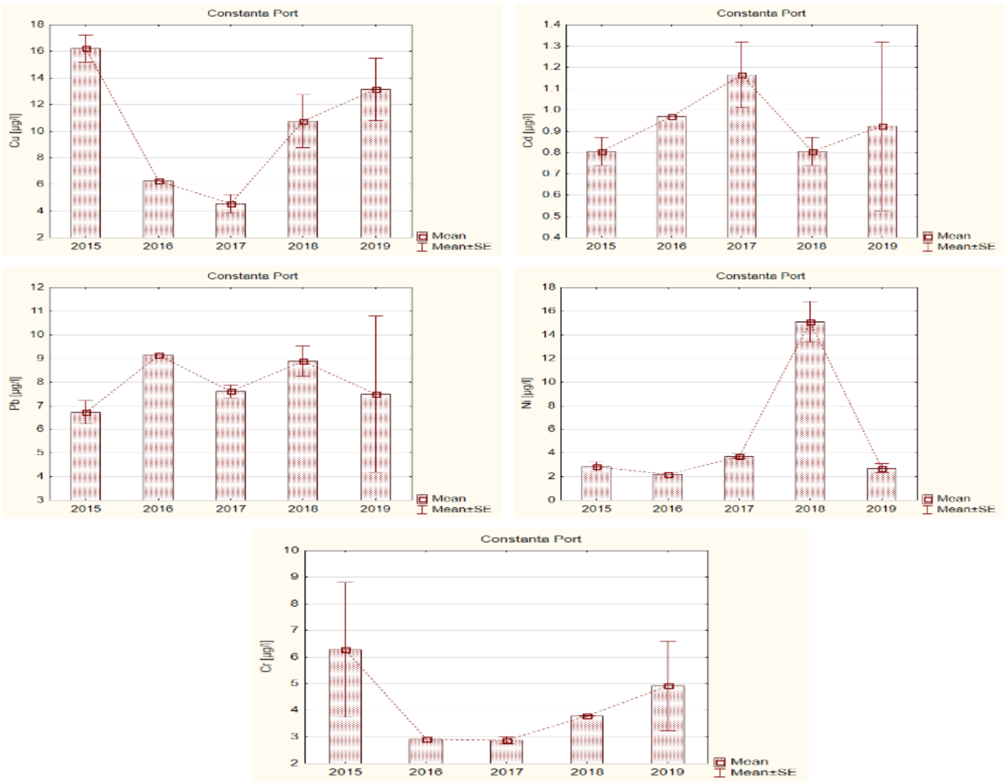


Figure 2.56 - Trends of heavy metals concentrations in surface waters - Constanta Port area, 2015 – 2019

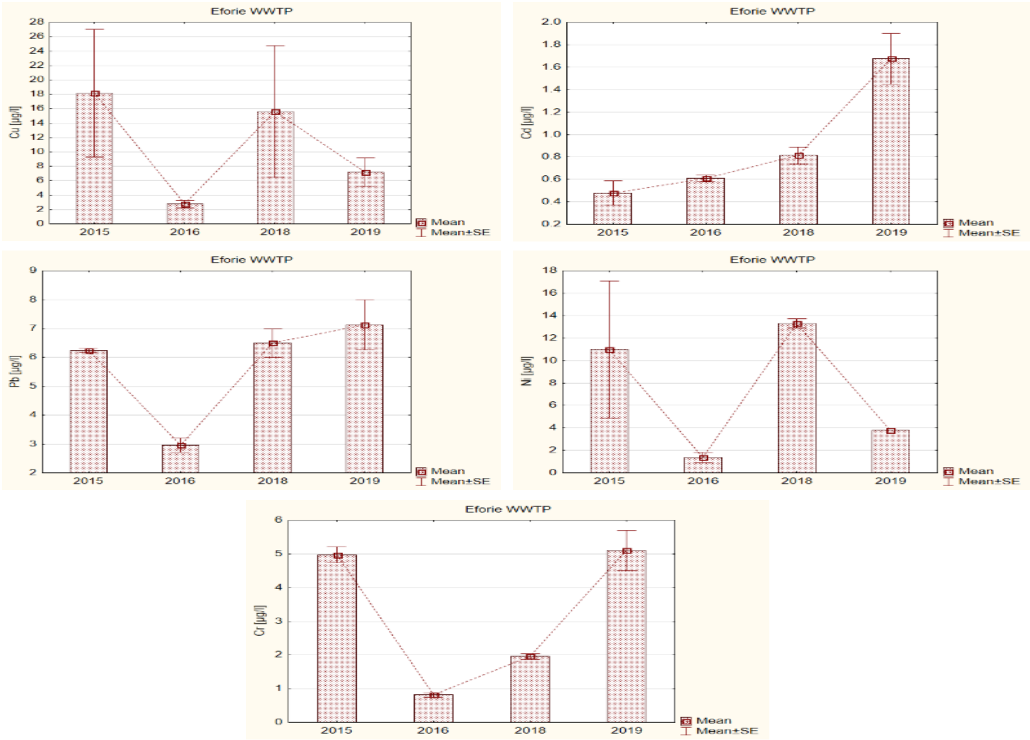


Figure 2.57 - Trends of heavy metals concentrations in surface waters – WWTP Eforie discharge area, 2015 – 2019

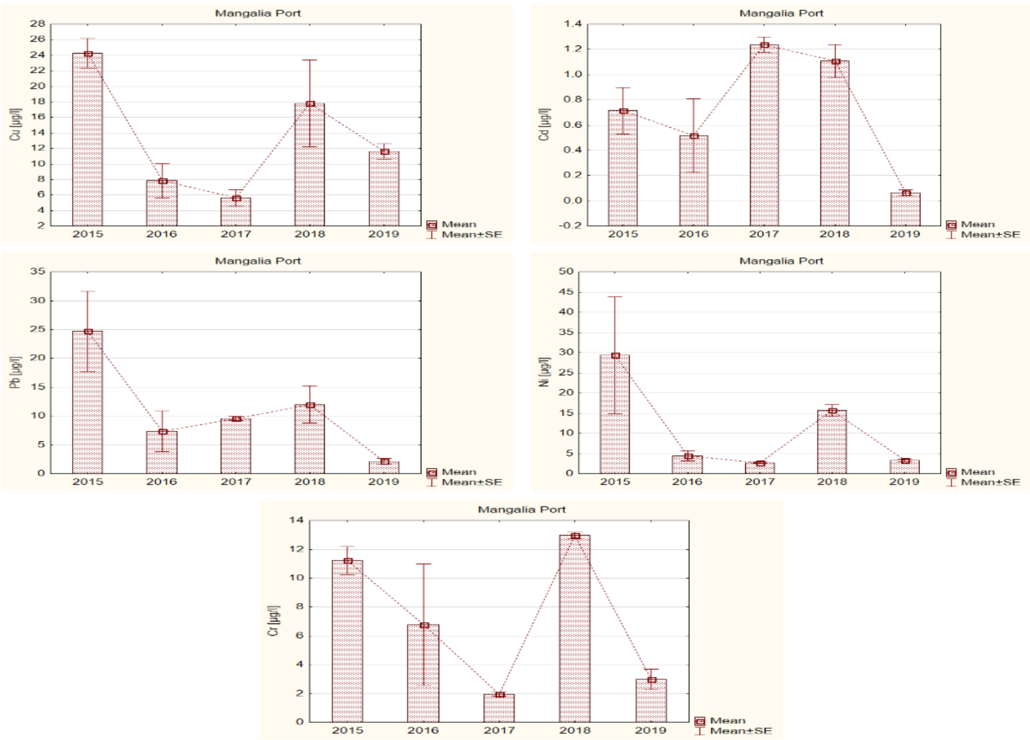


Figure 2.58 - Trends of heavy metals concentrations in surface waters – Mangalia Port area, 2015 – 2019

Higher concentrations were measured inside Constanta Port and Midia Port basins, in comparison with the surrounding areas, and in front of Eforie South WWTP discharge. In Mangalia Port, there were no significant differences between the inside and offshore port area.

Metals concentrations in surface seawater from the four hot-spots areas investigated in September 2019 indicated a low level of trace metal pollution, as no sample surpassed recommended EQS values.

In comparison with available monitoring data (2015 – 2018) from the same areas, in 2019 the results were generally maintained between similar variability ranges, with slightly increasing or decreasing trends, depending on the area or investigated element.

2.3.2.4 Organic Pollutants

Water samples were characterized by OCPs values between the detection limit and 32.40 µg/L. Heptachlor, aldrin, endrin, p,p' DDD and p,p' DDT concentrations were below the detection limit, except some values recorded for heptachlor and aldrin in Midia harbour (8.18 µg/L, and respectively 31.55 µg/L) and p,p' DDD in Constanta harbour (2.85 µg/L). The other individual compounds varied within the following ranges: 0.004 µg/L to 5.96 µg/L HCB, 0.003 µg/L to 32.40 µg/L lindane, 0.002 µg/L to11.89 µg/L dieldrin and 0.002 µg/L to 10.67 µg/L p,p' DDE (Table 7.10). Except for PCB 28 that had values between 0.004 µg/L and 59.38 µg/L, PCBs were below detection limits in all samples.

TPHs values ranged between 3.12 µg/L and 15.25 µg/L and the PAHs analysis highlighted the presence of six of the sixteen investigated compounds: naphthalene, acenaphthylene, acenaphthene, phenanthrene, anthracene and indeno(1,2,3-c,d)pyrene in concentrations between detection limit (0.0001 µg/L) and 1.72 µg/L (Table 7.11).

The distribution of POPs inside (stations MD_A, CT_A and MG_A) and outside (stations MD_M, MD_B, MD_ C, CT_M, CT_B, CT_ C, MG_M, MG_B, MG_ C) the port basin reveals as a contamination source, most likely, the atmospheric transportation or Danube input. Except for Midia where the highest levels (32.4 µg/L lindane, 31.54 µg/L endrin) of POPs were recorded inside the port, for the other areas, the highest values (59.38 µg/L, 52.12 µg/L PCB 28, 19.89 µg/L lindane, 11.89 µg/L dieldrin, 10.7 µg/L p,p' DDE, 4.12 µg/L HCB) were recorded outside the port basins (Figure 2.59). There is little doubt today that atmospheric transport and deposition via dry and wet deposition and air-water transfer are major drivers of POPs loading and inventories in both coastal and open marine systems (Jiménez et al., 2015). POPs undergo widespread distribution in the environment when they volatilize from source regions, undergo transport through the atmosphere to distant locations, and are then deposited to surface media by wet or dry deposition (Hageman et al., 2015). Also, except lindane (3.87 µg/L) and PCB 28 (26.64 µg/L), no other chlorinated compounds were detected in front of Eforie WWTP (Figure 2.59).

The distribution of TPHs and PAHs concentrations followed a similar pattern with no obvious differences between the stations inside and outside the port area. Maximum TPHs concentration were recorded in MG_A (15.3 µg/L), CT_B (13.3 µg/L), MD_A (10.9 µg/L) and MD_C (10.5 µg/L) stations (Figure 2.60). PAHs were homogeneously distributed in Midia and Mangalia port areas. Higher values were detected in Constanta area outside the port basin in CT_M (0.76 µg/L anthracene) and CT_C (0.48 µg/L naphthalene and 1.72 µg/L anthracene) stations and in Eforie WWTP discharge area (1.07 µg/L naphthalene and 0.70 µg/L anthracene) (Figure 2.61). Inputs of PAHs in seawater could be related to different sources such as untreated wastewater discharge, urban runoff, refinery effluents, vessel discharge and/or spills, vehicular emission, and atmospheric deposition as well as seasonal hydrological variation (Neff, 1979).

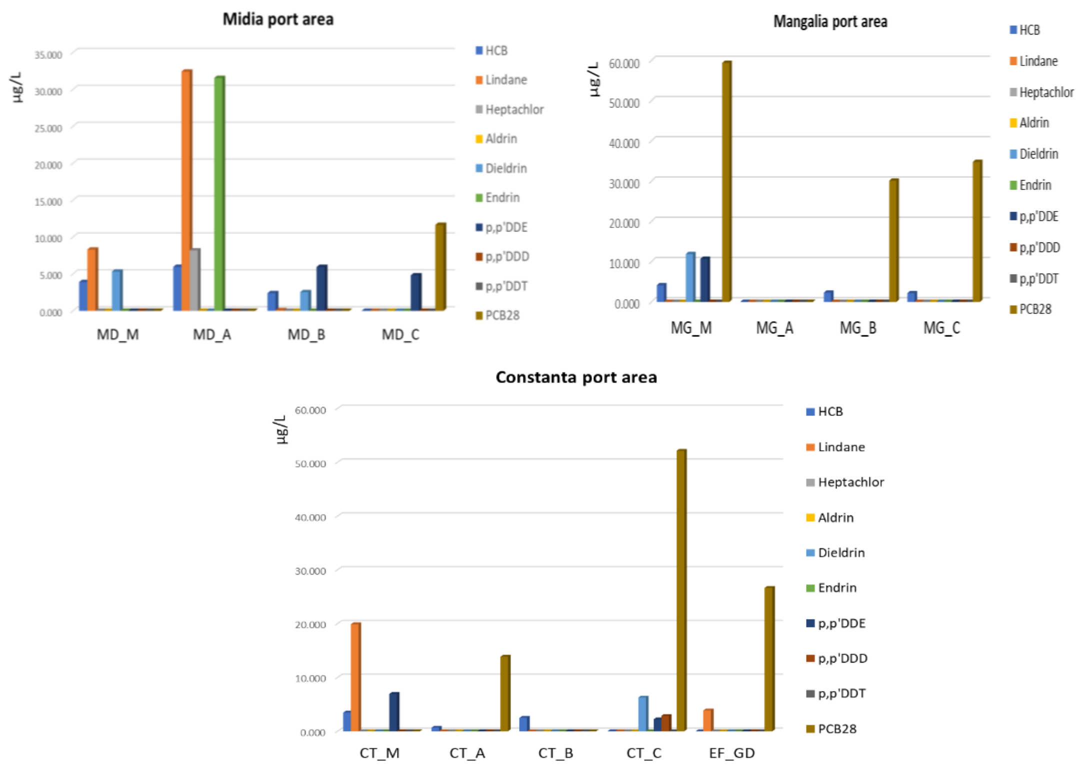


Figure 2.59 - Spatial distribution of chlorinated compounds concentrations in surface waters in hot-spots study areas, September 2019

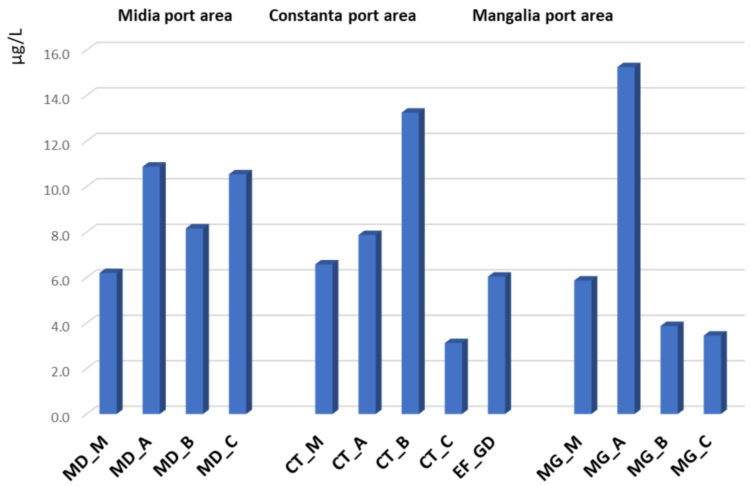


Figure 2.60 - Spatial distribution of TPHs concentrations in surface waters in hot-spots study areas, September 2019

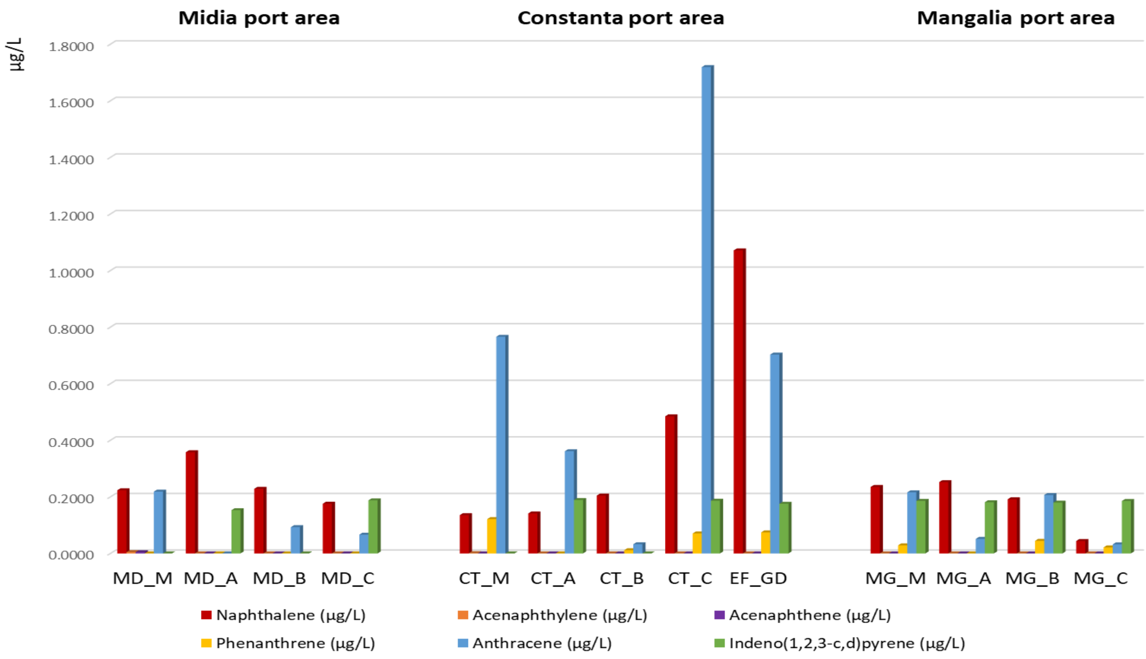


Figure 2.61 - Spatial distribution of PAHs concentrations in surface waters in hot-spots study areas, September 2019

The concentrations detected in seawater indicated a low level of hydrocarbon pollution. TPH values were much lower than the maximum admissible value (200 µg/L) stipulated by national legislation and anthracene was the only regulated compound that exceeded the threshold values proposed for PAHs in water to define good ecological status, according to Directive 2013/39/EU, in 50 % of the samples.

For organochlorine pesticides the pollution was high as the concentration of cyclodiene pesticides (aldrin, dieldrin, endrin), the sum of DDTs (DDT and metabolites) and lindane exceeded the threshold values proposed for water to define good ecological status (according to Directive 2013_39_EU) in 48 % of the samples, HCB in 70 % of the samples and heptachlor in 8 % of the samples.

In comparison with available monitoring data (2015 – 2018) from the same areas, in 2019 the results were generally maintained between similar variability ranges, with some increasing or decreasing trends, depending on the investigated area and class of compounds. Slightly increase of chlorinated compounds trends in the Mangalia area and PAHs in the Constanta area was noticed. Midia, Constanta and Eforie areas were characterized by lower concentrations in 2019 compared to 2018 for chlorinated compounds. All areas had a decreasing tendency for TPHs (Figure 2.62 - Figure 2.65).

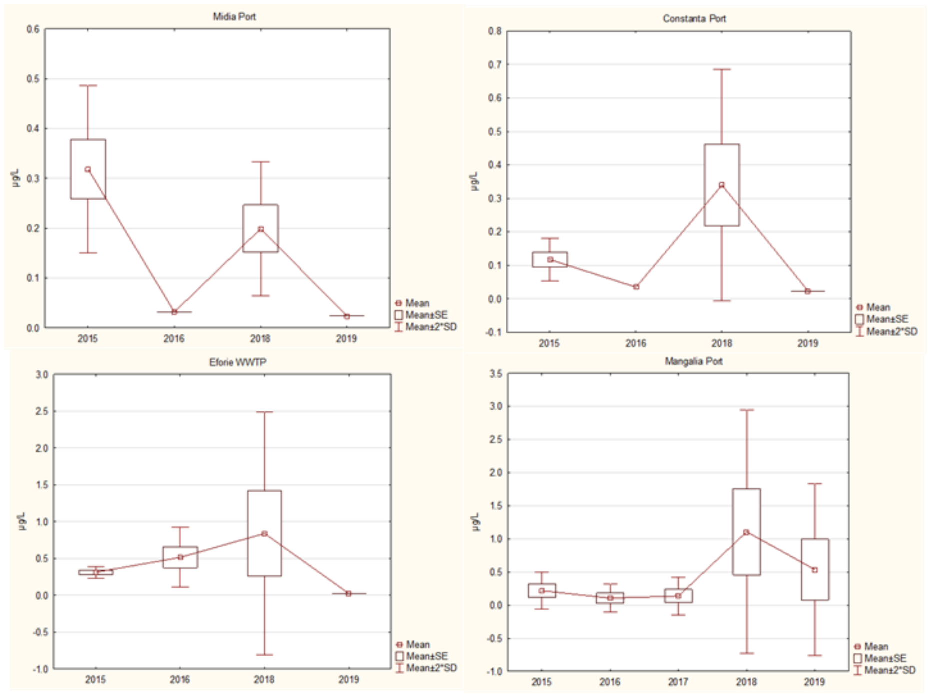


Figure 2.62 - Trends of total OCPs concentrations in surface waters in Midia, Constanta, Eforie and Mangalia areas, 2015 - 2019

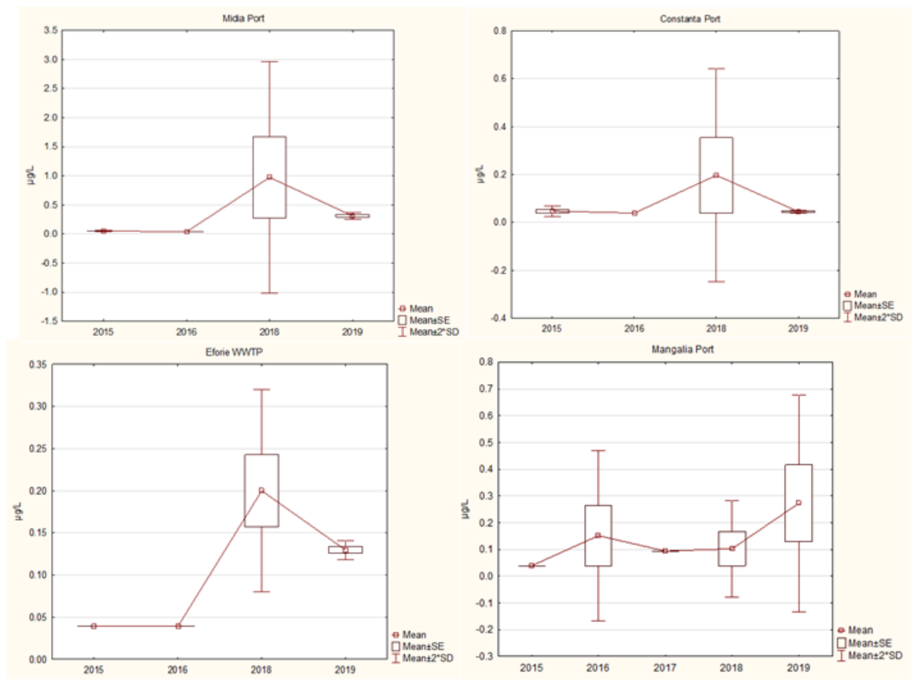


Figure 2.63 - Trends of total PCBs concentrations in surface waters in Midia, Constanta, Eforie and Mangalia areas, 2015 - 2019

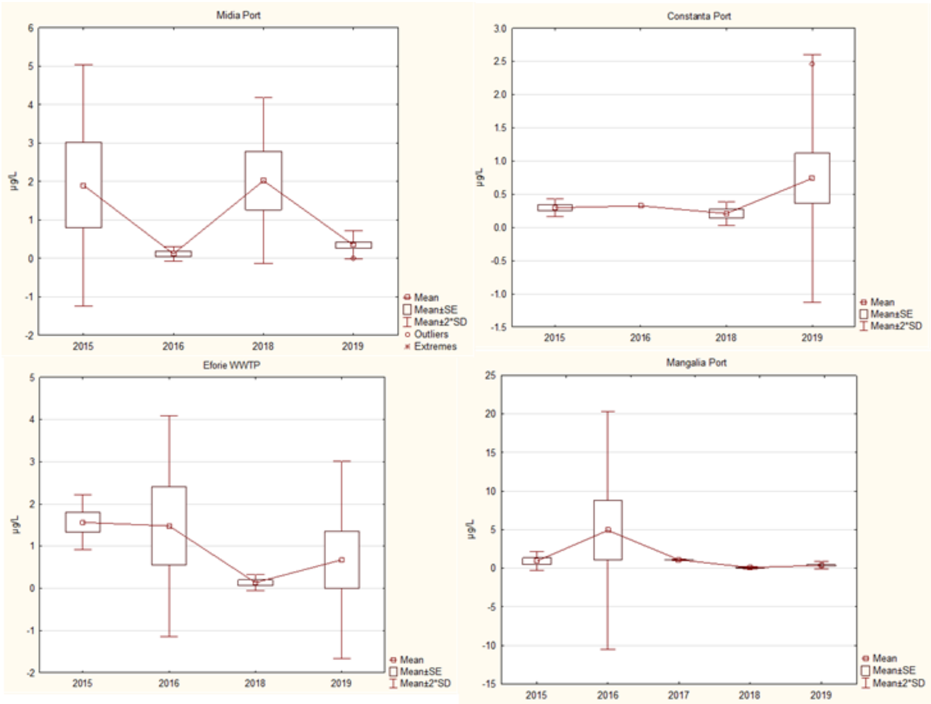


Figure 2.64 - Trends of total PAHs concentrations in surface waters in Midia, Constanta, Eforie and Mangalia areas, 2015 – 2019

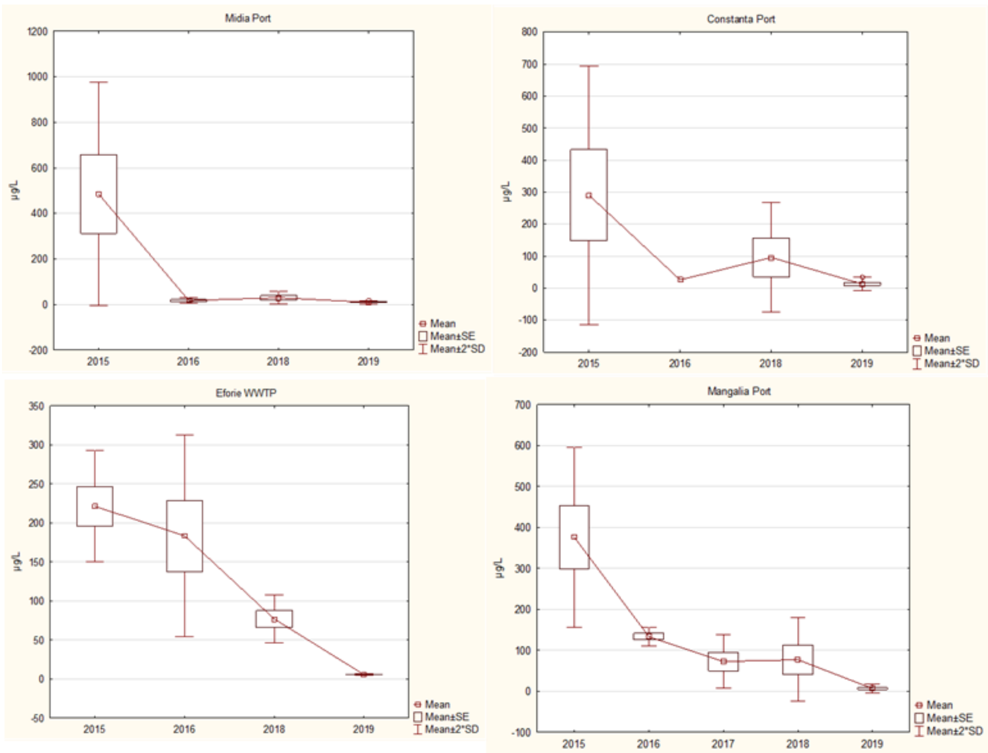


Figure 2.65 - Trends of TPHs concentrations in surface waters in Midia, Constanta, Eforie and Mangalia areas, 2015 – 2019

The distribution of organic pollutants concentrations showed no obvious differences between the stations inside and outside the port area.

The concentrations detected in the four hot spots areas, in September 2019 indicated a low level of hydrocarbon pollution, but a high level of pollution with organochlorine pesticides as their concentrations exceeded the threshold values proposed for water to define good ecological status (according to Directive 2013_39_EU) in 8 % to 70 % of the samples.

In comparison with available monitoring data (2015 – 2018) from the same areas, in 2019 the results were generally maintained between similar variability ranges, with some increasing or decreasing trends, depending on the investigated area and class of compounds.

2.3.3 Turkey

2.3.3.1 Physical-chemical parameters

Water column salinities at Samsun study site stations were in the range of 18.01-18.51 psu in summer whereas in winter it was in the range of 17.95-18.31 psu. The lowest salinities belonged to the SAAT01 that showed the lowest temperatures as well. Water column temperatures were recorded as 10.7-11.8°C in winter-2020 and 9.8-26.5°C in summer-2019 where strong thermocline was observed almost at all stations deeper than 15-20 m and the lowest temperatures (≅9-10°C) were recorded at the bottom waters of the deepest stations (e.g. SLI03, SLI06, SN03, SN06). The surface mixed layer depth was 10-11 m in summer with temperatures of 25.5-26.5°C and below these depths' thermocline layer was featured. In winter, almost all water column was mixed at all the stations.

2.3.3.2 Nutrients

NOx concentrations of the surface mixed layer (taken as 11 m both for winter and summer for comparison) waters varied from 0.24 µM to 2.13 µM (mean 0.9 µM) in winter (Figure 2.66) and <0.05 µM at all stations in summer (Figure 2.67). Concentrations at the station groups were in the order of SAAT>SN>SLI. These values are quite lower than the river coastal sites.

NH_4-N concentrations were in the range of 0.04-11.3 µM in winter, 0.04-2.9 µM in summer where the highest concentrations were found at the SAAT stations closer to the shoreline. Concentrations were again in the order of SAAT>SN>SLI.

Ortho-phosphate (PO_4-P) concentrations in the surface waters of the Samsun study site were measured <0.02 - 3.48 µM (0.08-3.80 µM for TP) in winter (Figure 2.66) and <0.02 – 8.3 µM (0.29-13.6 µM for TP) in summer (Figure 2.67). TP concentrations were again in the order of SAAT>SN>SLI by location, PO4-P was SN>SAAT>SLI. These values were quite higher than the river coastal sites and reflecting the influence of treated municipal wastewater discharges.

Silicate concentrations in the surface waters were measured in the range of 1.75 - 6.2 µM in winter (Figure 2.66) and <0.06 – 3.77 µM in summer (Figure 2.67) in the coastal waters of Samsun site. Concentrations were again in the order of SAAT>SN>SLI by location. These values are lower than the river coastal sites similar to the NOx as expectedly.

Dissolved oxygen concentrations in the water column (including bottom depths) were measured in the range of 5.3-9.5 mg/L in summer (Figure 2.66) and 7.4-9.2 mg/L in winter (Figure 2.67); not indicating any hypoxic conditions in both seasons. Slightly lower values were measured at SAAT bottom waters.

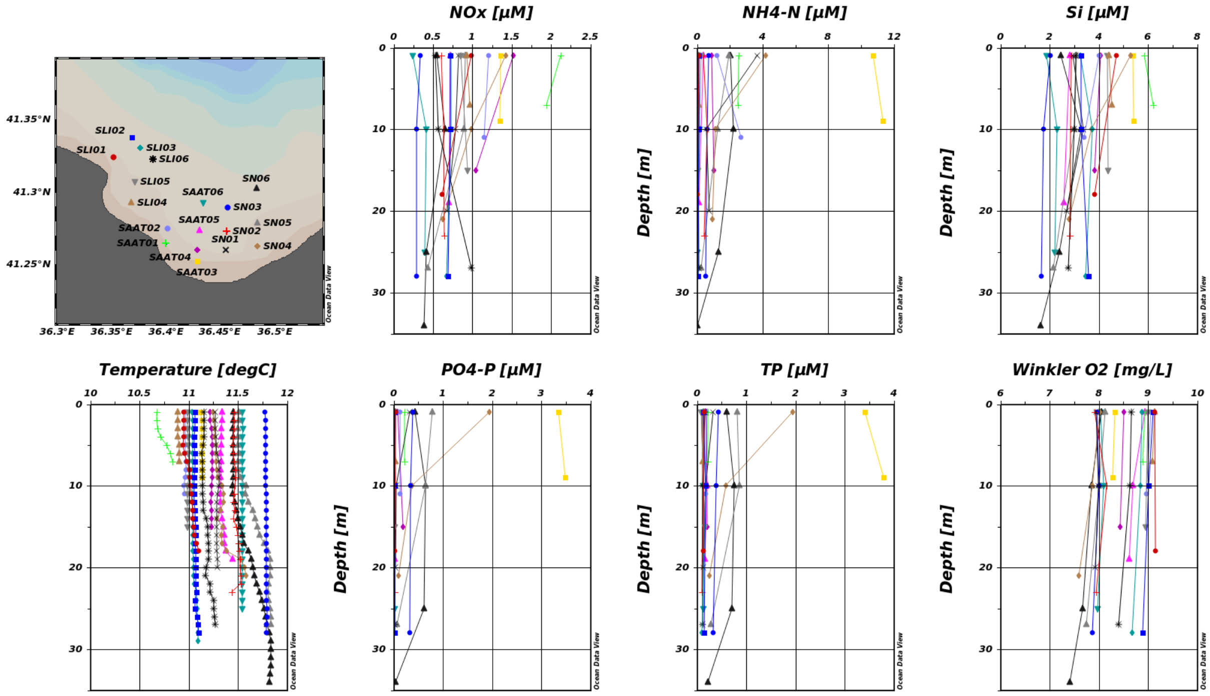


Figure 2.66 - The winter measurements of oxidised nitrogen (NOx), ammonium (NH4), silicate (Si), phosphate (PO_4), total phosphorus (TP), and dissolved oxygen (DO) at Samsun study site

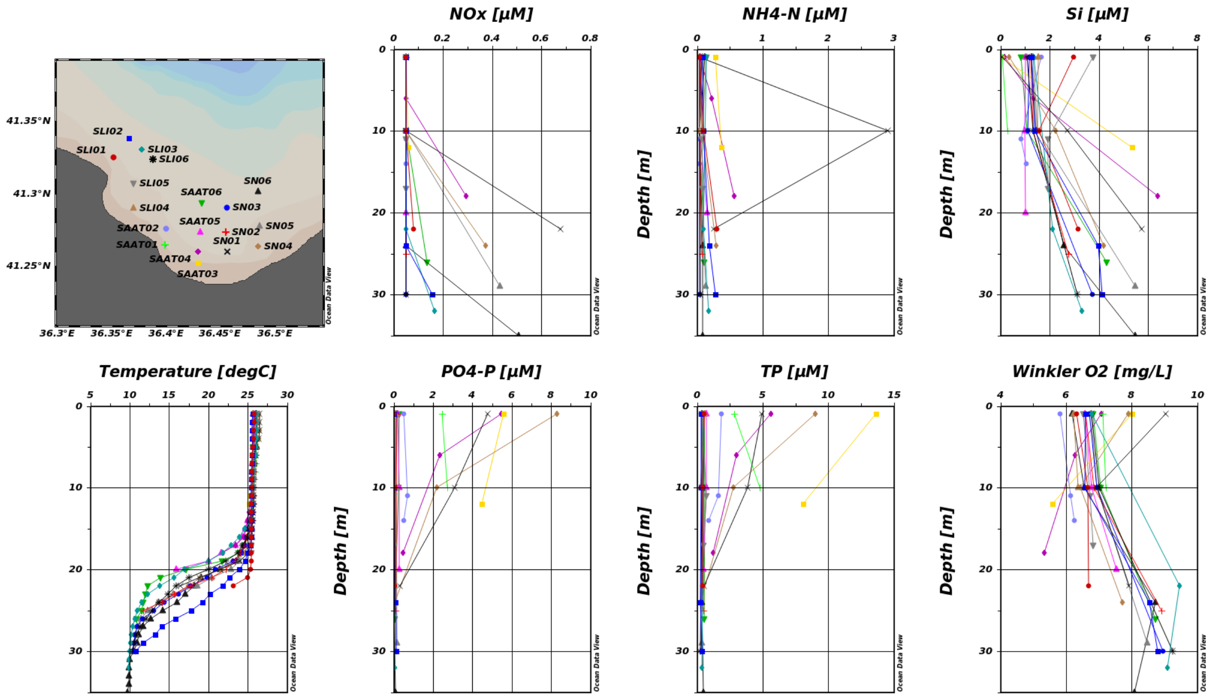


Figure 2.67 - The summer measurements of oxidised nitrogen (NOx), ammonium (NH4), silicate (Si), phosphate (PO_4), total phosphorus (TP), and dissolved oxygen (DO) at Samsun study site

The surface mixed layer chlorophyll *a* concentrations changed between 0.82 µg/L and 2.19 µg/L in winter and 0.08 and 23.4 µg/L in summer (Figure 2.69) at the Samsun study site. These values of both seasons are quite higher than the river coastal waters. The highest values were measured at the treatment plant discharge area (SAAT01, SAAT03, SAAT04 and eastern nearshore stations (SN01, SN04). The overall order of the concentrations by location is SAAT>SN>SLI. Chlorophyll *a* concentration of the stations, in which the phytoplankton sampling has been done, supports the change in phytoplankton biomass and abundance values. In parallel to the chlorophyll *a* changes, it was found that the eastern stations' phytoplankton biomass values are high in both sampling periods.

These high values resulted from the prymnesiophyceae species in winter and dinoflagellate species in summer. It was found that the high chlorophyll *a* values are caused by the dominance of dinoflagellate in SN01 station (located at eastern nearshore) in the summer.

SAAT01-04 and SN01, SN04, SN05 summer <5 m changed in the range of 1-8 m (Figure 2.68). In winter, the transparency changed almost homogeneously ranging at 3-5 meters (Figure 2.69).

Total Suspended Solids (TSS) were in the range of 0.7-5.3 mg/L in winter and 0.2-3.85 mg/L in summer. The Total Organic Carbon (TOC) contents varied from 2.32 mg/L to 2.67 mg/L in winter and 2.75 mg/ to 6.20 mg/L in summer (Figure 2.68, Figure 2.69). TOC values, especially summer values are quite high indicating the influence of municipal wastewaters.

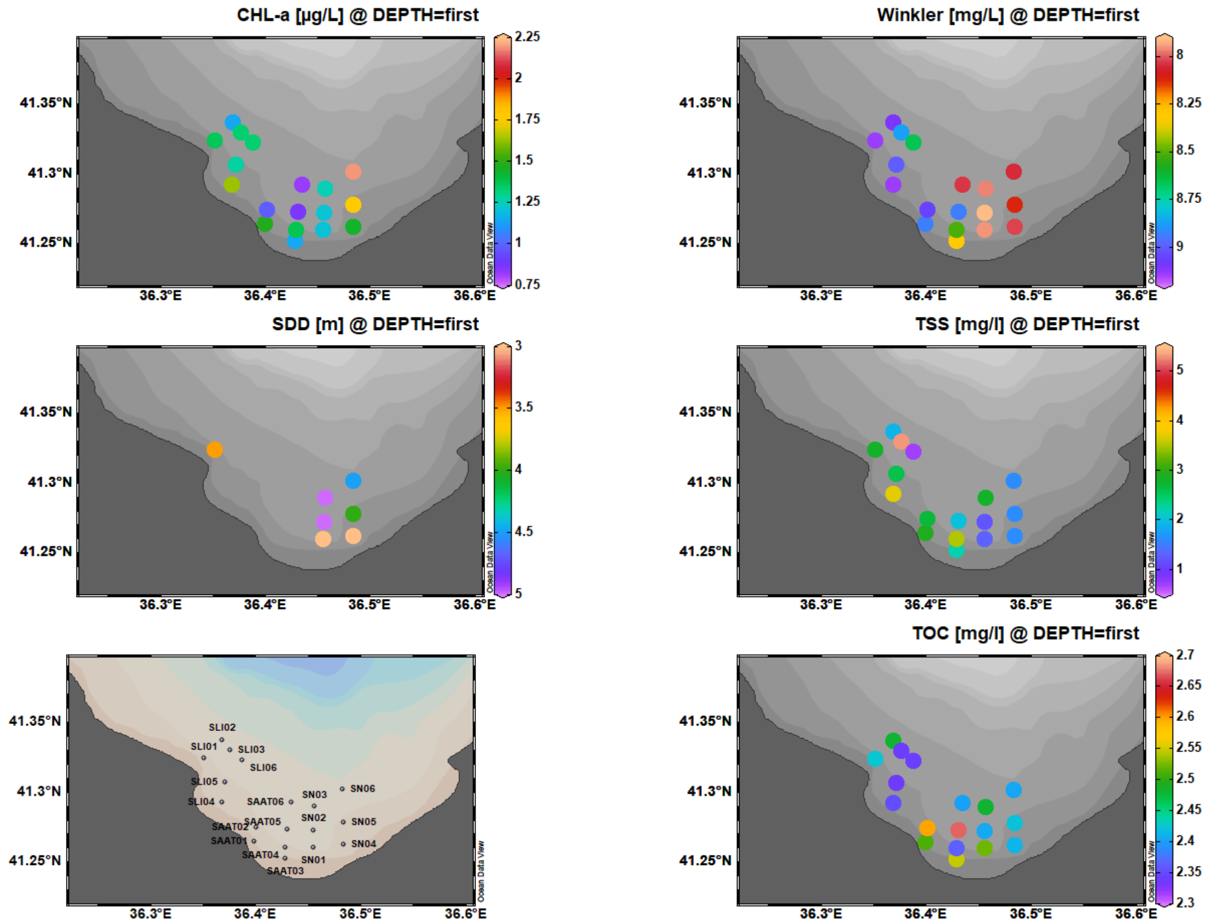


Figure 2.68 - The winter measurements of surface chlorophyll a, TSS, TOC, SDD and dissolved oxygen at Samsun study site

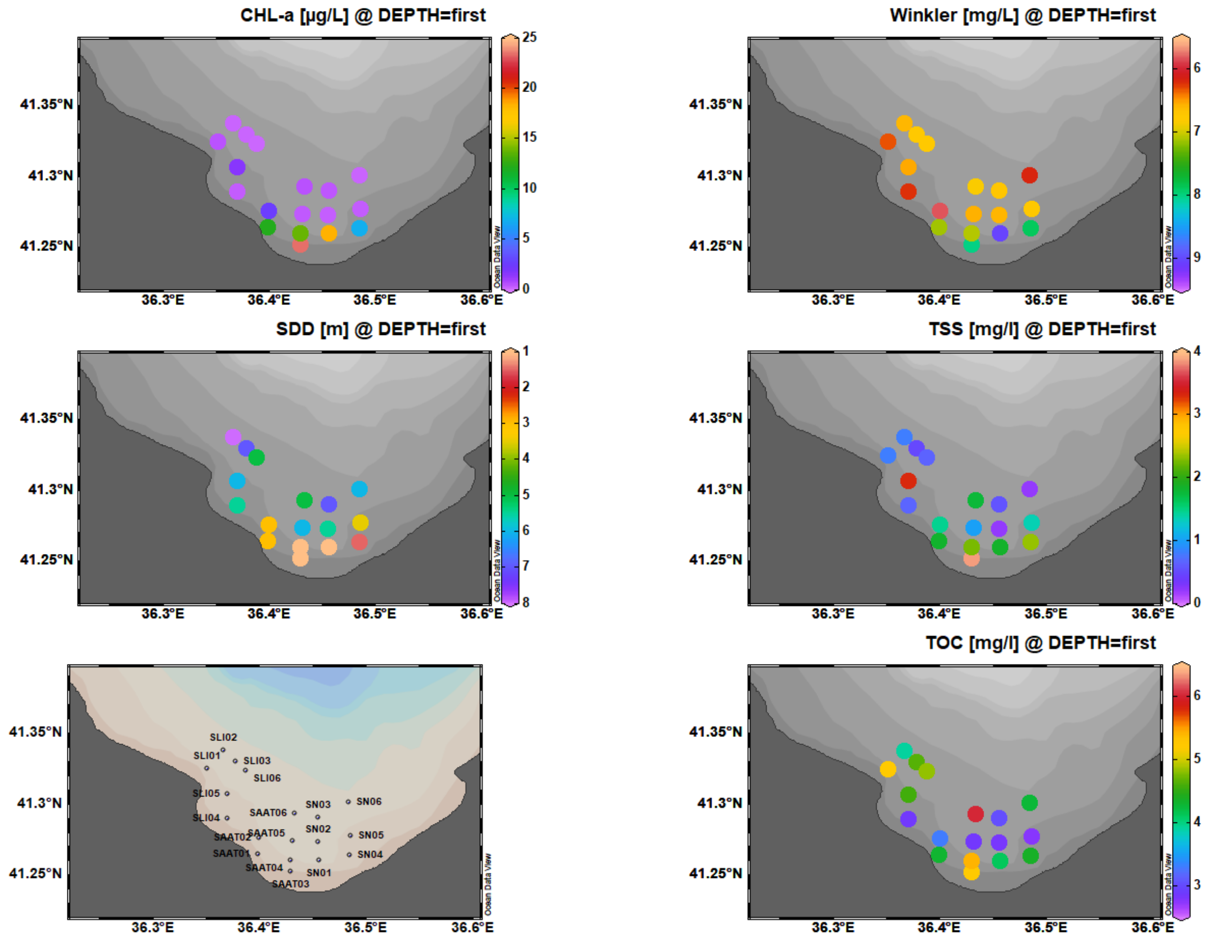


Figure 2.69 - The summer measurements of surface chlorophyll a, TSS, TOC, SDD and dissolved oxygen at Samsun study site

It can be predicted that SAAT site has higher concentrations than the other two sites showing the influence of WWTP discharge. Although it is known that the inner part of the port is heavily polluted, this does not affect the outer port waters (lowest values were measured at SLI stations). The effect of local small-scale currents was not considered in this evaluation and the cumulative effects of different pressures could not be differentiated.

2.3.3.3 Heavy Metals

Cd concentrations were detected between 0.02-1.33 µg/L. Maximum concentrations of Cd were determined in stations SN 6 in winter and summer seasons as 0.43 µg/L and 1.33 µg/L, respectively. Pb concentrations were detected between 0.03-2.31 µg/L. Similar to Cd, the maximum concentration of Pb was determined in the samples taken from the SN6 station in the summer season. Ni concentrations were measured between 0.57 µg/L and 1.08 µg/L. The maximum concentration of Ni was also measured in winter (SAAT1). Spatial distribution maps show that higher concentrations of the metals in the water matrix were dominated at the stations closer to the industrial area such as copper production and metal processing (Figure 2.70 and Figure 2.71).

All metals measured in the water matrix were found below the MAC-EQS values identified as Priority Substances (EU-2013/39) and Specific Pollutants (TR-2016/08) under the WFD (Water Framework Directive).

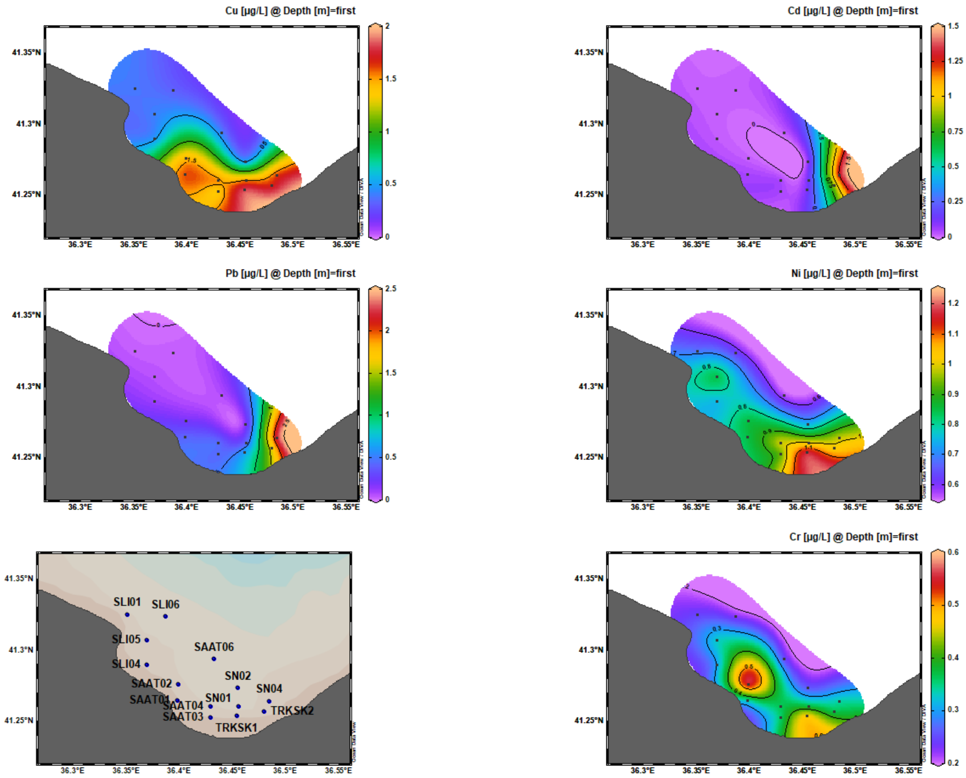


Figure 2.70 - Special distribution of the metals in water collected from Samsun Hot Spot area, summer 2019

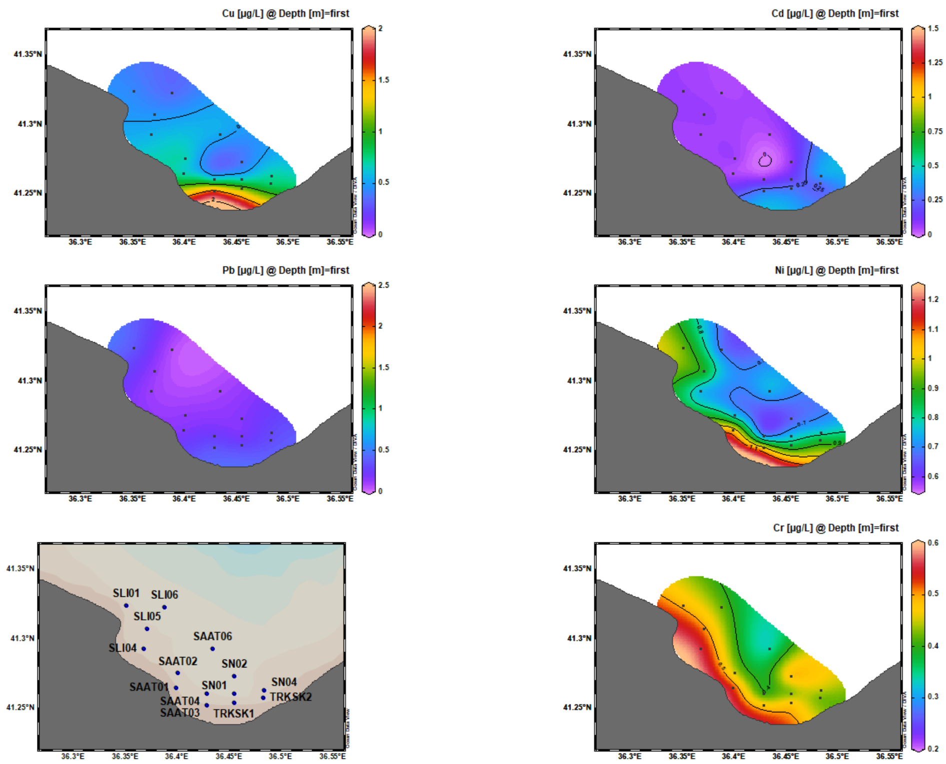


Figure 2.71 - Special distribution of the metals in water collected from Samsun Hot Spot area, winter 2020

Concentrations of metals in surface water samples (oxic layer) collected from all stations were detected below the EQS levels established by Directive 2013/39/EU and the National Surface Water Management Regulation of Turkey (2016) (Figure 2.72).

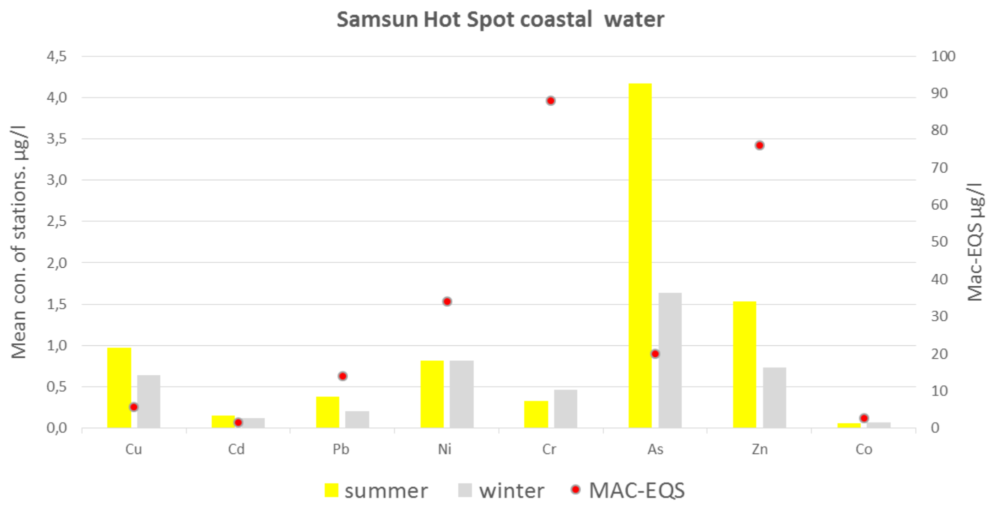


Figure 2.72 - Metal concentrations of the water samples collected in summer (2019) and winter (2020)

Most of the elements (As, Zn, Pb, Cu) were found in higher concentrations in the summer season or similar levels in both seasons such as Co, Ni and Cd. In general, higher metal concentrations (Cd, Pb, As, Zn and Cu) were observed in water samples collected from the Samsun Hot Spot coastal area than the river-sea impact areas of Yesilırmak and Sakarya (Figure 2.73).

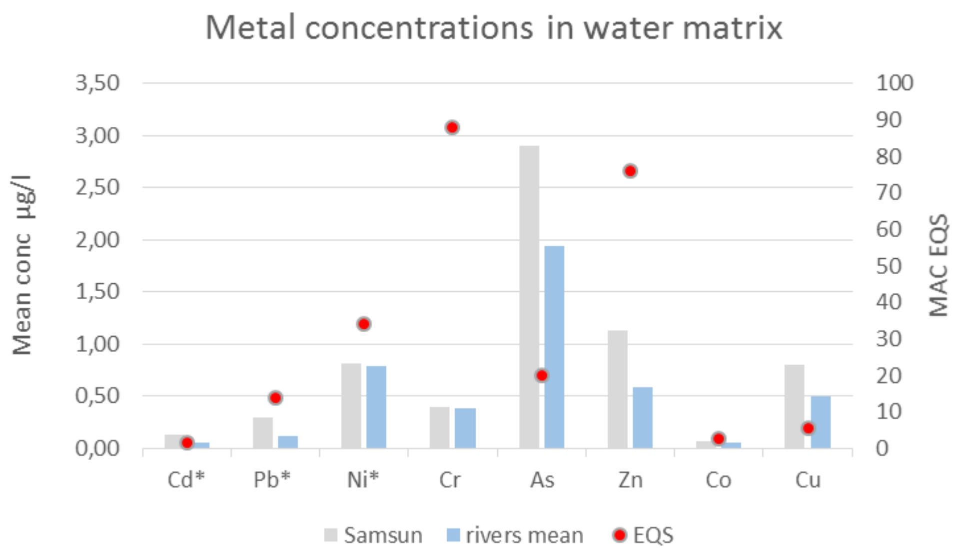


Figure 2.73 - Metal concentrations in Samsun coastal and RIAs (Yeşilırmak and Sakarya) waters

Metal concentrations measured in all surface seawater samples of the Samsun Hot Spot coastal area (in July 2019 and January 2020) were found below the MAC-EQS values identified as Priority Substances (EU-2013/39) and Specific Pollutants (TR-2016/08) under the WFD (Water Framework Directive). Generally, a decreasing gradient from coast industrialized area (eastern part of the Hot Spots) and WWT discharge (middle part of the Hot Spots area) to open area was noticed for most analysed metals, reflecting metal industry influence upon receiving zone. The seasonal difference was observed in Samsun HS water samples in terms of higher metal contents in summer sampling with minimum dilution effect of rivers and precipitation.

2.3.3.4 Organic Pollutants

Total Petroleum Hydrocarbon (TPH) in seawater ranged between 0.011 μg/L and 2.684 μg/L at Samsun Port and WWT impact areas. These values are lower than the Max-EQS value (100 μg/L) stated in the National Surface Water Management Regulation from 2016 (Figure 2.74, Figure 2.75).

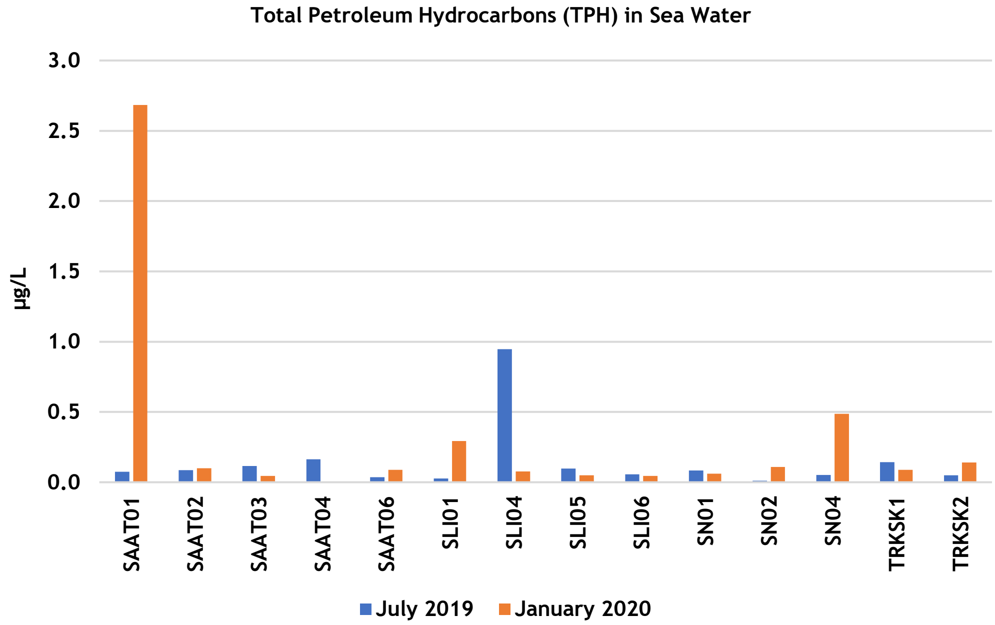


Figure 2.74 - TPH concentrations in seawater, Samsun Hot Spot

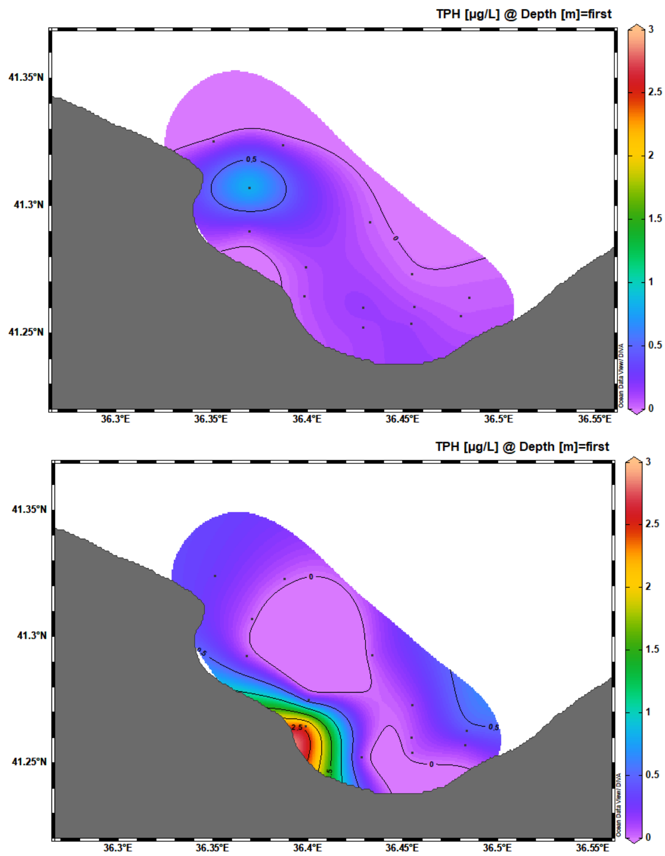


Figure 2.75 Spatial distribution of TPH in surface waters - summer 2019 (left) and winter 2020 (right), Samsun Hot Spot

Concentrations of most of the priority organic substances were found below the Max-EQS (Directive 2013/39/EU) except Benzo(a)Pyrene and Benzo[b]fluoranthene, one of the 16 polyaromatic hydrocarbons. The Benzo(a)Pyrene levels were found higher than the Max-EQS (0.027 µg/L) in the winter season at seven stations of Samsun Port and WWTP (SAAT01, SAAT02, SAAT03, SAAT04, SAAT06, SLI04 and SLI06: 0.177 µg/L, 0.087 µg/L, 0.305 µg/L, 0.032 µg/L, 0.125 µg/L, 0.064 µg/L and 0.035 µg/L respectively). Benzo(b)fluoranthene concentrations were also higher in the four stations of Samsun Port and WWTP (SAAT01, SAAT02, SAAT03, SAAT06 and SLI04: 0.157 µg/L, 0.053 µg/L, 0.322 µg/L, 0.313 µg/L and 0.061 µg/L) than the threshold value (Max-EQS 0.017 µg/L) (Directive 2013/39/EU) (Figure 2.76).

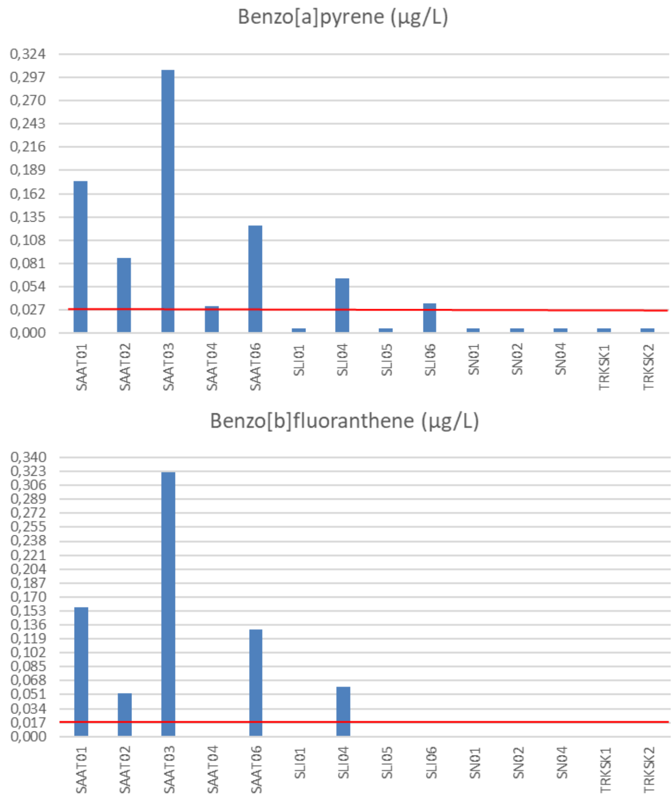


Figure 2.76 - Concentrations of benzo(a)pyrene and benzo(b)fluoranthene in surface waters of Samsun HS in relation to the proposed value to define good environmental status, January 2020

3 Benthic habitats

Benthic habitats play an important role in some of the key ecosystem processes (i.e., primary production, food webs, recycling, etc.), but they are subject to many human pressures which put at risk their functionality (Claudet & Fraschetti, 2010). The European Marine Strategy Framework Directive (MSFD; Directive 2008/56/EC) requires the European Member States to achieve a Good Environmental Status (GEnS) by 2020 (Borja (2006), Borja et al. (2011b) and Borja et al. (2013)). The AZTI Marine Biotic Index (AMBI; Borja et al., 2000) and M-AMBI (Muxica et al., 2007) are widely used in assessing the quality of the benthic environment all over the world and they were also reported as good approaches to assess the benthic ecological quality in the Black Sea. M-AMBI*(n) (Sigovini et al., 2013) is a simplified modification of the original method M-AMBI. It was proposed as one of the indicators for assessing the good environmental status of marine habitats in the Romanian and Bulgarian marine waters (Todorova et al., 2013, 2018; Abaza et al., 2018).

The assessment of the condition of benthic habitats is one of the evaluation criteria both in the WFD (as a biological quality element) and in the MSFD descriptors (Benthic Habitat - D1, D4, D6).

3.1 Macrozoobenthos

3.1.1 Ukraine

We observed the lowest species diversity - only ten taxa (Figure 3.1). The most abundant were *Mytilus galloprovincialis* (Lamarck, 1819), *Alitta succinea* (Leuckart, 1847), *Nephtys hombergii* (Savigny in Lamarck, 1818), *Palaemon elegans* (Rathke, 1836). The species compositions were similar to almost all marine stations because of the dominance of *Mytilus galloprovincialis* and *Alitta succinea* (Figure 3.2).

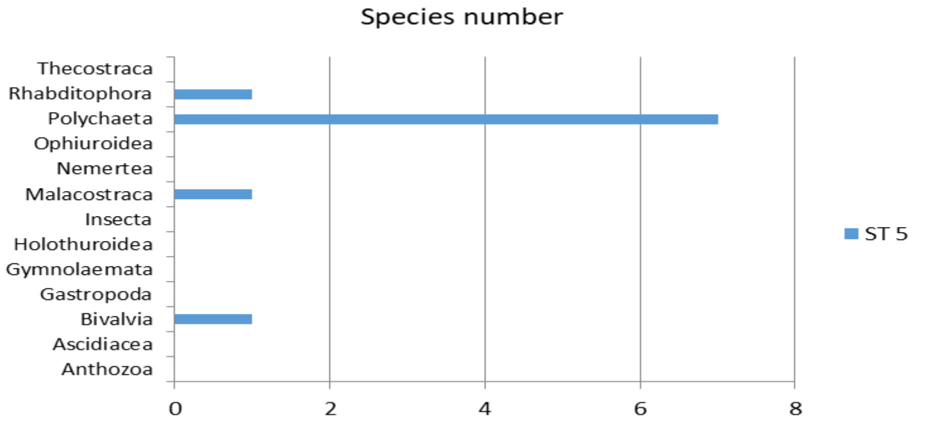


Figure 3.1 Taxa composition within "Hot spots."

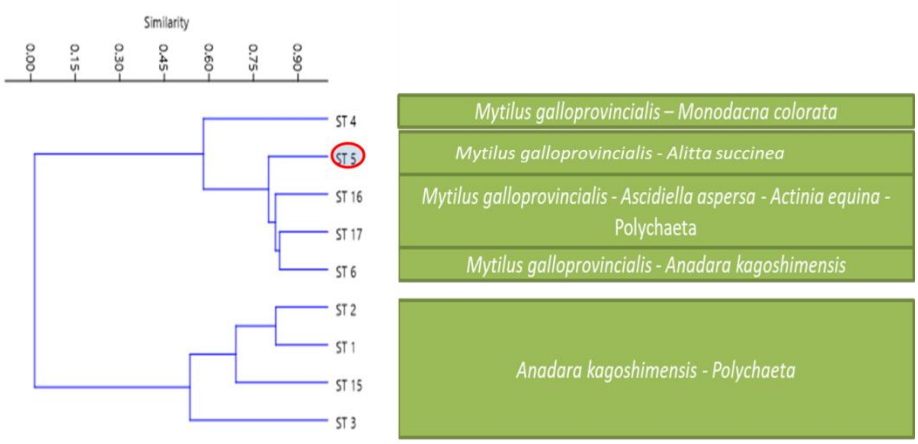


Figure 3.2-Bray Curtis similarity of macrozoobenthos based on % biomass data comparing "river-sea border" stations, "hot spots" (in circles), and marine stations

The community's abundance and biomass were relatively low and did not exceed 1000 ind/m^2 and 50 g/m^2 (Figure 3.3).

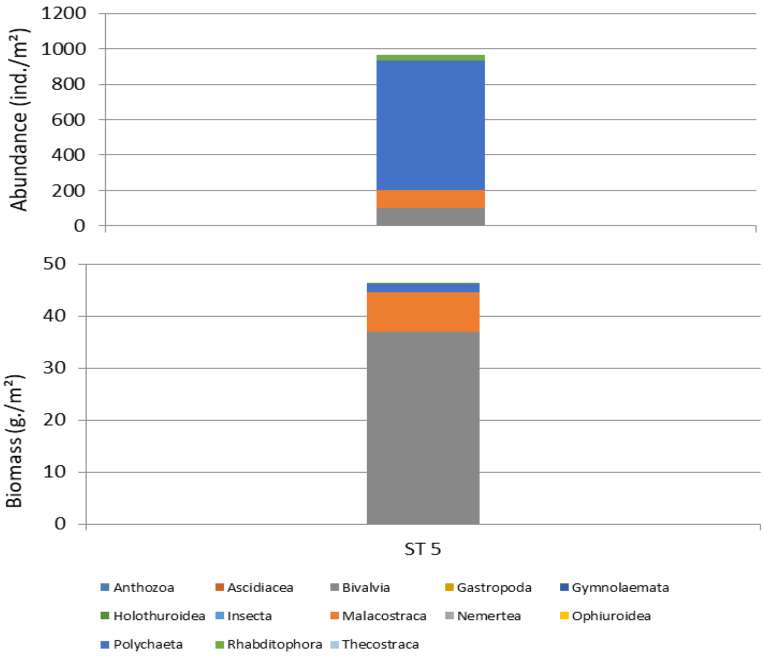


Figure 3.3 - Abundance and biomass within "Hot spot" - Ukrainian region of the Black Sea

The food web composition was like one of the river-sea border communities devote to mud as the main substrate. The species specialized on subsurface predation on meiobenthos dominated by biomass, but the share of different functional feeding groups in abundance was structured. On both scales, the share of epibenthic suspenser feeders was significant (Figure 3.4).

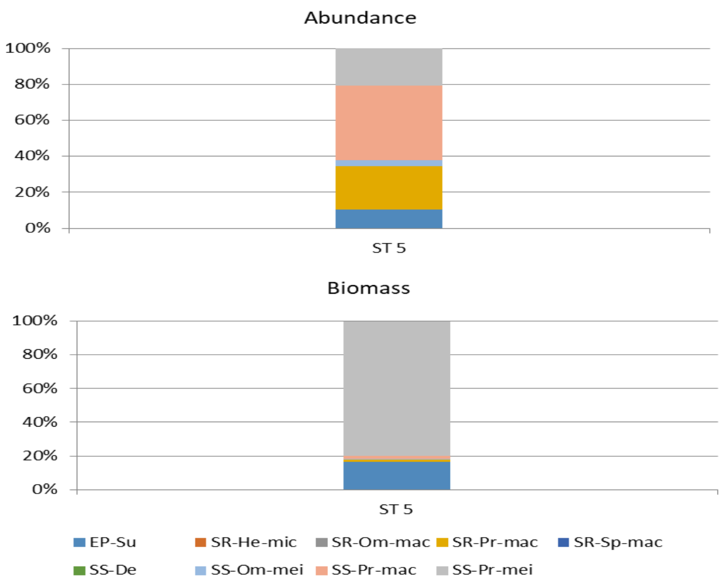


Figure 3.4 - The share (%) in abundance and biomass of different functional feeding groups within the "hot spots"

Despite the lack of diversity, the hotspots community had comparable indices values with a worst in all marine stations (Table 3.1).

Table 3.1 - Alpha diversity of hotspot

Station	S	iChao1	H'	I_{Mg}
5	10	10	2.038	1.31

S – species richness, iChao1 – lower bound of potential species richness, H` - Shannon index, IMg – Margalef index

A comparison of AMBI values revealed that most of the stations were slightly disturbed, but low species number and Shannon index values led to "moderate" class according to M-AMBI (n) (Table 3.2).

Table 3.2 - AMBI and M-AMBI values

Station	AMBI	Disturbance	M-AMBI(n)	Class
5	2.949	Slightly disturbed	0.658	Moderate

S – species richness, iChao1 – lower bound of potential species richness, H` - Shannon index, IMg – Margalef index

Conclusions

The poorest species composition (only ten taxa) occurred under anthropogenic impact within the hot spot area.

The dominant species composition was similar in all marine stations because of the significant share of *Mytilus galloprovincialis* (over 50 % of biomass).

The hot-spot area's trophic structure was closer to the river-sea border zone's trophic structure, devoted to soft muddy sediments there and a high share in the abundance of polychaete *Alitta succinea*.

3.1.2 Romania

The identified species were associated with one of the five ecological groups (EG) according to AMBI index: EGI: sensitive species; EGII: indifferent species; EGIII: tolerant to organic enrichment; EGIV: second-order opportunistic species; and EGV: first-order opportunistic species (Borja et al., 2000). The ecological group classifications consider feeding type, life habit, body size, life history, and response to disturbances (i.e., organic enrichment) (Borja et al. 2000). Before quantitative data analysis at each station, the average between replicates was done. For each harbour, Shannon Diversity Index was calculated. This is an index applied to biological systems derived from a mathematical formula used in the communication area by Shannon in 1948 (Mandaville, 2002). It is the most preferred index among the other diversity indices. The index values are between 0.0 – 5.0. The values above 3.0 indicate that the structure of the habitat is stable and balanced; the values under 1.0 indicate that there are pollution and degradation of habitat structure.

Bray-Curtis similarity analysis was performed with square-root transformed data using Primer package program version 7 (Clarke et al., 2014). SIMPER (similarity percentages – species composition) procedure, also available in Primer, was used to investigate the contribution of each species to mean Bray-Curtis dissimilarity between inner and outer sites.

Port of Midia

The macrofaunal community in the Midia area was comprised of 30 taxa belonging to five taxonomical groups (Annex C). The greatest diversity registered in the control station (MD_M – 20 species) and the lowest inside of the Midia Port (MD_A – 5 species). There was no considerable difference between outer stations (MD_B, MD_C, and MD_M) in terms of diversity.

Macrozoobentic diversity was dominated by the polychaetes (16 species) followed by molluscs (6 species) and crustaceans (5 species).

Benthic diversity was formed in the inner station (MD_A), by tolerant and opportunistic species, except *Nephtys hombergii* which is an indifferent one. High organic content in sediment can promote the abundance of some tolerant species and reduce sensitive species (Pearson & Rosenberg, 1978). In the other three stations species that belonged to all five ecological groups were present.

Shannon Diversity Index was between 0.579 and 2.032. The values less than 1.0, as in the case of inside the harbour (MD_A), indicate the presence of pollution and degradation of habitat structure (Figure 3.5).

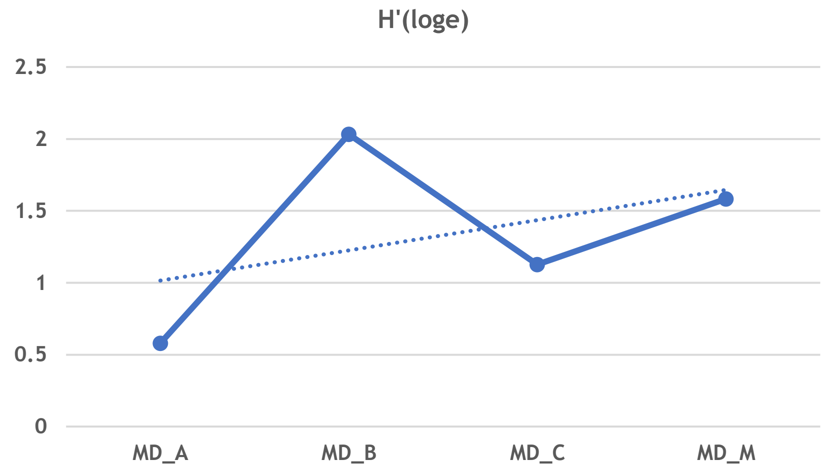


Figure 3.5 - Shannon Diversity Index values of Midia sites

The **density** of macrozoobenthic communities at Midia ranged from 410 ind./m^2 (MD_A) to 3920 ind/m^2 (MD_B). Molluscs were numerically dominant, accounting for 57 % of the total macrofauna. Their dominance is due to the presence in large numbers of the small bivalve *Lentidium mediterraneum* (max. density 2650 ind/m^2 at MD_C) which was present only in the stations outside the port (Figure 3.6). In the study area, where the predominant habitat is fine sand, *Lentidium mediterranem* is a key species.

Polychaetes were the second dominant group, representing 29 % of the total macrofauna density. Among the polychaetes, present in all four stations were the species *Capitella capitata* (first-order opportunistic species) and *Nephtys hombergii* (indifferent species). *Nephtys hombergii* was also numerical dominant species inside the harbour (MD_A).

Crustaceans, another important group in benthic communities, represented 14 % of the total macrofauna density. The crustacean species that recorded high-densities (77 ind/m^2 to 773 ind/m^2) was *Ampelisca diadema*, found just outside of the harbour. Cnidaria and Nemertea had a very low contribution, in terms of density.

Molluscs were also the dominant group accounting for 72 % biomass, followed by crustaceans (16 %) and polychaetes (1 2%) (Figure 3.7). Zoobenthic communities' biomasses ranged from 17.985 g/m^2 (MD_A) to 137.939 g/m^2 (MD_M).

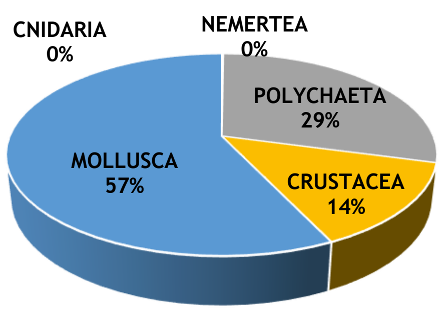


Figure 3.6 - Percentages of zoobenthic groups - abundance

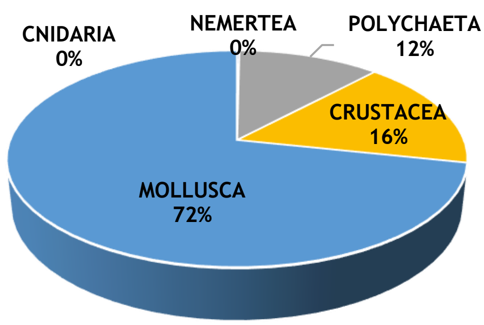


Figure 3.7 - Percentages of zoobenthic groups-biomass

An analysis of density and biomass data showed that the macrozoobenthic groups were distributed differently depending on the station (Figure 3.8). Inside the harbour (MD_A) polychaete worms dominated numerically (100 %), an expected feature of the polluted areas. In this inner station, the benthic community was represented by a few polychaete species that contributed with high values to the total density. At MD_B, the station closest to the port, the molluscs dominated (46 %) followed by polychaetes (32 %) and crustaceans (22 %). The dominance of molluscs was due to the presence in large numbers of two key bivalve species: *Lentidium metiterraneum* (880 ind/m^2) and *Chamelea gallina* (650 ind/m^2).

Molluscs also dominated (72 %) at outer station MD_C, followed by the polychaetes (26 %) and crustaceans (2 %). As in the case of the previous station, among the molluscs, the dominant species were *Lentidium mediterraneum* (2650 ind/m^2) and *Chamelea gallina* (80 ind/m^2).

At control station (MD_M) molluscs recorded 58 % from macrozoobenthic density followed by the polychaetes (22 %) and crustaceans (20 %). In this station, also appeared some new species of molluscs such as *Macomangulus tenuis* (3 ind/m^2) and *Parvicardium exigum* (7 ind/m^2), but the dominant remained *Lentidium mediterraneum* (2 090 ind/m^2). The presence of these molluscs (*Macomangulus tenuis* and *Parvicardium exigum*), which are sensitive species (EG I) shows an improvement of the ecological status in the control station compared to the other stations.

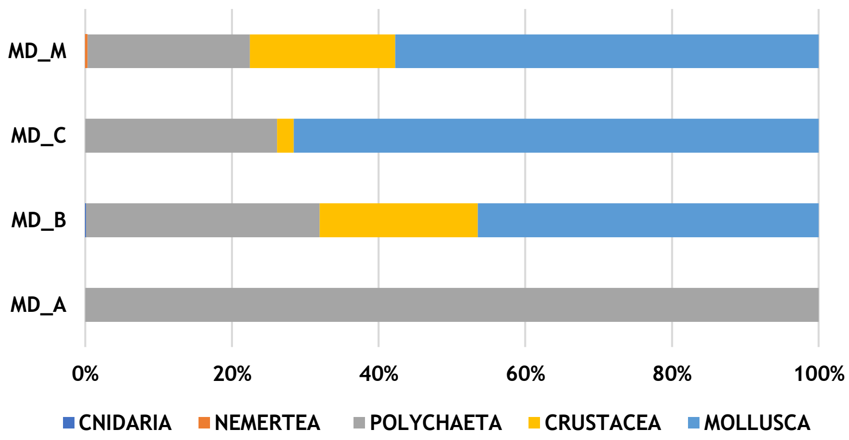


Figure 3.8 - Percentage of densities

In terms of biomass, at MD_A, the situation was almost similar as in the density case (Figure 3.9). At the other stations, biomass was dominated by molluscs and crustaceans. From the crustaceans biomass, the burrowing decapod *Upogebia pusilla* had a high contribution. It recorded values of 7 g/m^2 at MD_C and MD_M. *Upogebia pussila* is also considered a sensitive species (EG I).

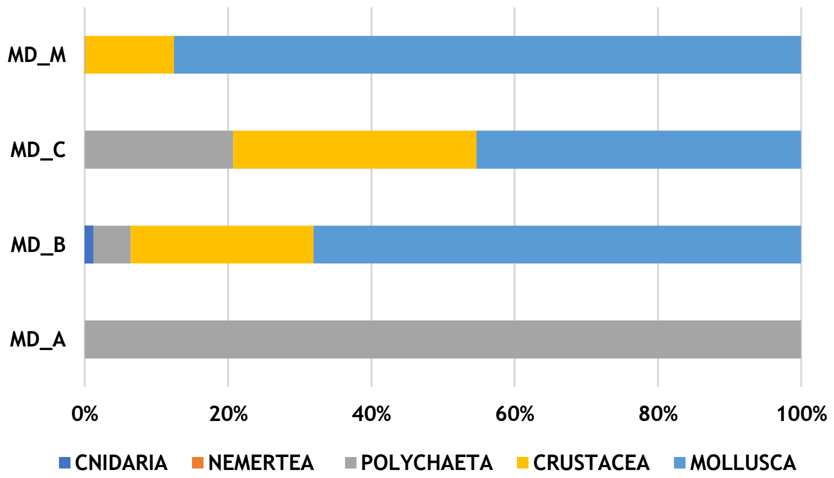


Figure 3.9 - Percentage of biomass

Abundances were subjected to Bray-Curtis cluster analyses and showed that the similarity between the station located inside the harbour and the other three stations located outside is less than 20 %.

A similarity of over 60 % was observed between the control station and the other two stations located outside the port (Figure 3.10).

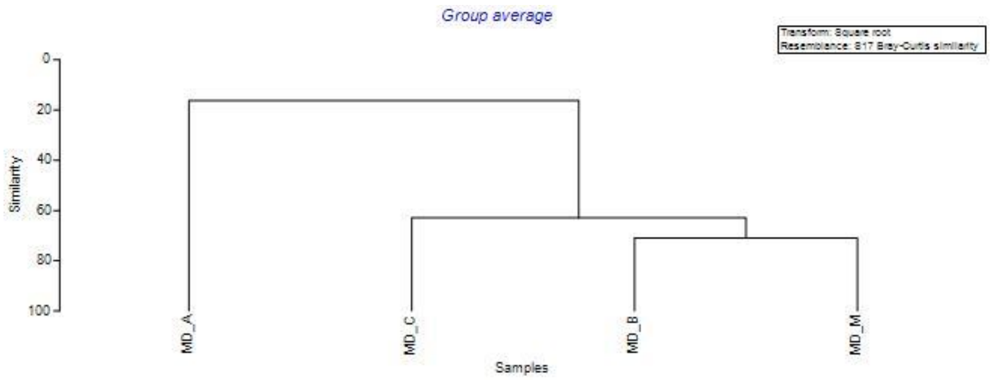


Figure 3.10 - Bray-Curtis similarities, square-root transformed abundance data

According to SIMPER analysis, the average dissimilarity between inner and outer stations is 83.75 %. The inner and outer stations difference is a sum of the high contribution from *Lentidium mediterraneum* (24.79 %) and *Ampelisca diadema* (11.79 %) and smaller contributions from other benthic species (Table 3.3).

Table 3.3 - SIMPER analyses based on abundance data in the Midia port area

InnerMD & OuterMD Average dissimilarity = 83.75	InnerMD	OuterMD				
Species	**Av.Abund**	**Av.Abund**	**Av.Diss**	**Diss/SD**	**Contrib%**	**Cum.%**
Lentidium mediterraneum	0	42.29	20.76	2.98	24.79	24.79
Ampelisca diadema	0	20.94	9.87	2.18	11.78	36.58
Scolelepis (Scolelepis) squamata	0	16.41	8.21	1.55	9.80	46.38
Chamelea gallina	0	15.52	7.35	1.96	8.78	55.15
Pygospio elegans	0	12.75	5.98	1.90	7.14	62.30
Prionospio cirrifera	0	10.76	5.16	3.75	6.16	68.46
Nephtys hombergii	18.71	9.70	4.37	10.20	5.21	73.67

Port of Constanta

The macrofaunal community at the Constanta area was comprised of 27 taxa belonging to five taxonomical groups (Annex C).

The greatest diversity was registered in the control station (CT_M – 22 species) and the lowest at the inner station (CT_A – 6 species). Benthic assemblage mirrored a diversity gradient from the inner station to the control station. Even in the case of the outer stations, significant differences were observed. In the CT_B station, 9 species were registered, in CT_C, 13 species and CT_M, 22 species.

Macrozoobentic communities were dominated by the polychaetes (11 species) followed by molluscs (7 species) and crustaceans (7 species).

Benthic communities from the inner station were formed just from polychaetes worms belonging to ecological groups II, III, IV, and V.

The values of the Shannon Diversity Index were between 1.125 and 2.011. The lowest value was for the inner station (CT_A) and increased to the control station (CT_M) (Figure 3.11).

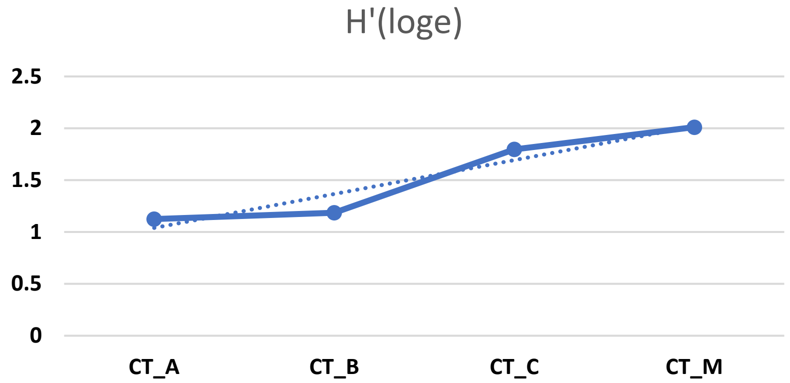


Figure 3.11 - Shannon Diversity Index values, Constanta Port

The density of macrozoobenthic communities at Constanta ranged from 407 ind/m^2 (CT_B) to 1 557 ind./m^2 (CT_M). Polychaetes were the dominant group representing 94 % of the total macrofauna density. Polychaetes density ranged from 353 ind/m^2 (CT_B) to 1470 ind/m^2 (CT_M) (Figure 3.12).
Crustaceans were the second dominant group representing 4 % of the total macrofauna density. Crustaceans density ranged from 0 ind/m^2 at CT_A to 47 ind/m^2 at CT_C and CT_M.
Molluscs represented 2 % of the macrofauna, with a density that ranged from 0 ind/m^2 (CT_A) to 33 ind/m^2 (CT_M).
Biomass was dominated by molluscs (76 % of the total) followed by crustaceans (20 %), polychaetes (3 %) and cnidarians (1 %) (Figure 3.13).

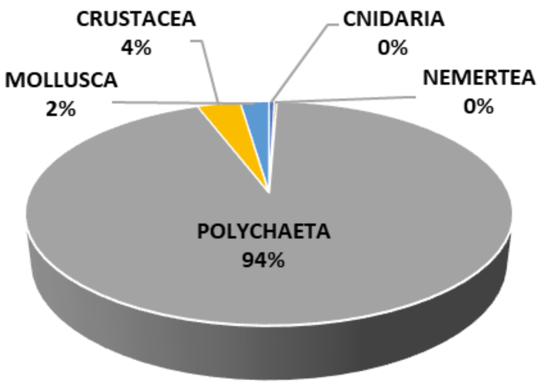


Figure 3.12 - Percentages of zoobenthic groups - abundance

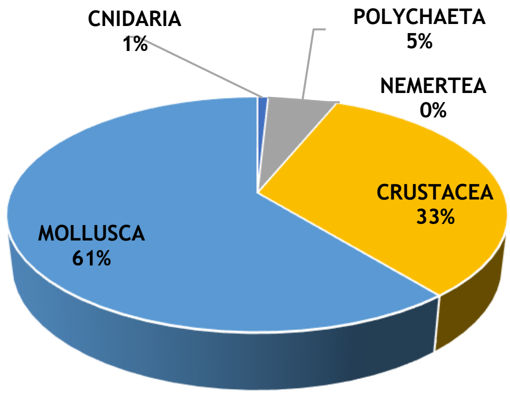


Figure 3.13 - Percentages of zoobenthic groups - biomass

Stations analysis based on quantitative data shows again a significant difference between inner and outer stations (Figure 3.14). At CT_A polychaetes were dominant (100 %). Among the polychaetes, the highest densities were recorded by *Nephtys hombergii* (270 ind/m^2) and the first-order opportunistic species *Capitella capitata* (123 ind/m^2).

At CT_B polychaetes dominated with 87 % followed by molluscs (6 %), crustaceans (4 %) and cnidarians (3 %). Cnidarian, *Diadumene lineata* is an indifferent (EG II) alien species often found inside Constanta harbour on hard substrata with mussels (*Mytilus galloprovincialis*) (Preda et al., 2012). This study found just at CT_B on different bivalve shells. The sensitive species *Upogebia pusilla,* 10 ind./m^2, was recorded at CT_B.

Polychaetes were also the dominant group at CT_C accounting for 92 % from density. Among polychaete species, *Nephtys hombergii* (277 ind/m^2) and *Capitella capitate* (237 ind/m^2) recorded the higher values. The second group were crustaceans (6 %), with *Upogebia pusilla* registering the highest density (27 ind/m^2). The third group were molluscs (2 %), represented by the sensitive species *Chamelea gallina* which recorded 17 ind/m^2.

At CT_M to the highest density contributed a great diversity. Polychaetes, the dominant group (94 %) was followed by the crustaceans (3 %) and molluscs (2 %). An important fact to mention is that many sensitive species have appeared here, such as *Nototropis guttatus* (7 ind/m^2), *Upogebia pusilla* (23 ind/m^2), *Chamelea gallina* (7 ind/m^2), *Parvicardium exiguum* (3 ind/m^2) and *Polititapes aureus* (13 ind/m^2).

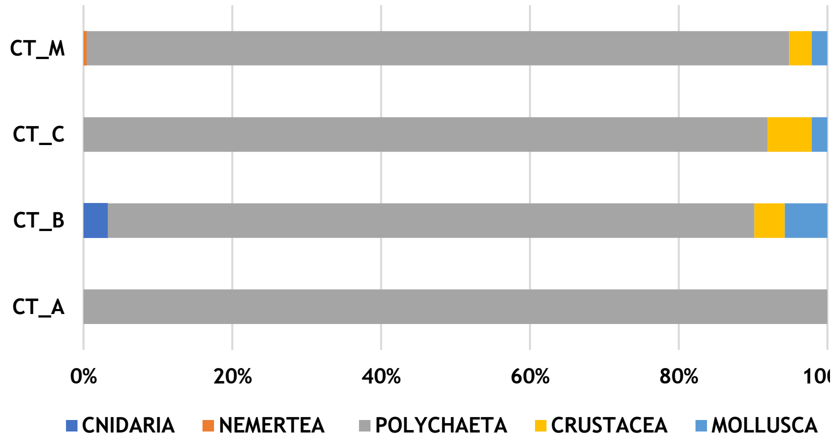


Figure 3.14 - Percentage of densities

In terms of biomass, except for the inner station CT_A, where polychaetes dominated, in all other stations, molluscs and crustaceans were dominant. Even though polychaetes have high densities in all stations, biomass has been dominated by large species of crustaceans and bivalves. Of these, the largest biomasses were recorded by species such as *Anadara kagoshimensis* (147.86 g/m^2, CT_B), *Chamelea gallina* (24.95 g/m^2, CT_C), *Upogebia pusilla* (49 g/m^2, CT_M) and *Polititapes aureus* (40.96 g/m^2, CT_M) (Figure 3.15).

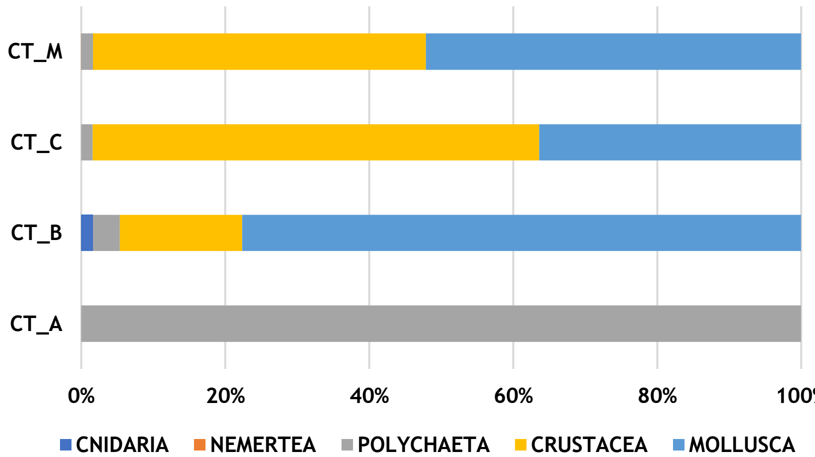


Figure 3.15 - Percentage of biomass

Because polychaetes dominated numerically in all stations, the Bray-Curtis analysis of abundance data was not relevant enough. Consequently, biomass data were subjected to Bray-Curtis analysis using the Primer software.

The Bray-Curtis cluster showed that similarity at the inner station and outer stations was less than 20 % (Figure 3.16). A low similarity was also registered between the station CT_ B and the other two outer stations. This may be due to very high biomass values recorded just at CT_B by the opportunistic species *Anadara kagoshimensis* (147.86 g/m^2). The greatest similarity (>50 %) was between CT_C and CT_M stations, both at distance from the inner harbour.

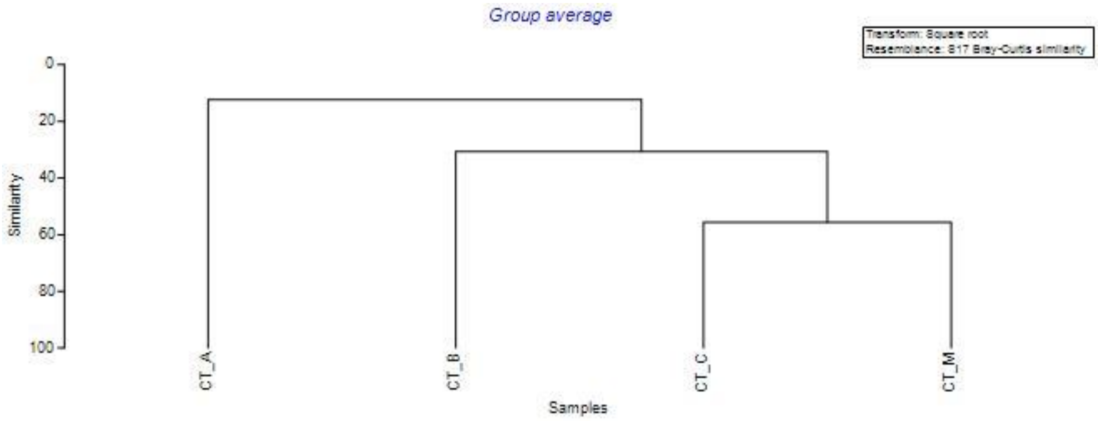


Figure 3.16 - Bray-Curtis similarities, square-root transformed biomass data

The average dissimilarity between inner and outer stations in the Constanta area was 41.44 %. To this difference contributed eleven species with percentages between 3.54 % and 15.07 % (Table 3.4).

Table 3.4 - SIMPER analyses

Groups InnerCT & OuterCT Average dissimilarity = 41.44	**InnerCT**	**OuterCT**				
Species	**Av. Abund**	**Av. Abund**	**Av. Diss**	**Diss/SD**	**Contrib. %**	**Cum. %**
Heteromastus filiformis	0.00	9.73	6.25	1.14	15.07	15.07
Prionospio cirrifera	6.32	5.76	3.74	1.20	9.03	24.10
Upogebia pusilla	0.00	4.39	3.45	4.75	8.32	32.42
Capitella capitata	11.11	11.45	3.21	1.42	7.74	40.16
Polydora cornuta	2.58	4.97	2.85	1.44	6.88	47.05
Scolelepis (Scolelepis) squamata	1.83	3.14	1.9	4.88	4.58	51.62
Pygospio elegans	0.00	2.97	1.86	1.05	4.48	56.10
Lagis koreni	0.00	2.22	1.56	0.96	3.77	59.87
Chamelea gallina	0.00	2.22	1.56	0.96	3.77	63.64
Anadara kagoshimensis	0.00	1.36	1.52	0.58	3.68	67.32
Nephtys hombergii	16.43	18.98	1.47	0.67	3.54	70.86

Eforie wastewater discharge

In the Eforie area, where the wastewater is discharged, the diversity was smaller compared to the control station (CT_C) (Annex C). It is important to mention that two of the six species identified at Eforie were sensitive species (*Upogebia pusilla* and *Abra prismatica*).

The Shannon Diversity Index at EF_WD has a lower value (1.108) compared to the control station (1.796).

Total macrozoobenthic density was dominated by the polychaetes (92 %) followed by the crustaceans (5 %), molluscs (2 %) and cnidarians (1 %) (Figure 3.17). Biomass was dominated by the crustaceans (65 %), molluscs (30 %), cnidarians (3 %) and polychaetes (2 %) (Figure 3.18).

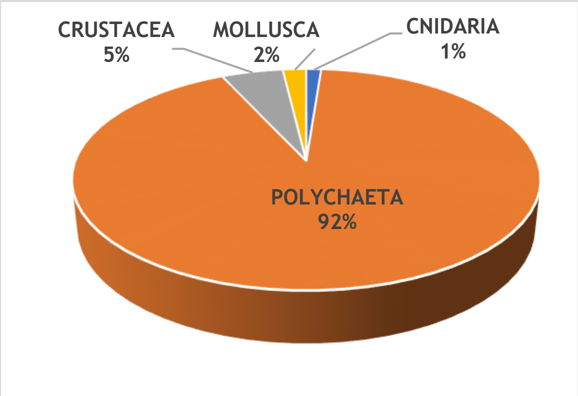


Figure 3.17 - Percentages of zoobenthic groups - abundance

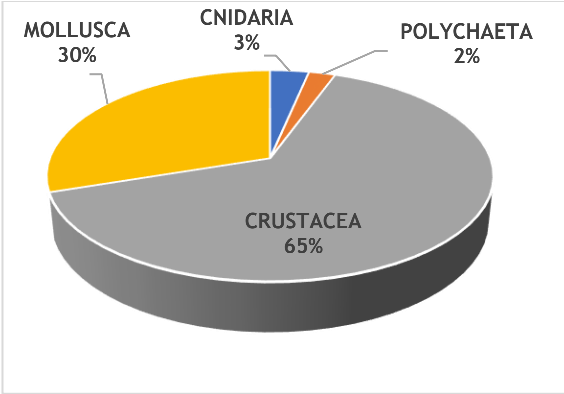


Figure 3.18 - Percentages of zoobenthic groups - biomass

In both stations, the density was dominated by polychaetes with 92 % (Figure 3.19).

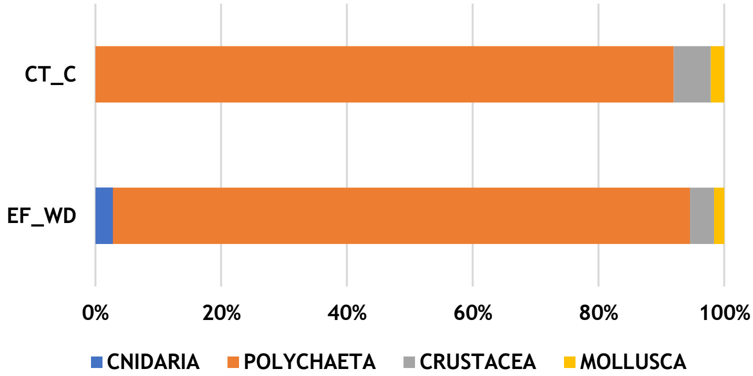


Figure 3.19 - Percentage of densities

In terms of biomass, at EF_WD crustaceans dominated with 73 % followed by cnidarians (16 %), molluscs (6 %) and polychaetes (5 %) (Figure 3.20).

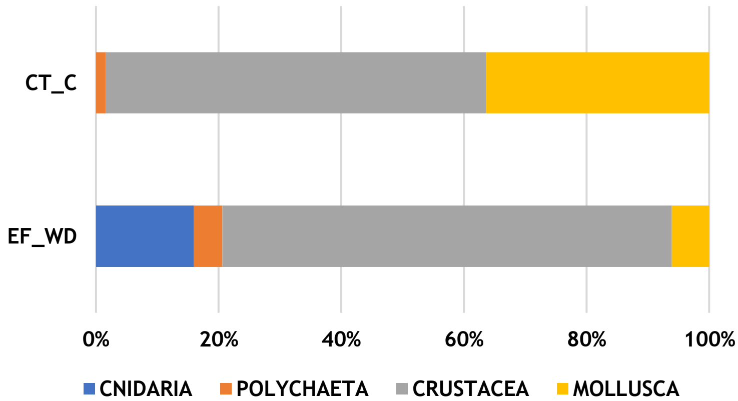


Figure 3.20 - Percentage of biomass

Port of Mangalia

The macrofaunal community at the Mangalia area comprised by 19 taxa belonging to four taxonomical groups (Annex C).

The greatest diversity was registered in the control station (MG_M – 16 species) and the lowest at the inner station (CT_A – 4 species). Two of the 4 polychaete species in MG_A station were sensitive species. Even if the two polychaetes (*Lindrilus flavocapitatus* and *Saccocirrus papillocercus*) are considered sensitive species to the content of organic matter in the sediment, at the Romanian coast they are very common species in the sandy infralittoral at depths between 0.5 m and 20 m.

The values of Shannon Diversity Index were between 0.974 and 1.833. The lowest value was recorded inside the harbour (MG_A) and the highest at MG_C. The value of 0.974, less than 1.0, indicates the pollution and degradation of the habitat structure (Figure 3.21).

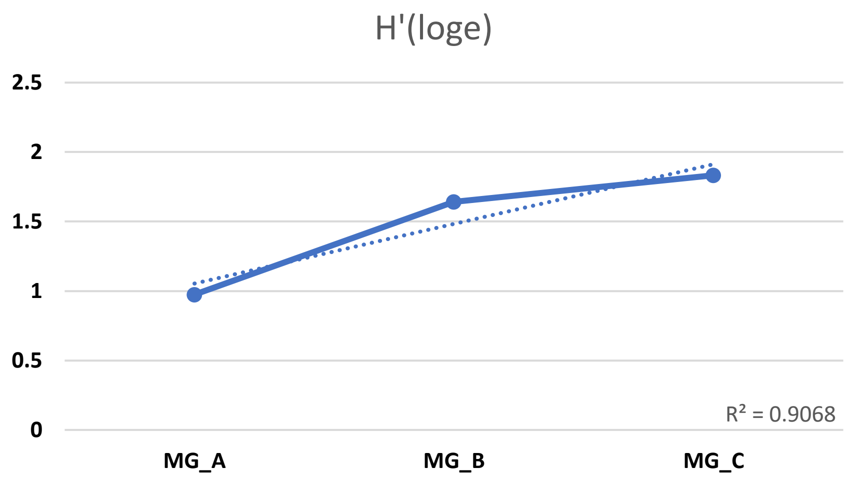


Figure 3.21 - Shannon Diversity Index values, Mangalia Port

The density of macrozoobenthic communities at Mangalia ranged from 410 ind/m^2 (MG_A) to 1 057 ind/m^2 (MG_C). Polychaetes were the dominant group representing 97 % of the total macrofauna density followed by the crustaceans (2 %) and nemerteans (1 %) (Figure 3.22). In terms of biomass, crustaceans were the dominant group (74 %) followed by polychaetes (26 %) (Figure 3.23).

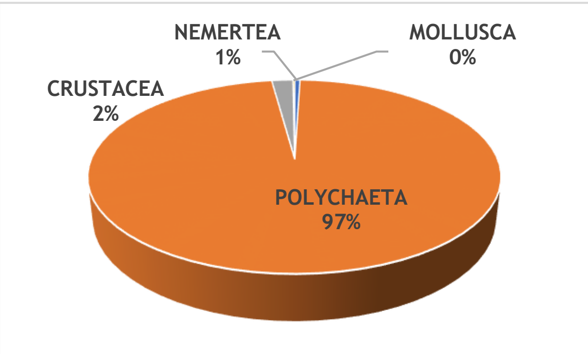


Figure 3.22 - Percentages of zoobenthic groups - abundance

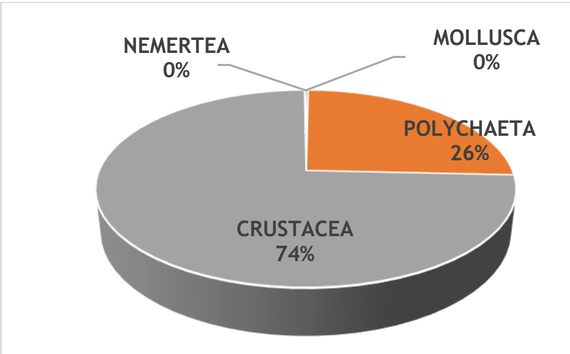


Figure 3.23 - Percentages of zoobenthic groups (biomass)

In the central part of Mangalia harbour (MG_A), polychaetes dominated with 100 %. Of the polychaetes dominant was *Nephtys hombergii* (197 ind./m^2) and *Saccocirrus papillocercus* (180 ind/m^2) (Figure 3.23). At distance (MG_B), macrozoobenthic communities were dominated by polychaetes (98 %) and crustaceans (2 %). Polychaetes group was dominated by *Lindrilus flavocapitatus* (210 ind/m^2) and *Scolelepis (Scolelepis) squamata* (120 ind/m^2). At MG_C benthic communities were dominated by the polychaetes (96 %) followed by the crustaceans (3 %) and nemerteans (1 %). Polychaetes group was represented by some species which were present in large number: *Capitella capitate* (377 ind/m^2), *Prionospio cirrifera* (233 ind/m^2), and *Nephtys hombergii* (190 ind/m^2). Crustaceans group was represented by two sensitive species *Iphinoe maeotica* (23 ind/m^2) and *Upogebia pusilla* (7 ind/m^2).

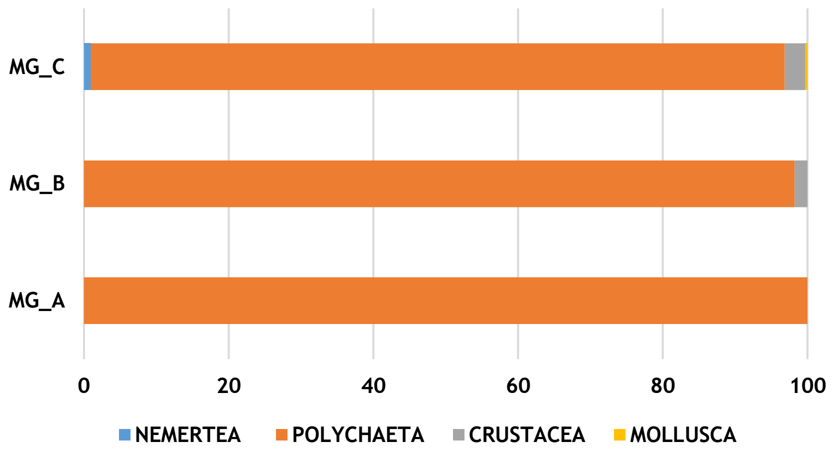


Figure 3.24 - Percentage of densities

Biomass was also dominated by the polychaete at MG_A and MG_B and by crustaceans at MG_C. An important contribution to crustaceans domination at MG_C was due to the presence in samples of the decapod *Upogebia pusilla* (Figure 3.24).

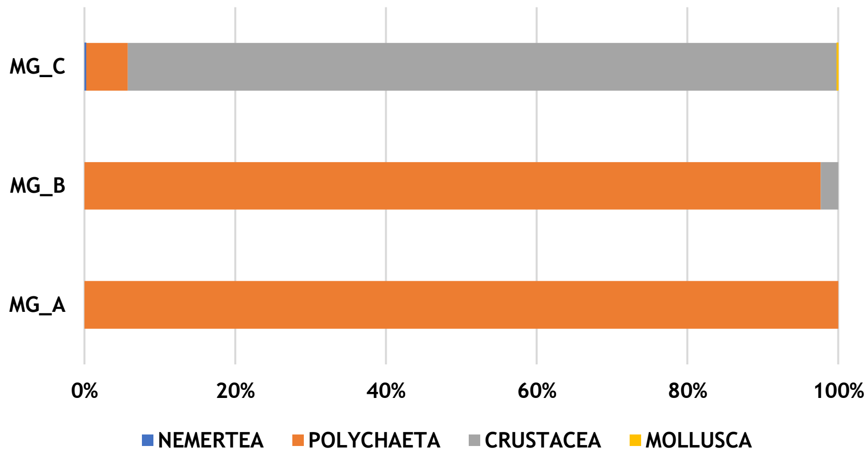


Figure 3.25 - Percentage of biomass

The abundance data were subjected to Bray-Curtis cluster analyses and showed that the similarity between the station located inside the harbour and the other three stations located outside is 20 %. Between the outer stations similarity is 50 % (Figure 3.26).

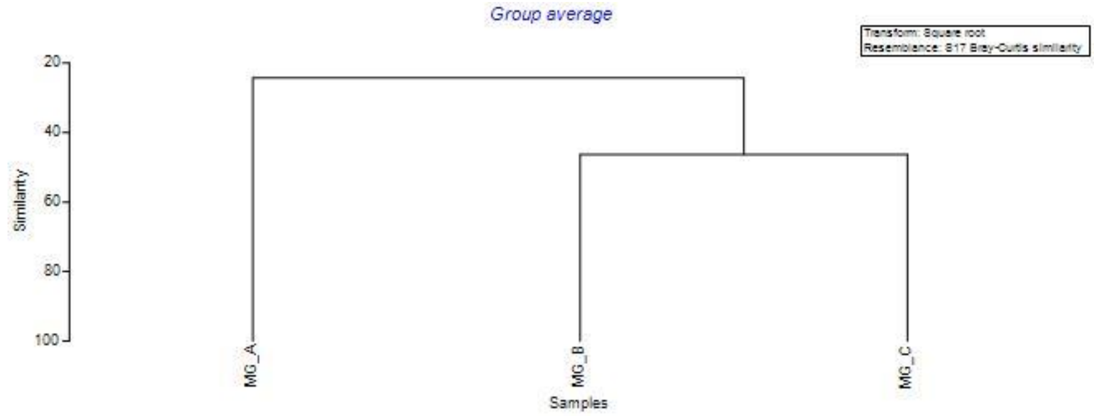


Figure 3.26 - Bray-Curtis similarities, square-root transformed abundance data

The average dissimilarity between inner and outer stations in the Mangalia area was 75.68 %. At dissimilarity contributed a little number of species with a high contribution. Of the seven species that contributed to this difference, *Saccocirrus papillocercus* had the highest percentage (16.16 %) (Table 3.5).

Table 3.5 - SIMPER analyses

Groups InnerMG & OuterMG Average dissimilarity = 75.68	InnerMG	OuterMG				
Species	**Av. Abund**	**Av. Abund**	**Av.Diss**	**Diss/SD**	**Contrib. %**	**Cum.%**
Saccocirrus papillocercus	13.42	0.00	12.23	3.96	16.16	16.16
Prionospio cirrifera	0.00	11.82	10.21	5.90	13.50	29.66
Scolelepis (Scolelepis) squamata	0.00	10.48	9.63	3.18	12.72	42.38
Capitella capitata	0.00	9.70	7.27	0.71	9.60	51.99
Lindrilus flavocapitatus	4.08	7.25	7.12	1.24	9.41	61.40
Sphaerosyllis bulbosa	0.00	6.27	5.85	2.37	7.73	69.13
Spionidae varia	4.08	0.00	3.72	3.96	4.92	74.04

Conclusions

Although the stations bottom depths were almost similar, macrofauna showed significant variation in composition and abundance between inner and outer stations. One reason may be that some parameters are very different inside the port. During the visual analysis of the samples was observed that the sediment inside the harbours was muddy with a blackish colour. Especially in the Midia harbour, after sample washing, a large amount of detritus was observed. In outer stations, the sediment parameters such as grain size, organic content, and food availability are among the important factors which can decisively influence benthic community structure.

Environmental disturbance generated by human pressure may cause structural changes in macrobenthic communities and influence species diversity due to different species stress tolerance (Gray and Pearson 1982). Tolerant and opportunistic species dominate stressed assemblage and less tolerant become rare or extinct.

Polychaetes often comprise over one-third of the total number of macrobenthic species (Fauchald & Jumars, 1979). In this study, they showed high diversity as well as high density, usually over 80 % of the total benthos abundance. Moreover, in the inner stations, the polychaetes had low diversity and dominated the density by 100 %. The 100 % dominance of polychaetes can be associated with a high level of tolerance of many species to adverse effects of anthropogenic perturbation (Borja et al., 2000). For example, *Capitella capitata,* species found in almost all stations, is considered in many studies the most common species acting as an indicator of high organic matter (Dean, 2008). Regarding this aspect, it should be mentioned that as long as the input of organic matter did not conduct to anoxia benthos seemed to be little affected (Dean, 2008).

3.1.3 Turkey

As a result of the analyses of benthic material collected during the samplings in July 2019 at the survey area, we identified 47 species belonging to eight taxonomic groups (Cnidaria, Nemertea, Oligochaeta, Polychaeta, Crustacea, Phoronida, Mollusca and Echinodermata) (Annex C).

The distribution of the species among taxonomic groups was examined, Crustacea ranked first with 17 species and followed by Mollusca (14 species), Polychaeta (11 species). “Other” groups were represented by fewer species (Figure 3.27).

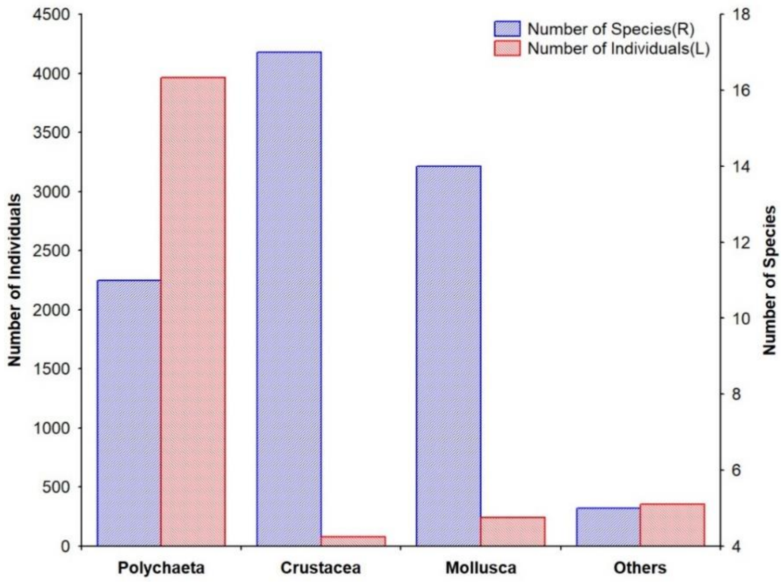


Figure 3.27 - Distribution of the number of species and mean of individuals among taxonomic groups – Samsun, July 2019

We found the highest mean of species number at station SLI06 (18) and the lowest at station SLI04 (13). Regarding the individuals, station SLI06 had the highest mean (5846.7 ind/m^2), while station SLI04 the lowest densities (2296.7 ind/m^2) (Figure 2.28).

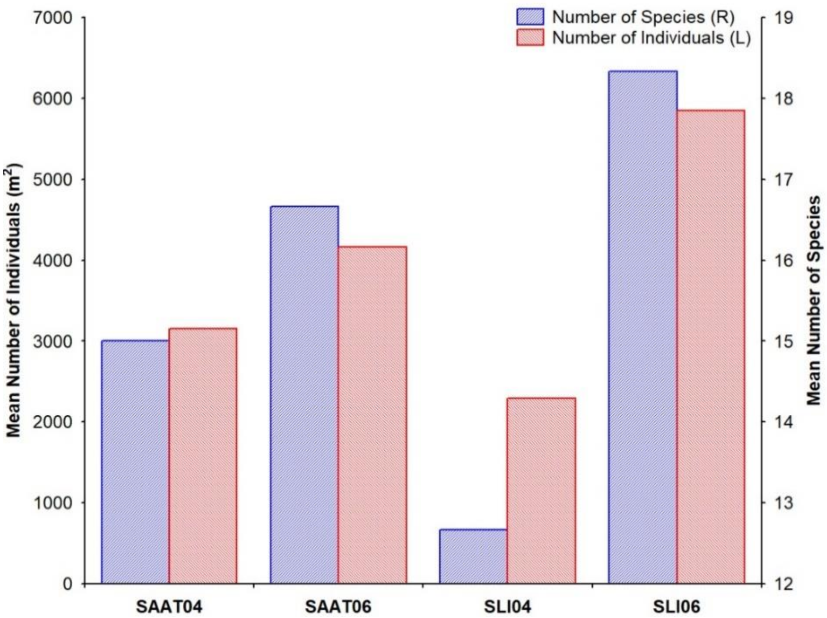


Figure 3.28 - Distribution of the mean number of species and individuals among stations - Samsun, July 2019

The dominant taxon was Crustacea (36 %), followed by Mollusca (30 %) and Polychaeta (23 %). Other groups represented 11 % dominance (Figure 3.29).

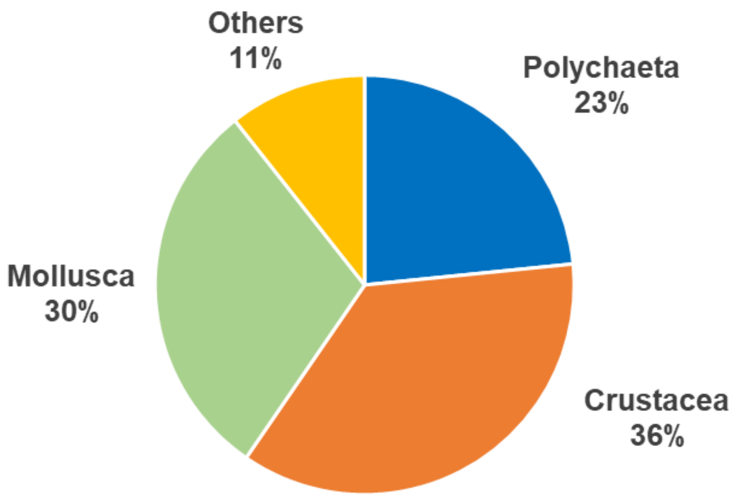


Figure 3.29 - Dominance (%) of zoobenthic taxa based on the species' number-Samsun, July 2019

The most abundant group was Polychaeta (85 %), followed by densities of others (8 %), Mollusca (5 %) and Crustacea (2 %), respectively (Figure 3.30).

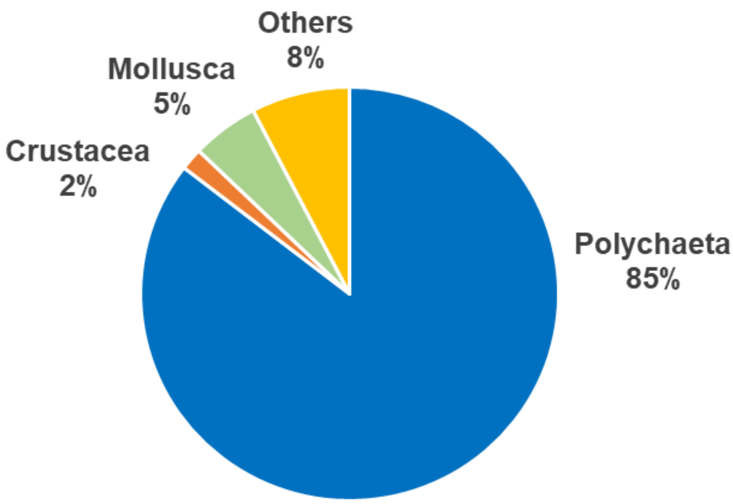


Figure 3.30 - Dominance (%) of zoobenthic taxa number of individuals – Samsun, July 2019

According to the Soyer's Frequency Index, the most constant taxa with 100 % frequency index value were polychaetes *Aricidea claudiae, Heteromastus filiformis*, *Micronephyts longicornis*, *Prionospio maciolekae* and mollusc *Abra alba* in summer. The other frequent species were molluscs *Polititapes aureus*, *Abra nitida* (92 %) and polychaete *Sigambra tentaculata* (75 %).

The highest mean diversity index value among the stations was at station SAAT04 (H'= 2.63), and the lowest at SLI06 (H'=1.74). Evenness index values ranged between (J') 0.41 (SAK10) and 0.67 (SAAT04) (Figure 3.31). In the station SLI06 with the lowest species diversity, the evenness index value was also found to be the lowest. When the species diversity index value is low and there is single-species dominance, the evenness index value is also low; the evenness index value is high at stations with higher species diversity.

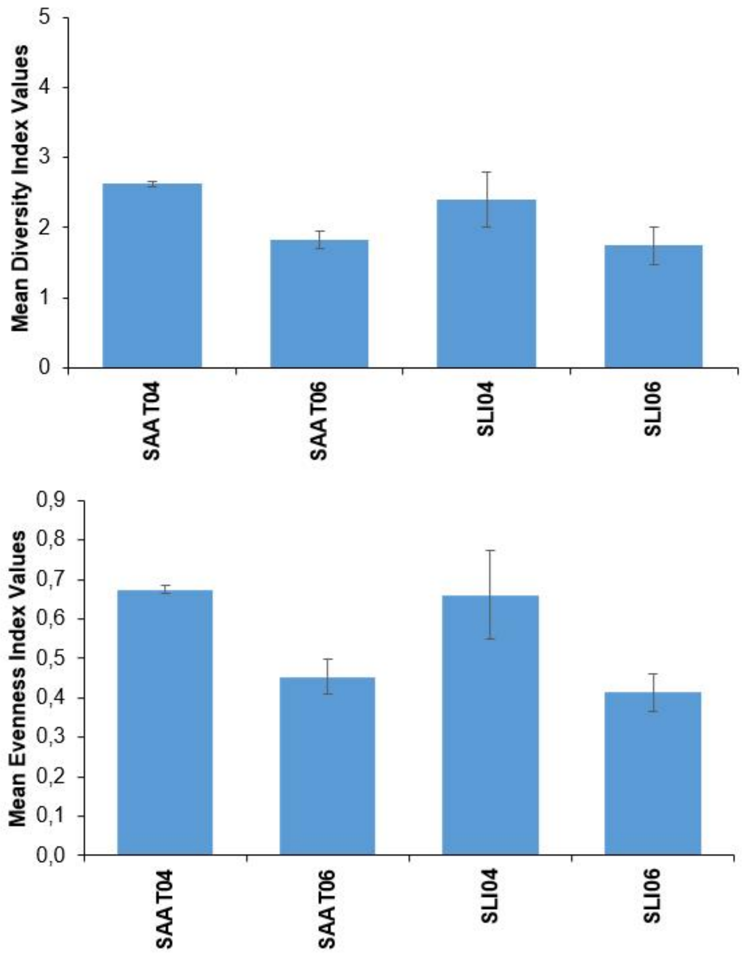


Figure 3.31 - Diversity and evenness index (mean± SE) – Samsun, July 2019

Turkish Benthic index TUBI values among the stations ranged between 1.85 (SAAT06) and 2.09 (SLI04). The station SAAT06 had the lowest TUBI scores in the area, thus classifying the water body's benthic quality status as "poor"; three stations possessed TUBI scores that indicated "moderate" ecological status (Figure 3.31).

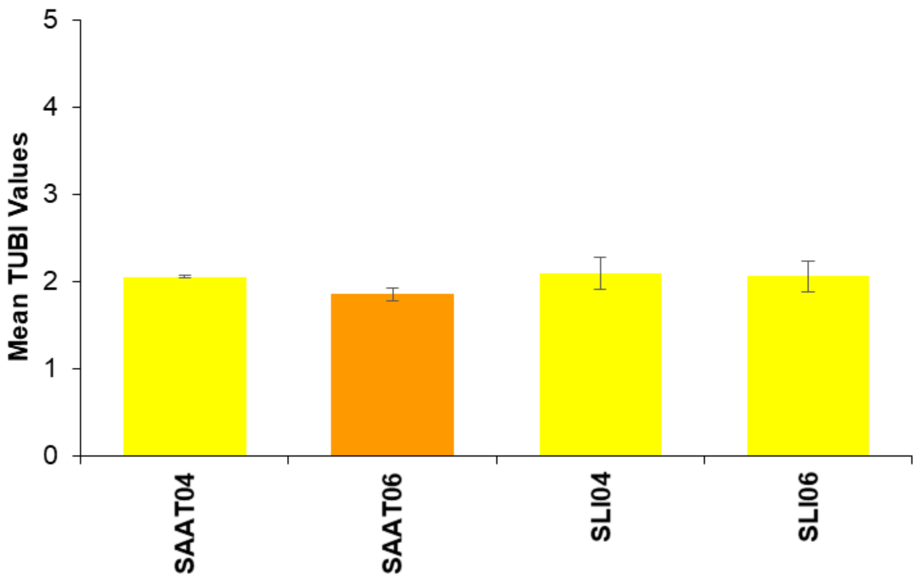


Figure 3.32 - TUBI (mean± SE) – Samsun, July 2019

In winter, we identified 49 species belonging to eight taxonomic groups (Cnidaria, Nemertea, Oligochaeta, Polychaeta, Phoronida, Crustacea, Mollusca, Echinodermata and Tunicata) (Annex C). The community structure of the soft-bottom zoobenthos' area is described seasonally using some ecological analyses. Crustacea ranked first with 17 species, followed by Mollusca (14) and Polychaeta (12). "Other" groups were represented by a smaller number of species (Figure 3.33).

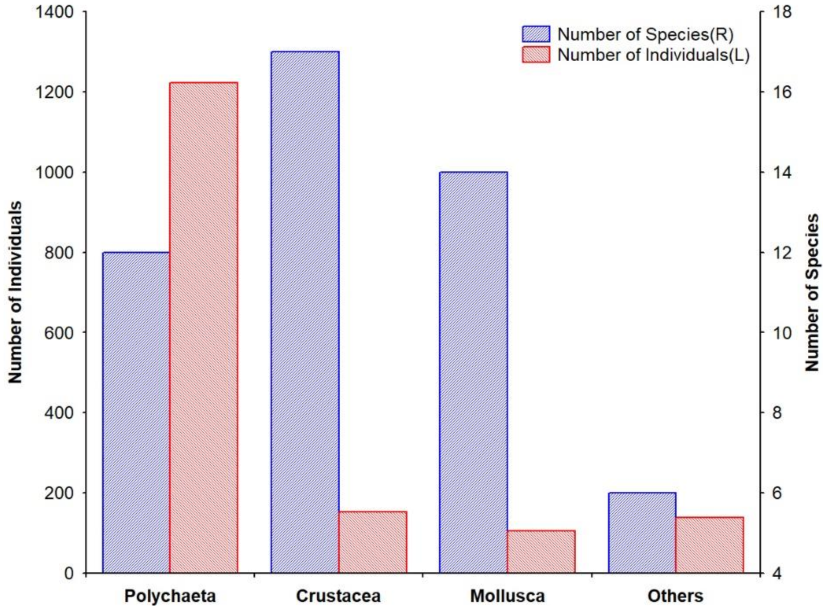


Figure 3.33 - Distribution of the number of species and mean of individuals among taxonomic groups-Samsun, January 2020

The highest mean of species number was determined at station SLI06 (15 species) and the lowest at station SAAT04 (11 species). The highest mean of individuals was encountered at station SAAT04 (1626.7 ind/m^2), and station SLI04 (1093.3 ind/m^2) were observed to have the lowest number of individuals (Figure 3.34).

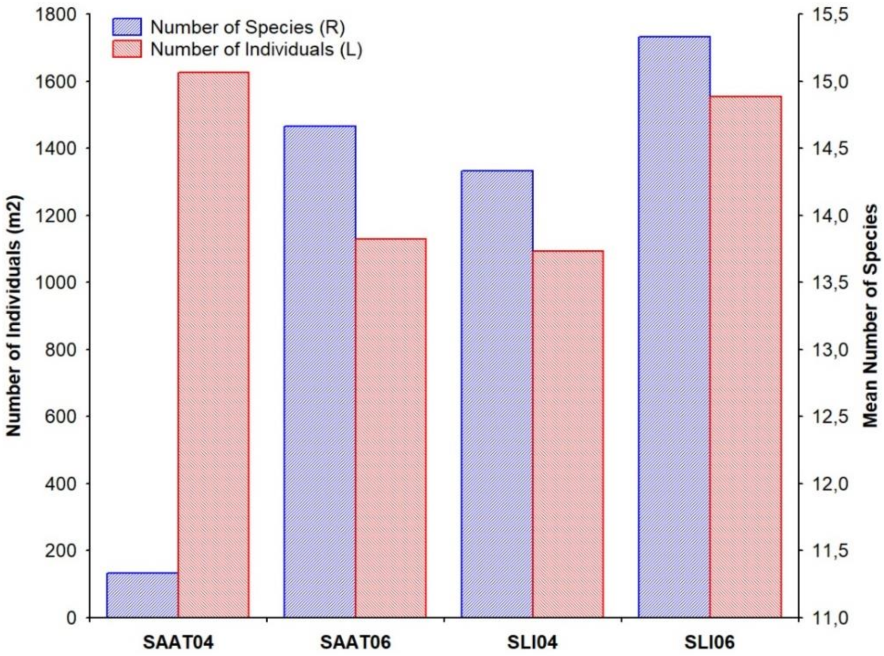


Figure 3.34- Distribution of the mean number of species and individuals among stations- Samsun, January 2020

As the proportion of species, Crustacea was the dominant taxon (35 %), followed by Mollusca (29 %) and Polychaeta (24 %). Other groups represented by 12 % dominance (Figure 3.35).

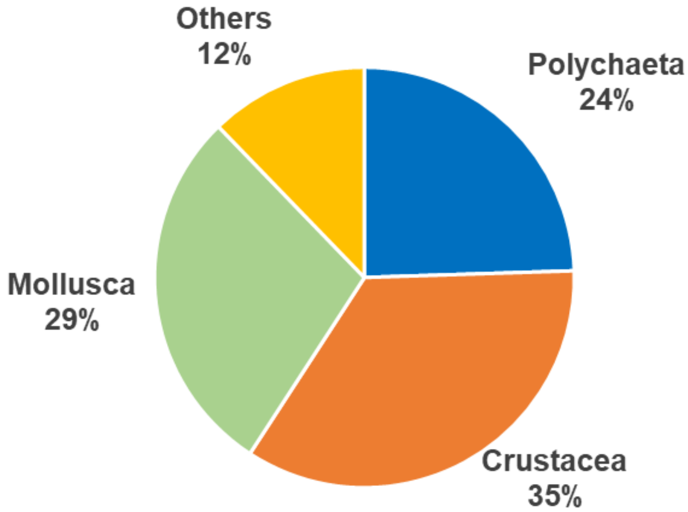


Figure 3.35 - Dominance (%) of zoobenthic taxa based on the number of species - Samsun, January 2020

Based on the number of individuals, Polychaeta was the dominant group (76 %), followed by Crustacea (9 %), Mollusca (6 %), and Others (9 %), respectively (Figure 3.36).

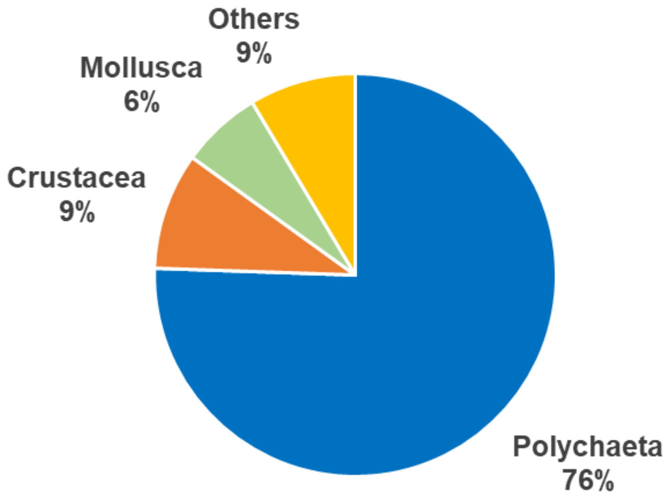


Figure 3.36 - Dominance (%) of zoobenthic taxa number of individuals- Samsun, January 2020

In winter, polychaetes *Heteromastus filiformis* and *Aricidea claudiae* were the most constant taxon with a frequency index of 100 %. The other frequent species were mollusks *Abra alba* (91.7 %), polychaetes *Micronephyts longicornis* (67 %), and *Sigambra tentaculata* (67 %).

The highest mean diversity index value among the stations occurred at station SLI04 (H'= 2.83), and the lowest at station SAAT04 (H'=1.81). Evenness index values ranged between (J') 0.53 (SAAT04) and 0.74 (SLI04) (Figure 3.37). In stations with low species diversity, species show heterogeneous distribution.

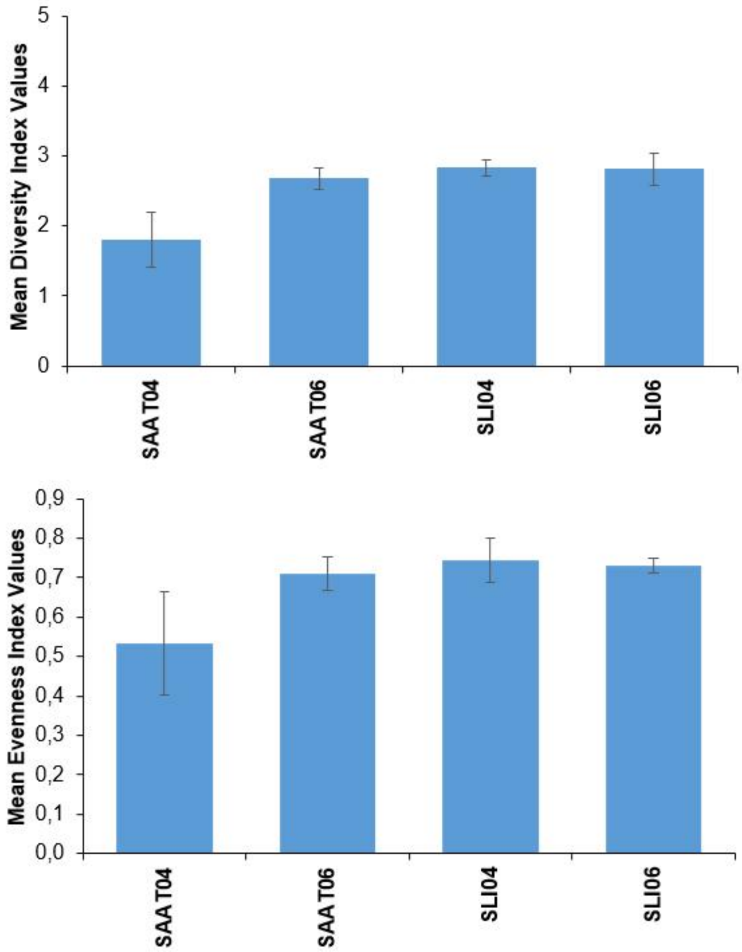


Figure 3.37 - Diversity and evenness index (mean± SE) – Samsun, January 2020

Turkish Benthic index TUBI values among the stations ranged between 1.38 (SAAT04) and 2.49 (SLI06). The station SAAT04 had the lowest TUBI scores in the area, thus classifying the water body's benthic quality status as “poor”; three stations possessed TUBI scores that indicated “moderate” ecological status (Figure 3.38).

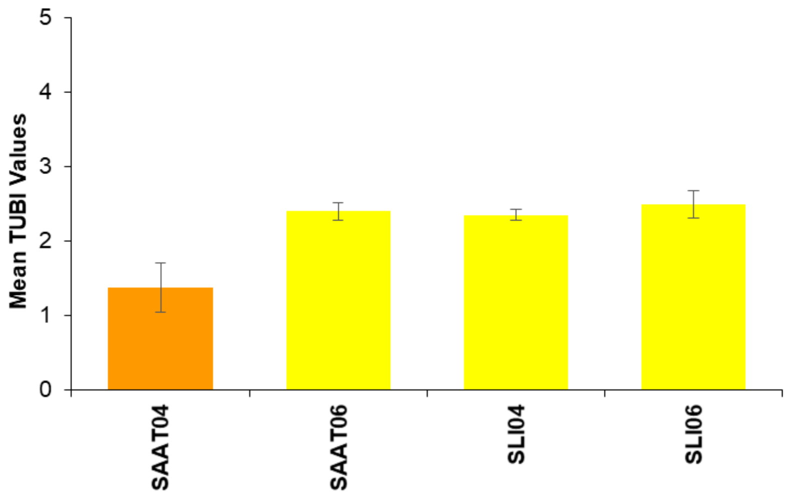


Figure 3.38 - TUBI (Mean± SE), – Samsun, January 2020

Conclusions

A total of 69 macrozoobenthic species belonging to nine taxonomic groups (Cnidaria, Nemertea, Oligochaeta, Polychaeta, Phoronida, Crustacea, Mollusca, Echinodermata and Tunicata) occurred in the research area (Annex C). Among species, we found two alien species - molluscs *Arcuatula senhousia* and *Rapana venosa*. *Arcuatula senhousia (Benson, 1842)* was reported first time from the Black Sea coast of Turkey in this study. It is an opportunistic species with high reproductive and fast growth ability and distributed in bays, estuaries and brackish waters (Doğan et al., 2014; Kovalev et al., 2017; Zhulidov et al., 2021).

The presence of this species in the Black Sea was reported for the first time from the Romanian coast (Micu 2004), then it was recorded in the Kerch Strait in the Azov Sea by Kovalev et al. (2017), in the Bulgarian coasts by Chartosia et al. (2018), in the Ukraine coast and Tuapse River in Russian Federation by Zhulidov et al. (2021). *Arcuatula senhousia* has been known from Turkey's coast since 2008 (Uysal et al., 2008; Eleftheriou et al., 2011; Doğan et al., 2014) and Sea of Marmara since 2012 (Öztürk et al., 2017).

The introduction pathways of this species in the Mediterranean and the Black Sea is by shipping. In terms of the individual's number of alien species, the research area is not considered endangered. Characteristic species for the area were polychaetes *Aricidea claudiae, Heteromastus filiformis, Micronephyts longicornis, Prionospio maciolekae* and mollusc *Abra alba*. *Heteromastus filiformis* is known as first-order opportunistic species. Others are also known as tolerant species to organic enrichment. In the stations, Crustacea represented a high number of species and Polychaeta a high number of individuals in the sampling periods. The distribution of the species and individuals by stations shows that the highest mean number of species in the summer and winter period was found at station SLI06 (18, 15 species, respectively) and the lowest mean number of species SLI04 (13, 11 species, respectively). Regarding individuals, station SLI06 had the highest average density (5846.7 ind/m^2) in summer, while station SAAT04 in winter (1626.7 ind/m^2. We used the Turkish Benthic Index TUBI developed by Çinar et al. (2015) to assess the ecological quality of stations. The stations' ecological quality conditions were determined to be the same in the summer and winter seasons. SAAT06 was in "poor" condition. The ecological quality status of the other stations was “moderate”. However, threshold values of TUBI need to be calibrated for the Black Sea.

3.2 Chemistry - sediments

Harbours in all parts of the globe have sediments contaminated with heavy metals and organic pollutants. Sources include shipping activities (including anti-fouling paints, dry dock, loading and bunkering operations, and ship repair and building), industry (e.g. pyrogenic processes, spills and leaks), urbanisation (e.g. sewage outfall, urban run-off, stormwater inputs) and agricultural waste. The distribution of contaminant enrichment in harbour sediments, the risk to benthic communities that these contaminants present and, where possible, the relationship between enrichment, risk and infaunal diversity should be investigated.

Marine ports are always significant sources of environmental pollution because their activities are associated with particular contamination of aquatic areas and bottom sediments. Contaminants get into the aquatic environment through shipping traffic, loading, repairs, and dredging, as well as rainwater runoff, effluent discharge, dust, etc. Heavy metals are regarded as especially dangerous contaminants because of their environmental persistence, toxicity, and ability to be incorporated into food chains. After getting into the water, heavy metals tend to be sequestered in the bottom sediments. The fluctuation in the spectrum and quantities of heavy metals in bottom sediments is not as rapid as in water and therefore the investigation of heavy metals in a relatively stable state enables the integral specific features of the heavy metal contamination of a water basin to be determined for a specific interval of time (Galkus et al., 2012).

Measurements of heavy metals only in marine water are insufficient for assessing the state of the ecosystem due to high variability, fluctuating inputs, and low residence time. With a combined action of adsorption, hydrolysis and co-precipitation, only a small part of the free metal ions remains dissolved in water, while a large amount of them is stored in sediments. However, when environmental conditions change, sediments can be converted from heavy metal deposits into sources for the water column. Therefore, the content of heavy metals in sediments is measured to provide vital information for the assessment of environmental risks in a long term (Zhuang & Gao, 2014).

Persistent organic pollutants (POPs) are organic substances with extremely toxic, bioaccumulative and persistent properties. They have been accepted as emerging substance and decided to be reduced by global and regional conventions (UNEP 1995; UNEP Stockholm convention 2001). Their different intrinsic physical-chemical properties, control their behaviour in the environment (Lohmann et al., 2007).

Sources of pollution from POPs include the improper use and/or disposal of agrochemicals and industrial chemicals, elevated temperatures and combustion processes, and unwanted by-products of industrial processes or combustion. Some of the POPs occur in nature but at the same time, they have been introduced from emissions (i.e., Poly Aromatic Hydrocarbons –PAHs) but most of them produced by industries for a variety of application (i.e., pesticides, polychlorinated biphenyls-PCBs). Others such as BFRs (Brominated Flame Retardants) are still produced while others accidentally formed or released as industrial byproducts or combustion (PCDDs- dibenzo-p-dioxins).

The POPs were also included in the list of priority substances WFD (2000/60/EC), due to their significant risk to or via the aquatic environment. Article 16 of the WFD requires determining the chemical status of surface waters including coastal waters. The Environmental Quality Standard Directive (EQS) (WFD daughter directive) establishes a maximum allowable concentration (MAC) for priority substances and certain other pollutants including some POPs. The EQS is based on the lowest toxic effect observed for aquatic organisms during testing in the laboratory with standard organisms. The POPs are concentrated in sediment and biota matrix at higher levels than the water matrix due to their hydrophobic nature. Environmental threshold values were provided by EPA to assess sediments status (Long et al., 1995).

3.2.1 Ukraine

Bottom sediments were studied at only one station (St. 5). At station 4, bottom sediments were represented only by shell fragments. The assessment was done by the UkrSCES methodology using the maximum available concentrations contained in the Ecological Norms (EN).
Kz reflects the concentration of all pollutants of the same type in a certain period in a given area. This factor represents the sum of the ratios of the concentration of each pollutant to its maximum available concentration (MAC), according to Ukrainian legislation for sediment, to the number of

measurements performed in a given period. There are five quality classes (very good, good, satisfactory, bad and very bad) and the overall assessment of the ecological condition of bottom sediments in the study area is determined by the worst assessment of the group of pollutants.
The ecological condition of bottom sediments is estimated by means of Kz:

for TM:		for organic compounds:
Kz<0.5	Very Good	Kz<0.2
Kz=0.5-1.0	Good	Kz=0.2-1.0
Kz=1.0-1.25	Satisfactory	Kz=1.0-5.0
Kz =1.25 - 2.5	Bad	Kz =5-25
Kz>2.5	Very Bad	Kz>25

Bottom sediments are heavily polluted by OCPs and PAHs, Kz OCPs and Kz PAHs correspond to a very "bad" ecological state (Table 3.6). As for organic compounds, sediments are more polluted by OCPs than by other groups of pollutants (Figure 3.39).

Table 3.6 Kz groups of pollutants in sediment in the areas of influence of WWTP "South"

Station	Kz TM	Kz OCPs	Kz PAHs
ST 5	0.46	75.31	31.5

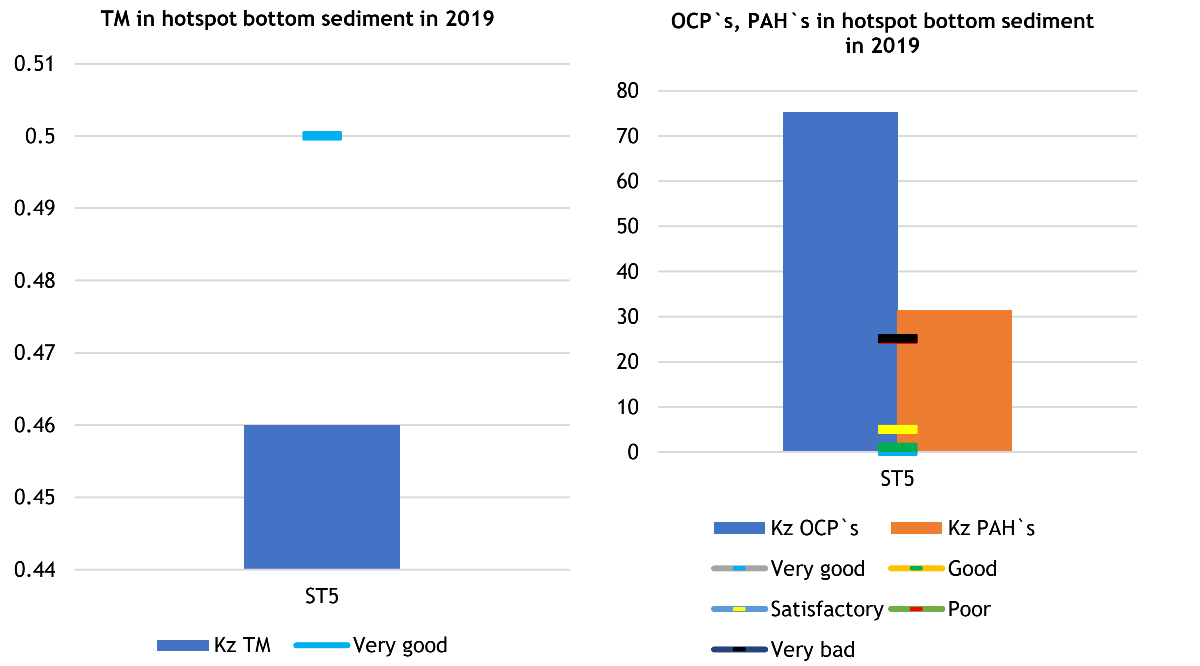


Figure 3.39 - Kz groups pollutants in sediment in the areas of influence of WWTP "South"

Among the pollutants, the concentrations of trace metals are at a low level. Among the individual PAHs, phenanthrene and fluoranthene were found in the highest concentrations, which correspond to a very bad ecological status. Concentrations of anthracene, benzo[a]anthracene, crysene, benzo[k]fluoranthene, benzo[a]pyrene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene correspond to a "bad" ecological status. Among the individual OCPs, lindane, dieldrin and DDT were found in the highest concentrations in bottom sediments, which correspond to a "very bad" ecological status (Table 3.7).

Table 3.7 Kz individual pollutants in sediment in the areas of influence of WWTP "South"

Station	Kz Cu	Kz Cd	Kz Pb	Kz Ni	Kz Cr	Kz Zn	Kz Co	Kz As	Kz Hg
ST 5	0.73	0.29	0.21	0.63	0.5	0.51	0.34	0.25	0.68

Station	Kz Naphthalene	Kz Phenanthrene	Kz Anthracene	Kz Fluoranthene	Kz Benzo[a]anthracene	Kz Crysene	Kz Benzo[k]fluoranthene	Kz Benzo[a]pyrene	Kz Benzo(g,h,i)perylene	Kz Indeno(1,2,3-c,d) pyrene
ST 5	2.65	201.1	9.72	34.4	11.6	16.6	7.8	9.84	9.70	11.64

Station	Kz HCB	Kz α-HCH	Kz β-HCH	Kz Lindane	Kz HCH total	Kz Heptachlor	Kz Aldrin	Kz Dieldrin	Kz DDT total
ST 5	0	0	0	208	2.08	7.72	0	24.4	435.6

In the TM group mercury, copper, nickel has the greatest contribution to pollution. In the OCPs group, DDT total and lindane make the greatest contribution to pollution (Figure 3.40).

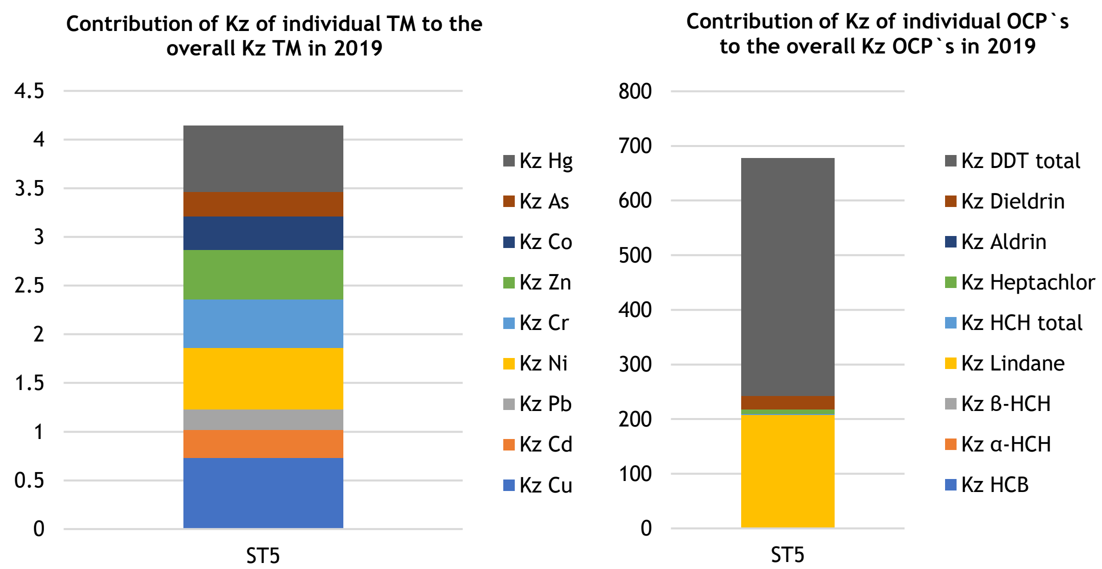


Figure 3.40 - Contribution of individual pollutants to the overall Kz groups in sediment

In the PAHs group, phenanthrene contributes the most to the pollution (Figure 3.41).

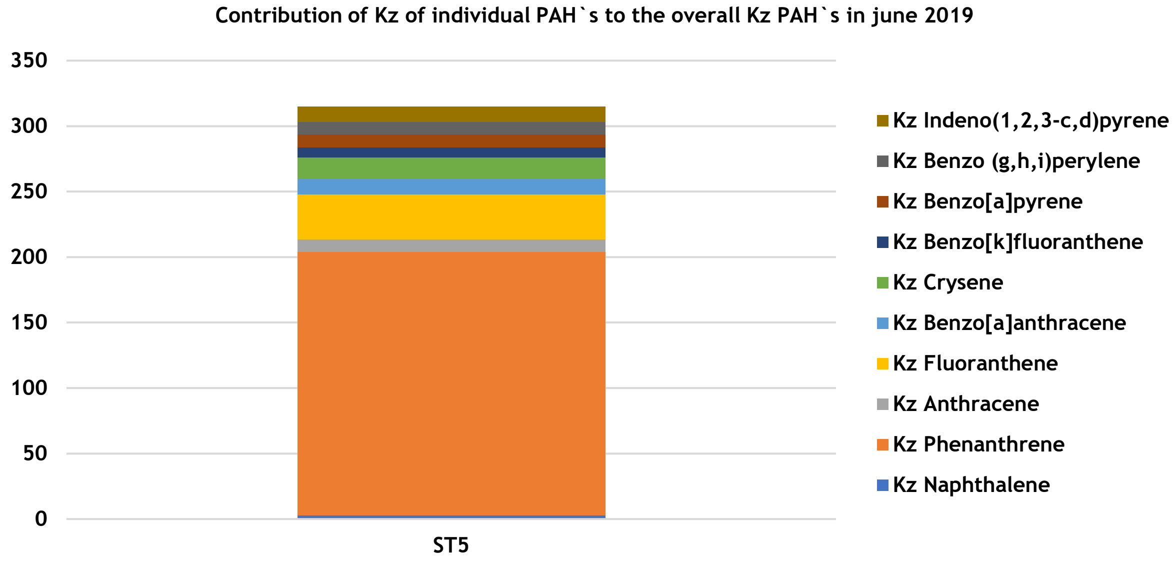


Figure 3.41 Contribution of PAHs to the overall Kz groups in sediment

Bottom sediments quality, in the investigated areas of influence of "Hot Spots", corresponds to a “very bad” ecological state.

The bottom sediments contain high concentrations of OCPs and PAHs. All of the investigated priority PAHs have high concentrations, with phenanthrene contributing the most to the pollution. Among OCPs, DDT total and lindane contribute the most to the group's pollution.

High concentrations of OCPs and PAHs in bottom sediments can be explained by the fact that the discharge from the treatment facilities is carried out into the bottom layer of water and poorly soluble pollutants are immediately precipitated. But this can lead to secondary pollution of seawater in the areas of influence of "Hot Spots" due to the roiling of bottom sediments and reverse diffusion of pollutants into the water.

3.2.2 Romania

Heavy Metals in sediments

Concentrations of heavy metals (Cu, Cd, Pb, Ni, Cr) measured in surface sediments from the studied areas were characterized by some degree of variability, reflecting not only the impact of various anthropogenic inputs but also the diversity of mineralogical and granulometric characteristics of sediments.

The following variation ranges were observed: 1.36 – 47.10 µg/g Cu; 0.001 – 0.95 µg/g Cd; 3.92 – 36.84 µg/g Pb; 9.01 – 57.84 µg/g Ni; 5.65 – 55.06 µg/g Cr. Data obtained during this cruise for the hot-spots areas (average values 12.95 µg/g Cu, 0.11 µg/g Cd, 13.32 µg/g Pb, 31.33 µg/g Ni, 25.66 µg/g Cr) are comparable with typical ranges reported for Black Sea marine sediments (even lower, in case of Cu, Cd, Ni, Cr), for instance, the limit of predominant values (75th percentile of 2012 – 2017 monitoring data) being as follows: 51.08 µg/g Cu; 1.15 µg/g Cd; 15.09 µg/g Pb; 78.09 µg/g Ni; 69.74 µg/g Cr (Oros, 2019).

The specific port morphology and hydrodynamic conditions occurring both inside and offshore port area represent factors influencing the transport of sediments, especially the finest ones, which are the main vehicles for contaminant dispersion. Thus, hydrodynamic features inside the port have an important role in facilitating the settling down of fine particles (Mali et al., 2018). It should be noted that sediments from all 3 ports basins (Midia, Constanta and Mangalia) presented significantly higher concentrations for all investigated elements in comparison with the surrounding areas. For instances, maximum concentrations for Cu (47.10 µg/g), Cd (0.95 µg/g), and Pb (36.84 µg/g) were registered inside Constanta Port, whereas maximum concentrations of Ni (57.84 µg/g) and Cr (55.06 µg/g) were measured inside Midia Harbour. Sediments in front of Eforie South WWTP discharge were characterized by moderate levels. (Table 7.12, Figure 3.42).

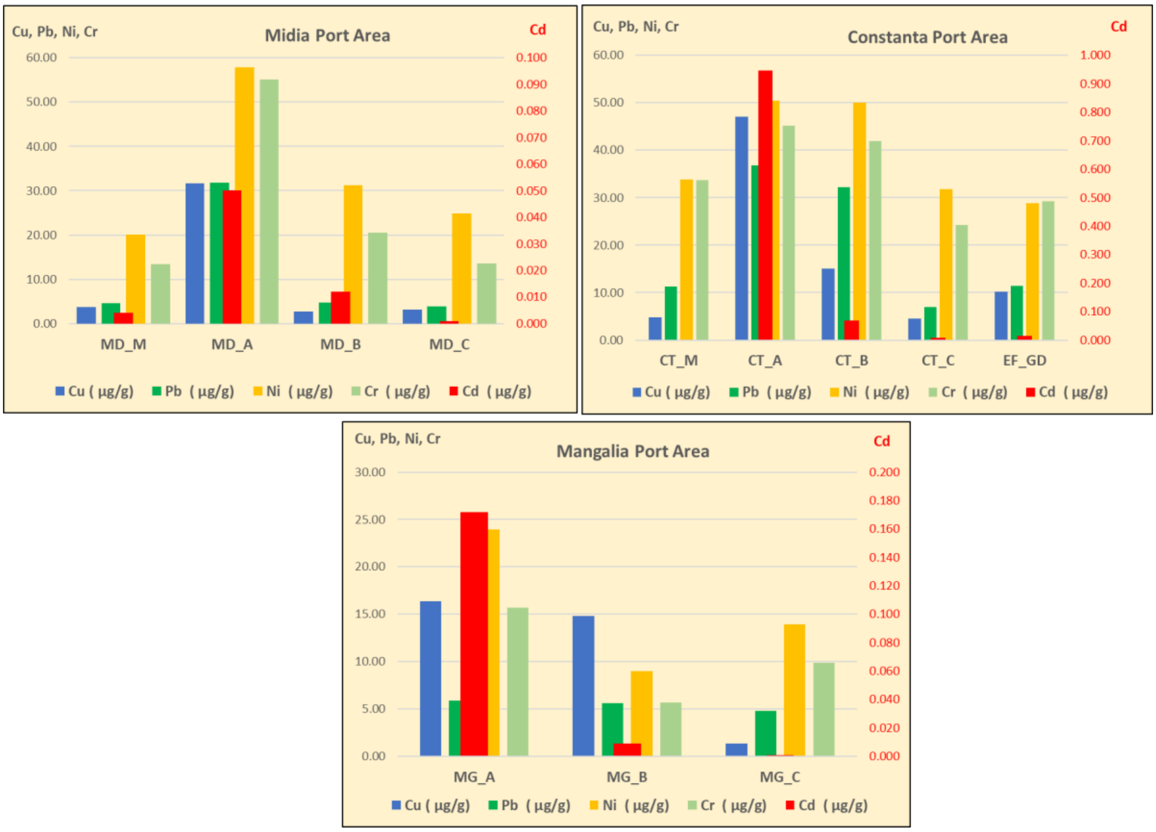


Figure 3.42 - Spatial distribution of heavy metals concentrations in surface sediments in hot-spots study areas, September 2019

Sediments are an important repository for various pollutants and also play a significant role as sensitive indicators for monitoring contaminants in aquatic systems. (Ozkan & Buyukisik, 2012). Sediments are an important carrier as well as a sink of heavy metals in the hydrological cycle and reflect the current quality of the system as well as provide information on the impact of pollution sources (Kruopiene, 2007). The distribution of heavy metals in sediments is influenced by the contribution of natural and anthropogenic sources and depends on the mineralogic and granulometric characteristics of sediments. Sediments with a finer texture and a higher organic content tend to accumulate higher concentrations of heavy metals compared to coarse sediments and this depends on specific hydrodynamic conditions that influence the fine particle (silt and clay) distribution (Naifar et al., 2018). In marine areas characterized by low depositional energy (like harbours) the accumulation of fine particles and pollutant is facilitated, whereas, in coastal areas characterized by high depositional energy (wave, currents), sediments are dominated by coarse-grained particles (sand).

The measurements from the 4 Romanian hot-spots areas indicated a “moderate” level of trace metal pollution since only 4 % of copper concentrations and 27 % of nickel concentrations in surface sediments surpassed recommended values (EQS), whereas the other investigated elements had levels below EQS (ERLs: 1.2 µg/g Cd, 47 µg/g Pb, 81 µg/g Cr; national legislation: 40 µg/g Cu, 35 µg/g Ni).

In comparison with available monitoring data (2015 – 2018) from the same areas, in 2019 the results were generally maintained between similar variability ranges, with some increasing or decreasing trends, depending on the investigated area and element (Figure 3.43 - Figure 3.46).

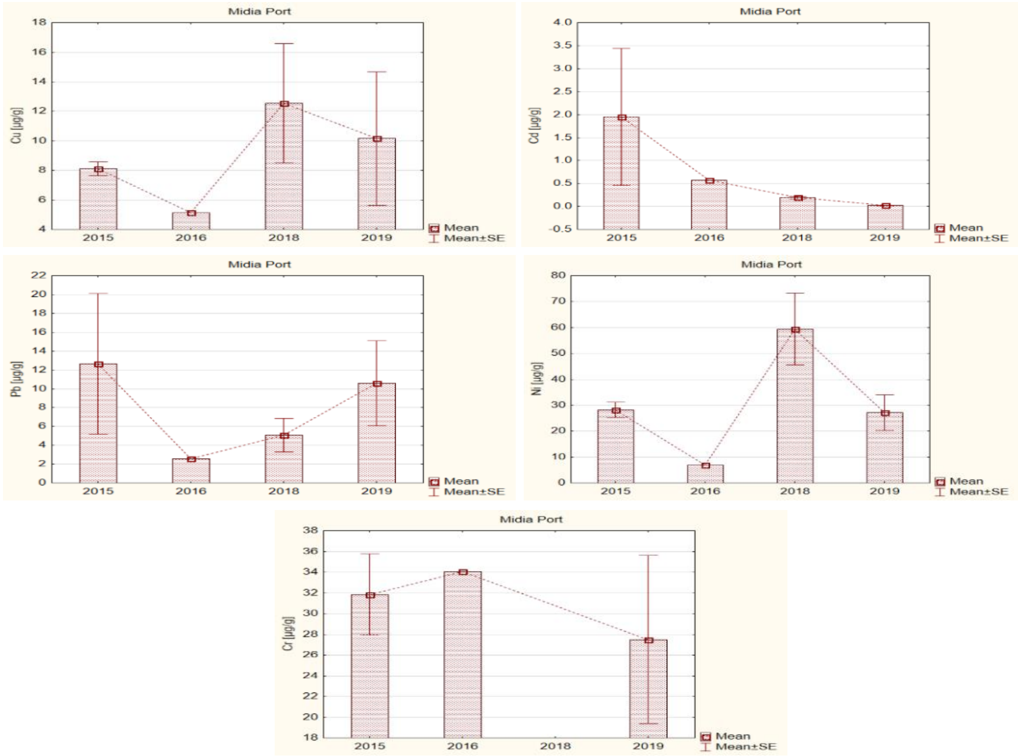


Figure 3.43 - Trends of heavy metals concentrations in surface sediments inside and surrounding area - Midia Port, 2015 – 2019

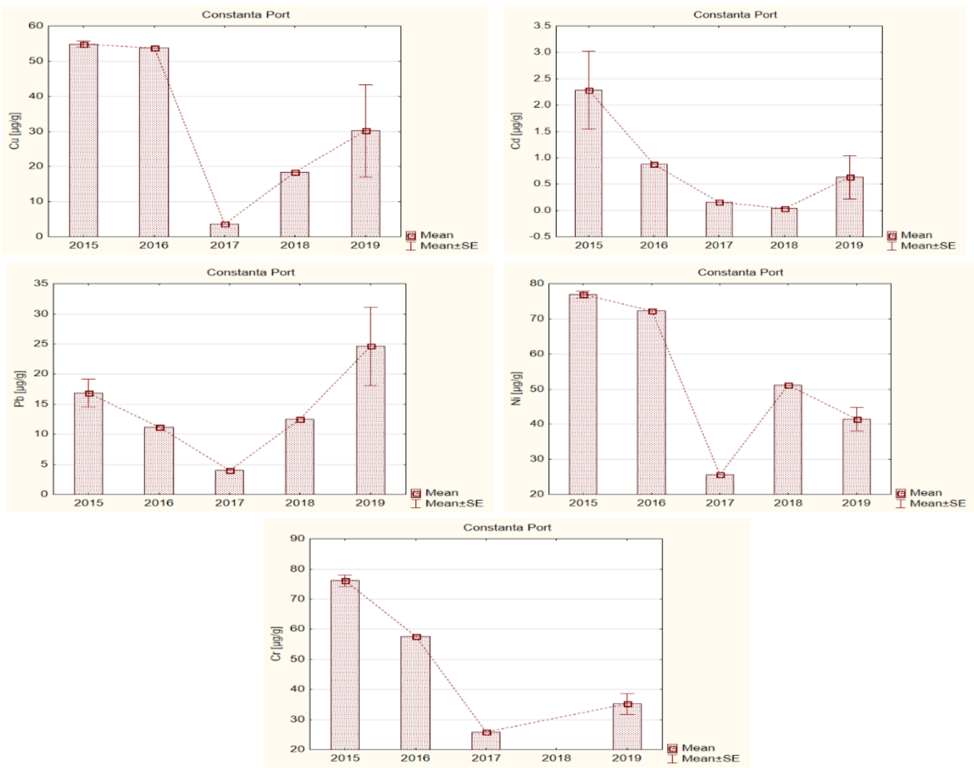


Figure 3.44 - Trends of heavy metals concentrations in surface sediments inside and surrounding area - Constanta Port, 2015 – 2019

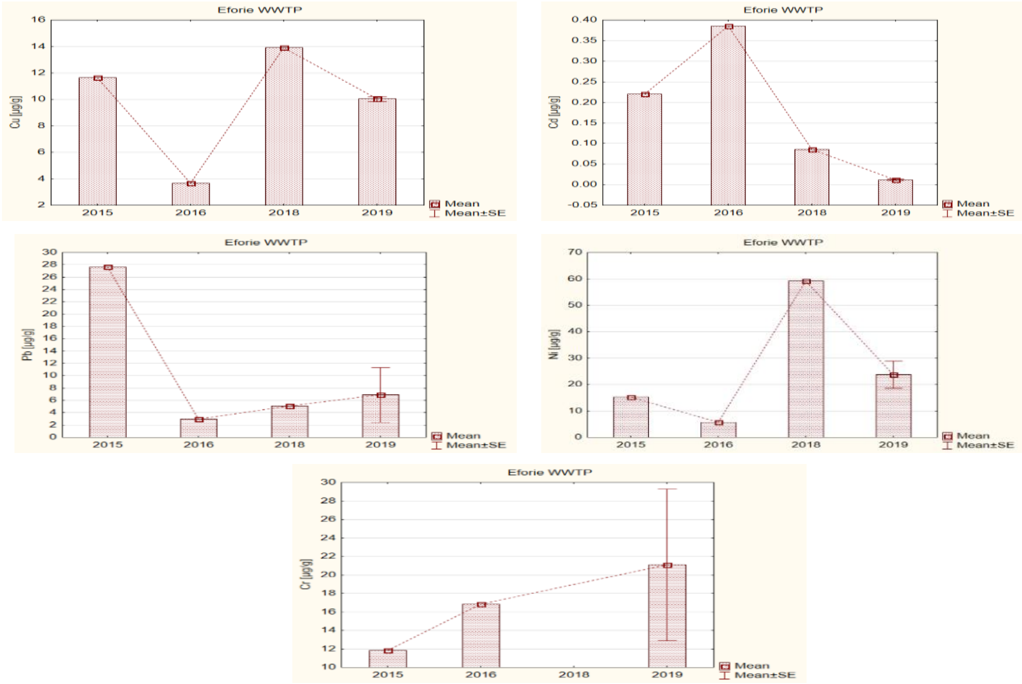


Figure 3.45 - Trends of heavy metals concentrations in surface waters in the vicinity of Eforie South WWTP discharge, 2015 – 2019

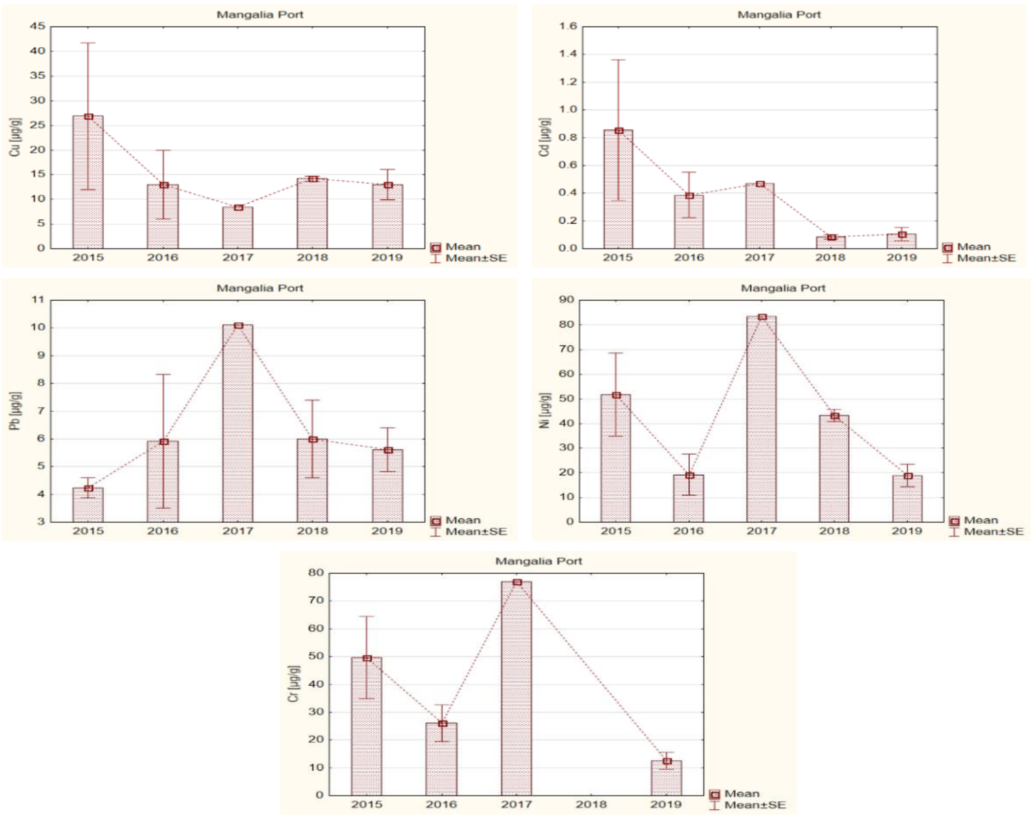


Figure 3.46 - Trends of heavy metals concentrations in surface sediments inside and surrounding area - Mangalia Port, 2015 – 2019

For instance, in Midia Port, basin and surrounding areas, a pronounced decreasing tendency was observed for Cd, whereas Pb slightly increased. Also in the Constanta Port area, Pb levels were higher in 2019, and concentrations of Cd, Ni and Cr were lower. In Mangalia port and surrounding area, all elements presented a slightly decreasing trend. The same decreasing trend for Cd was noticed in sediments from the Eforie WWTP discharge area.

Conclusions

Sediments from all 3 ports basins (Midia, Constanta and Mangalia) presented significantly higher concentrations for all investigated elements in comparison with the surrounding areas.

Metals concentrations in sediments from the 4 hot-spots areas investigated in September 2019 indicated a moderate level of trace metal pollution since only 4 % of copper concentrations and 27 % of nickel concentrations surpassed recommended values (EQS), whereas the other investigated elements had levels below EQS.

In comparison with available monitoring data (2015 – 2018) from the same areas, in 2019 the results were generally maintained between similar variability ranges, with some increasing or decreasing trends, depending on the investigated area and element.

Organic pollutants in sediments

Sediments samples collected in September 2019 from the 4 study areas were characterized by OCPs and PCBs values below detection limits in all samples.

TPHs values ranged between 11.57 and 413.04 µg/g dry sediment and the PAHs analysis highlighted the presence of twelve of the sixteen investigated compounds in concentrations between detection limit (0.1 ng/g dry sediment) and 271.43 ng/g dry sediment.

Some of the polyaromatic hydrocarbons were observed only in Mangalia port area: naphthalene - 1.43 ng/g dry sediment in MG_A station; chrysene - 23.68 ng/g dry sediment in MG_A station and 101.32 ng/g dry sediment in MG_B station; and indeno(1,2,3-c,d)pyrene- 117.55 ng/g dry sediment in MG_B station. Fluorene was detected mainly outside Midia port (129.99 ng/g dry sediment in MD_M station, 131.77 ng/g dry sediment in MD_B station and 130.52 ng/g dry sediment in MD_C station). Some compounds were found also in Mangalia port area and inside Midia port: benzo[a]anthracene – 24.12 ng/g dry sediment in MG_A station, 125.80 ng/g dry sediment in MG_B station and 127.32 ng/g dry sediment in MD_A station; benzo[b]fluoranthene – 15.22 ng/g dry sediment in MG_A station, 140.19 ng/g dry sediment in MG_B station and 144.74 ng/g dry sediment in MD_A station; benzo[k]fluoranthene – 120.004 ng/g dry sediment in MG_B station and 124.59 ng/g dry sediment in MD_A station and benzo (g,h,i)perylene – 267.51 ng/g dry sediment in MG_B station and 271.43 ng/g dry sediment in MD_A station (Figure 3.47). Compounds like phenanthrene, fluoranthene, pyrene and benzo[a]pyrene were detected in all studied areas and represented dominated compounds in Constanta and Eforie area.

In coastal environments most PAHs derive from petroleum spillage, industrial discharges, atmospheric deposition, and urban run-off (Fathallah et al., 2012).

In general, two - three ringed and some alkyl-substituted PAHs are good for distinguishing petrogenic contamination (Saha et al., 2009), whereas four- six ringed PAHs which are more toxic and thermodynamically stable than those from petrogenic sources are appropriate for identifying those from pyrogenic origins (Jiang et al., 2009; Adeniji et al., 2017).

In addition to contamination source, particle size may affect PAH composition (Helmstetter & Alden, 1994). Organic matter in finer particles is often more degraded than that in coarser particles (Leboeuf & Weber, 1997), so PAHs may sorb differently to particles with different sizes. High-molecular weight PAHs, which are more hydrophobic, may preferentially bind with finer mineral grains rich in degraded organic matter, and low-molecular-weight PAHs with coarser mineral grains with fresher organic matter (Wang et al., 2014).

The highest TPHs concentrations were detected outside Mangalia harbor (MG_C station - 413.035 µg/g dry sediment) and inside Constanta (CT_A station - 299.75 µg/g dry sediment) and Midia harbor (MD_A station- 78.90 µg/g dry sediment) (Figure 3.48).The values recorded in the other stations were lower than typical ranges reported for Black Sea marine sediments in coastal area, for instance the limit of predominant values (91.70 µg/g dry sediment - 75th percentile of 2009 – 2018 monitoring data).

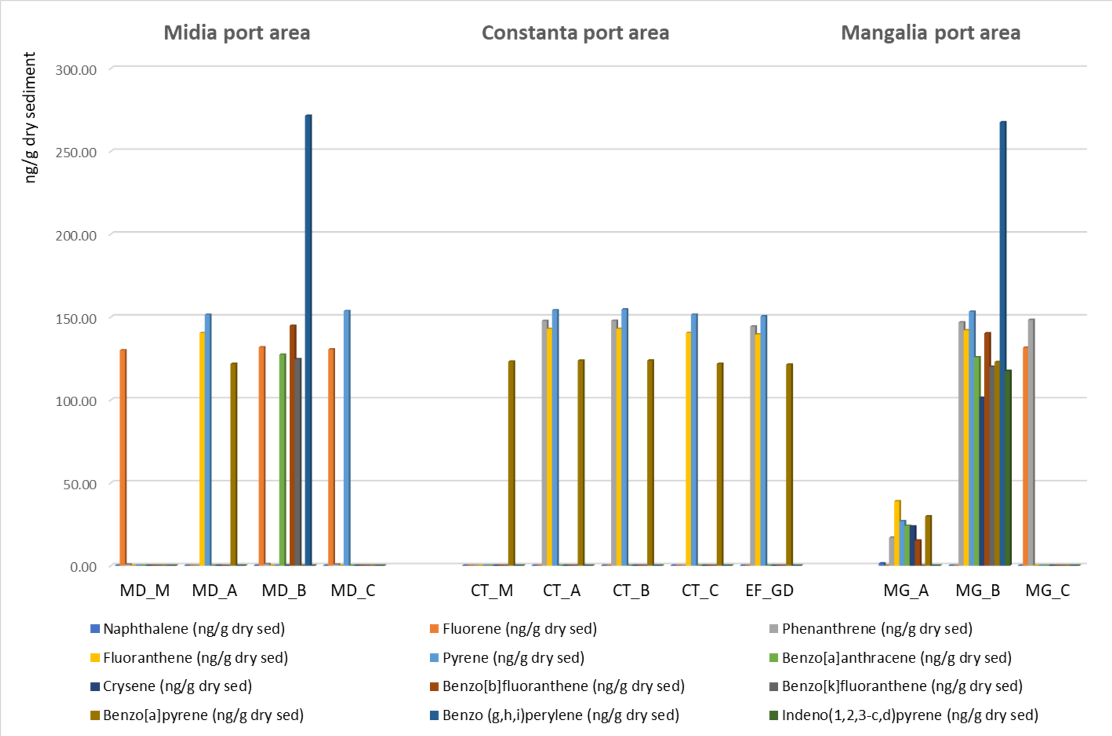


Figure 3.47 - Spatial distribution of PAHs concentrations in surface sediments in hot-spots study areas, September 2019

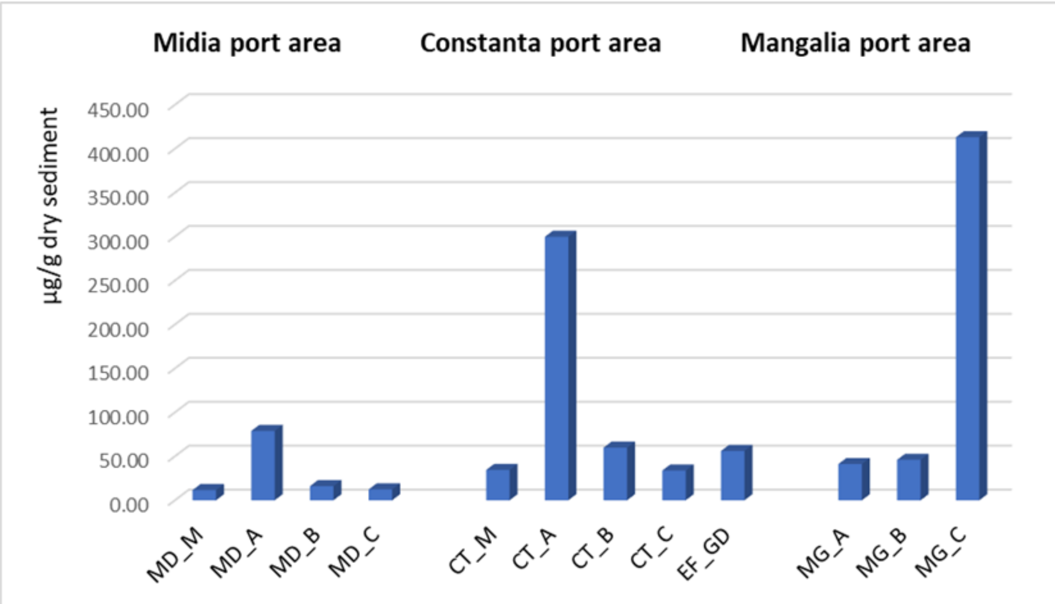


Figure 3.48 - Spatial distribution of TPHs concentrations in surface sediments in hot-spots study areas, September 2019

The concentrations detected in September 2019 in the 4 hot-spots areas indicated a low level of organic pollution, as no exceeding of EQS values were noted for chlorinated compounds and only 17% of benzo (g,h,i)perylene concentrations and 8% of total PAHs concentrations in surface sediments surpassed recommended values.

In comparison with available monitoring data (2015 – 2018) from the same areas, in 2019 the results were generally maintained between similar variability ranges, with some increasing trends of HPTs in Mangalia and Eforie areas (Figure 3.49, Figure 3.50, Figure 3.51, Figure 3.52).

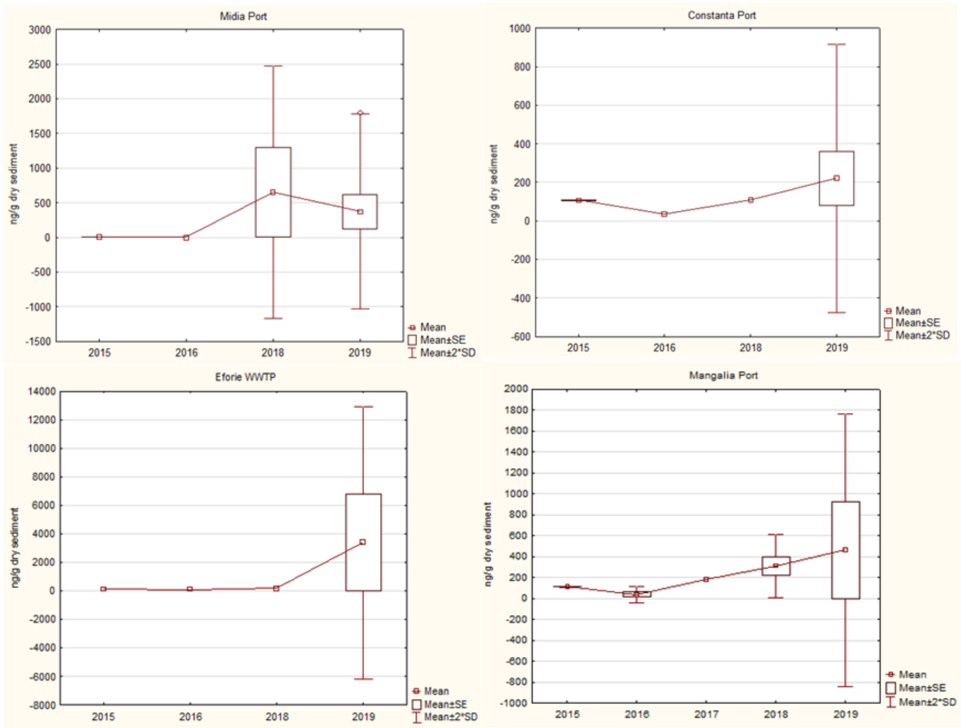


Figure 3.49 - Trends of total OCPs concentrations in surface sediments in Midia, Constanta, Eforie and Mangalia areas, 2015 - 2019

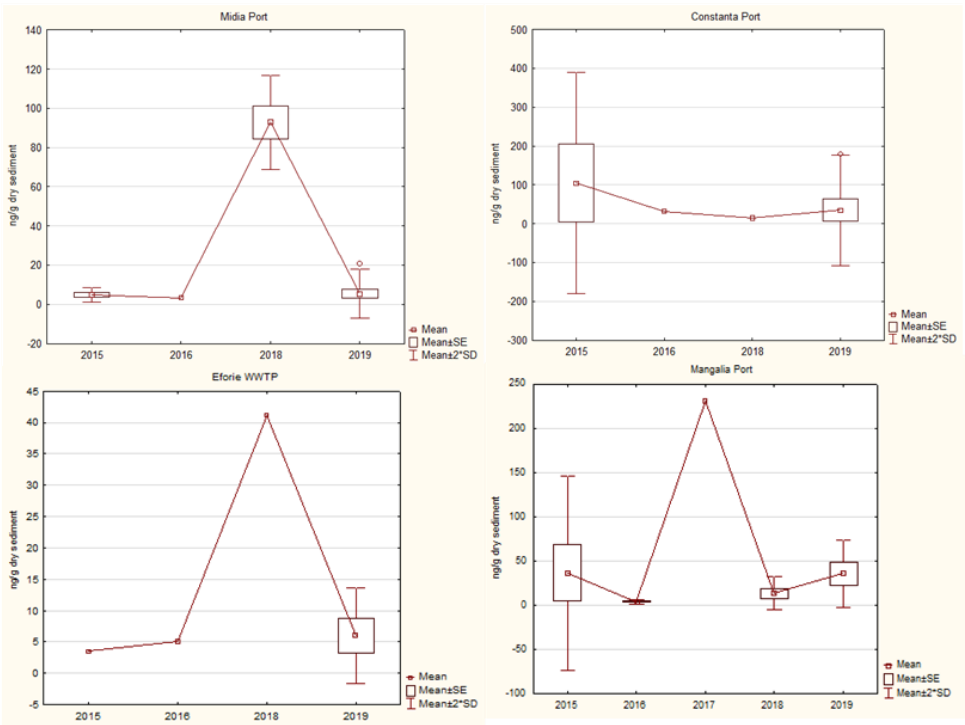


Figure 3.50 - Trends of total PCBs concentrations in surface sediments in Midia, Constanta, Eforie and Mangalia areas, 2015 - 2019

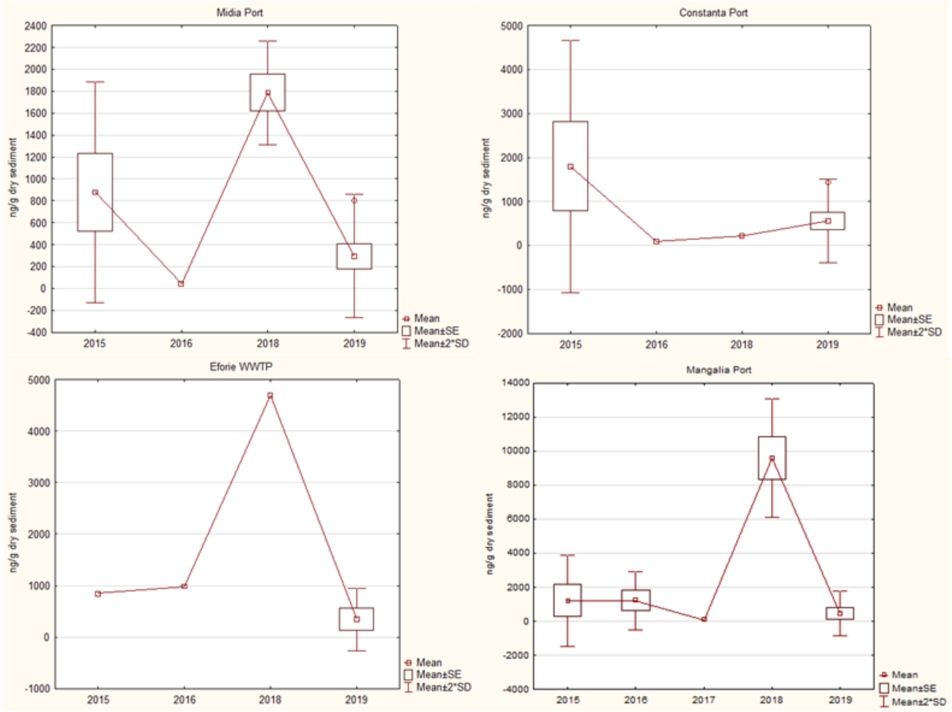


Figure 3.51 - Trends of total PAHs concentrations in surface sediments in Midia, Constanta, Eforie and Mangalia areas, 2015 - 2019

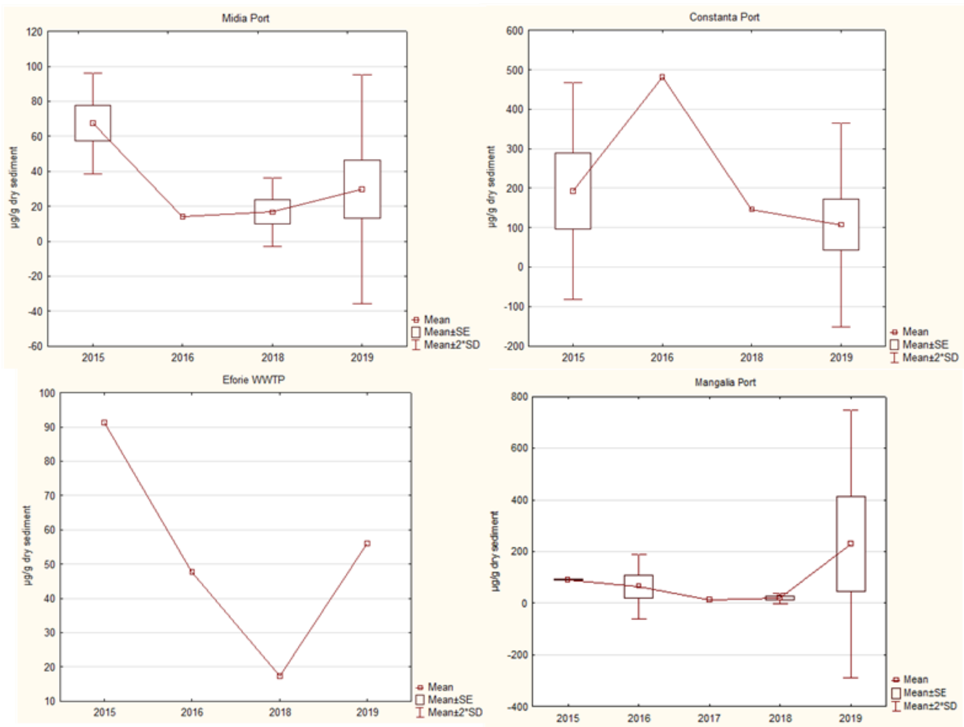


Figure 3.52 - Trends of TPHs concentrations in surface sediments in Midia, Constanta, Eforie and Mangalia areas, 2015 - 2019

Conclusions

Sediments samples collected in September 2019 from the 4 study areas were characterized by OCPs and PCBs values below detection limits in all samples. TPHs values were lower than typical ranges reported for Black Sea marine sediments in coastal area and PAHs distribution was characteristic to each area.
The concentrations detected in the four hot spots areas, in September 2019 indicated a low level of organic pollution, as no exceeding of EQS values were noted for chlorinated compounds and only 17% of benzo (g,h,i)perylene concentrations and 8% of total PAHs concentrations in surface sediments surpassed recommended values.
In comparison with available monitoring data (2015 – 2018) from the same areas, in 2019 the results were generally maintained between similar variability ranges, with some increasing trends of HPTs in Mangalia and Eforie areas.

3.2.3 Turkey

Heavy Metals in sediments

Previous studies carried out at the southern Black Sea coastal area have provided important information about metals' pollution. However few studies were concentrated on POPs pollution (MISIS project). One of the studies has shown that the concentrations of the OCs and PCBs in mussels were higher in coastal areas close to the largest city of the region, the Samsun harbour area (Kurt & Ozkoc, 2004). Recently, significant amounts of PAHs and TPHs were detected in sediment samples collected from the Samsun coastal area within the scope of the national monitoring program. In addition, the sum of PCBs (ICES 7) was found to be higher than the proposed ERL threshold for sediment (Atabay et al., 2019).

The typical surficial bottom of the Samsun sediments consisted of silty, organic-rich mud material. The water contents of the sediment samples range from approximately 38 % to 50 % in the Samsun port and WWTP area. Sand contents ranged between 0.05 % and 51.9 % (mean 5 %) in the samples. The highest sand concentrations (51.8 %) were found in SAAT03 of Samsun WWTP stations, this is followed by Samsun Port (SLI04) and again WWTP station (SAAT01). Mud contents ranged from 45.4 % to 99.7 % (mean 88.9 %) in domination with more than 90 % (at 10 stations over 18). A small amount of gravel was found only in the samples at the treatment plant of Samsun and station out of the port (SLI02 and SAAT02), with contents of up to 4.2 % (Figure 3.53).

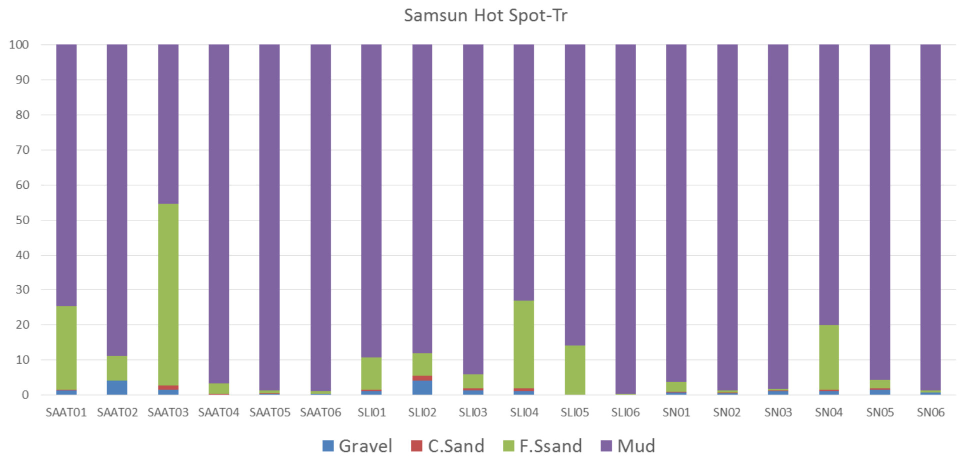


Figure 3.53 - Particle size distribution of sediment samples collected from Samsun HS

The heavy metal concentrations (As, Cu, Cr, Cd, Pb, Ni, Hg) measured in surface sediments collected from Samsun Hot Spot areas in June 2019 reflect the impact of various anthropogenic inputs.

The following variation ranges (in dry weight) were observed: 8.82-20.45 µg/g As; 78.63-464.33 µg/g Cu; 0.15 – 0.71 µg/g Cd; 86.24 – 207.08 µg/g Cr; 18.34-66.59 µg/g Pb; 55.53-158.07µg/g Ni; 87.07-223.40 µg/g Zn and 0.57-20.75 µg/g Hg (Table 7.12). Metal contents (mean values) of the sediments collected from the Samsun hot spot area were also compared in the graphics with the ecosystem impact threshold values (US ERL and ERM) (Long et al. 1995). Most of the sediment metal contents (75th percentile) such as: As, Cr, Cu, Ni, Zn and Hg, were find above the ERL values. Furthermore, most of the Ni and Hg contents of the samples (75 percentile) were above ERM values.

It is observed that mean Ni and Hg values of the sediment samples are higher than and about the ERM values (Figure 3.54). The mean As, Cr, Cu, and Zn concentrations are higher than and similar to the ERL values. Only mean Cd and Pb contents of the samples were detected below the ERL values.

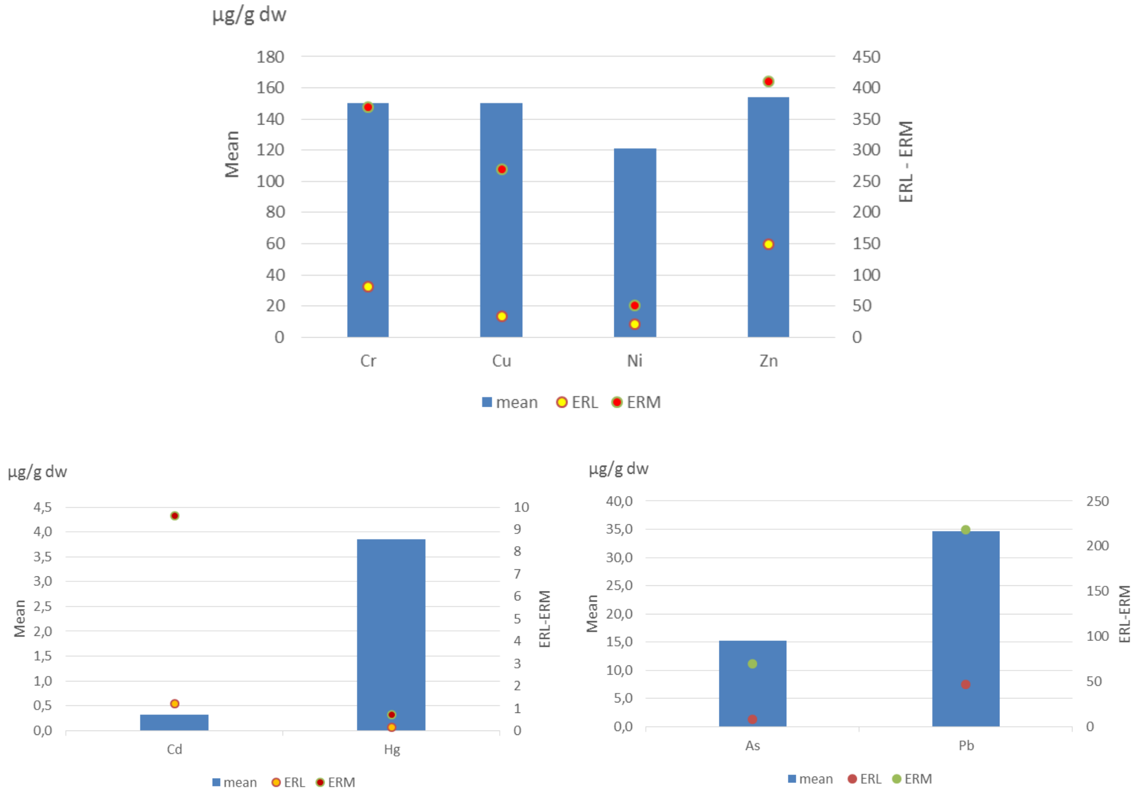


Figure 3.54 - Comparison of the mean metal contents of sediment with the threshold values

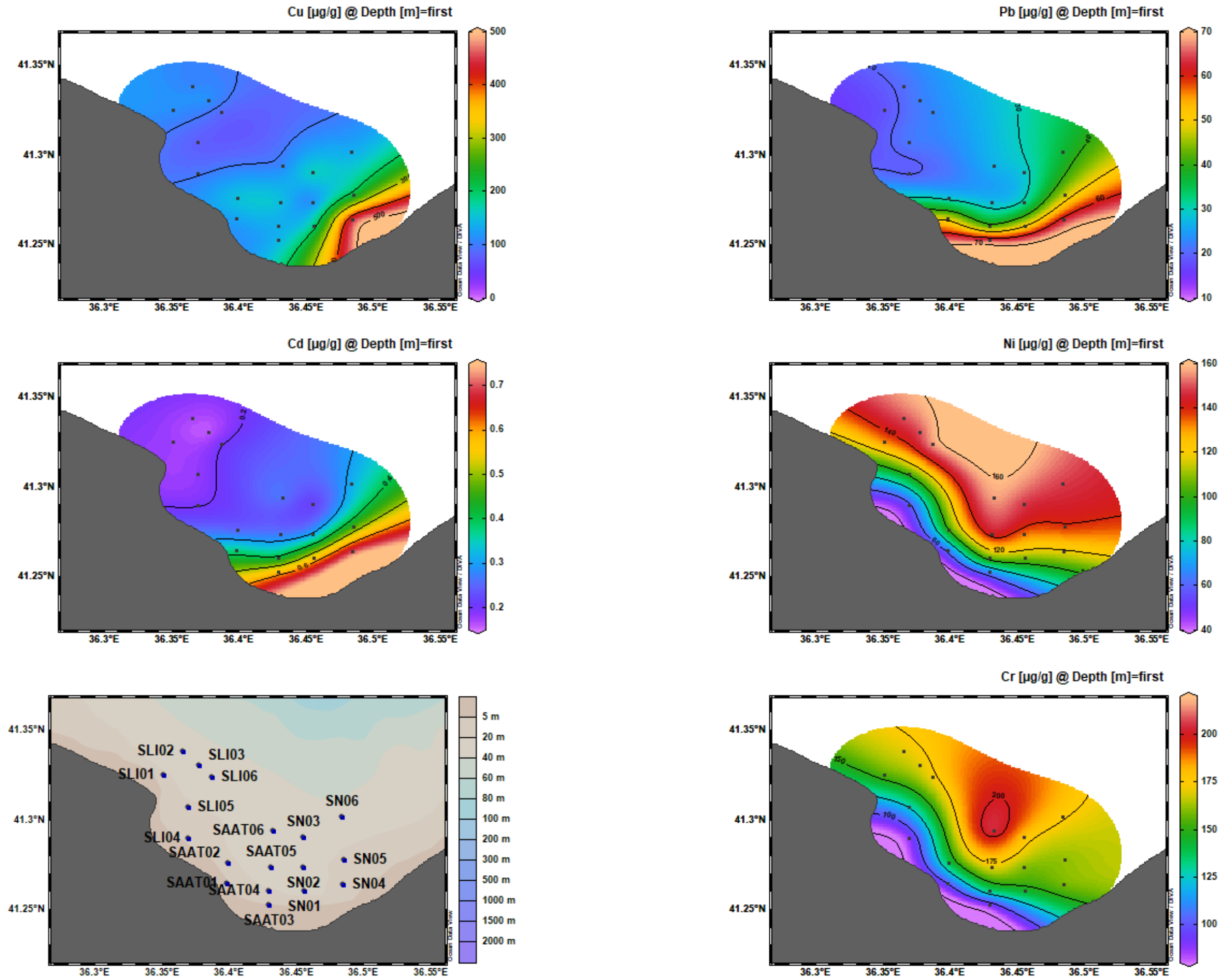


Figure 3.55 - Spatial distribution of heavy metals concentrations in surface sediments of Samsun hot spot

Higher metal concentrations (Cu, Cd, Pb and Hg) were detected at the easternmost stations with copper production facilities on the land side and innermost stations close to wastewater treatment plant discharge. The concentrations of these elements gradually decrease outward. Reversely the Ni and Cr elements were found in higher contents at the deeper (>40 m) locations (Figure 3.55).

For the region affected by the Samsun Hot Point, the data obtained in this study are generally higher than those reported for Black Sea sediments. For instance, the limit of predominant values (75th percentile of 2017 – 2018 monitoring data) being as follows: 14.67 µg/g As; 56.40 µg/g Cu; 0.17 µg/g Cd; 22.91 µg/g Pb; 41.307 µg/g Ni; 74.57µg/g Cr. However, the dominance of Pb, Ni, Cu, Cr, Zn and Hg contents in the Samsun Hot Spot coastal area samples are much higher than the 75th percentile values of 2018 monitoring values (Figure 3.56). Especially the high difference (72 times higher) in mercury (Hg) concentrations is striking.

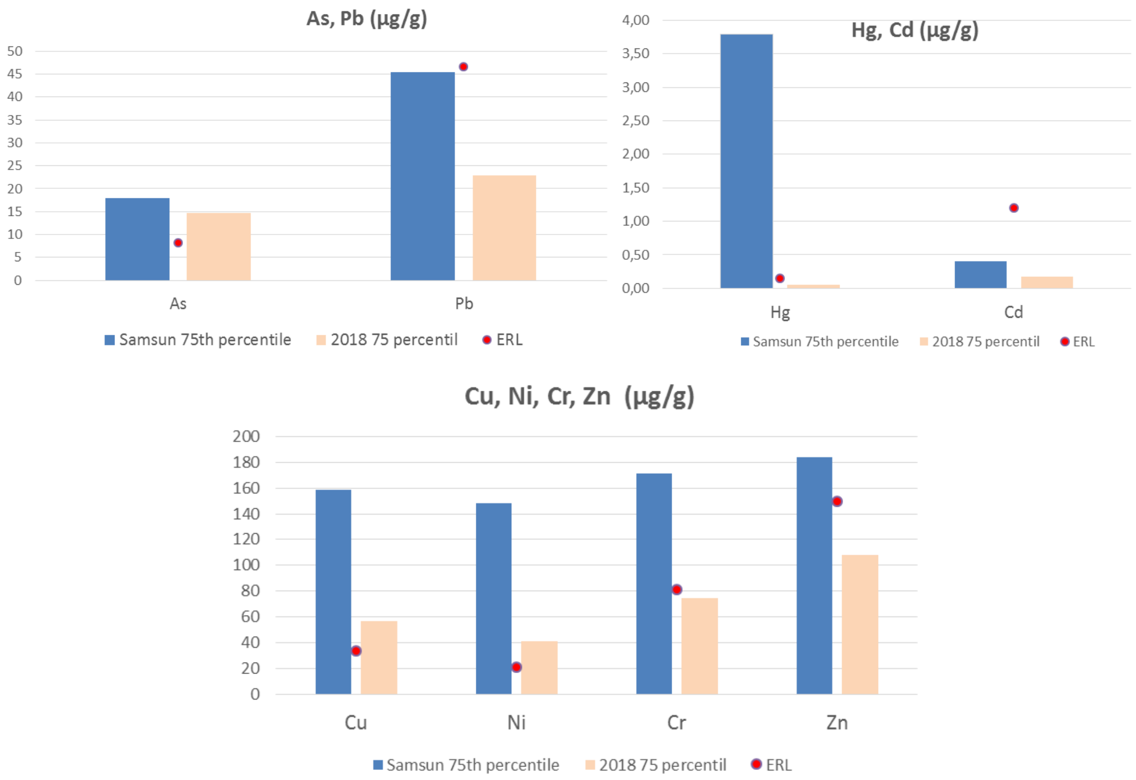


Figure 3.56 - Comparison of 75 percentiles of sediment metal contents (Samsun HS and 2017-18 BS stations)

In general, higher concentrations were observed at the stations close to the wastewater treatment plant and metal industries (SAAT and SN stations) than at the stations close to the Samsun port (SL stations). A decreasing trend from coast to open stations was observed for Hg, Zn, Pb at the SAAT stations (Figure 3.55 and Figure 3.57). For Cu, a similar decrease was observed at the stations SN 4, 5, 6 (eastern side) (Figure 3.55, Figure 3.57). From side to open increasing trend was observed for Cr, Ni at the SAAT and SN stations. At the port stations (SL) increasing was observed for Hg, Ni and Cr (Figure 3.55, Figure 3.57).

Figure 3.57 - Metal contents of sediments collected from Samsun Hot Spot area

Assessment of sediment metal contamination by comparing only with threshold values can be misleading, especially in the absence of background values. For this reason, in addition to the ERL comparison given above, an evaluation was conducted using the enrichment factors (EF). The enrichment factor is calculated by proportioning the amounts of an element in the sample and the earth's crust (shale average: Krauskopf, 1985). In this calculation, values are normalized with Al contents of samples and shale. Enrichment values are classified according to six categories (<1, 1-3, 3-5, 5-10, 10-25, 25-50 and >50) suggested by Sakan (Sakan et al. 2014). In this classification, an enrichment factor of 1 indicates that the element in question is of lithogenic origin. EF values 10-25, 25-50 and above 50 indicate, severe, very severe and extremely severe enrichments respectively. EF classifications are shown in Figure 3.58, for Samsun Hot Spot coastal area sediments.

In general, the highest EF values of Samsun Hot Spot sediments were calculated for Hg implying the extremely severe enrichment (EF>50) (5 stations from 18 stations). The stations have EF>50 for Hg are: SN4> SAAT3> SN5> SN6 > SN1 in decreasing order. Other higher EF values (25-50) were detected for Cu at st SN4 and Hg at stations SN2 and SAAT1 indicating very severe enrichments. “Severe enrichments” were observed in 3 stations for Hg, 5 stations for Cu, 2 stations for Pb and 1 station in As.

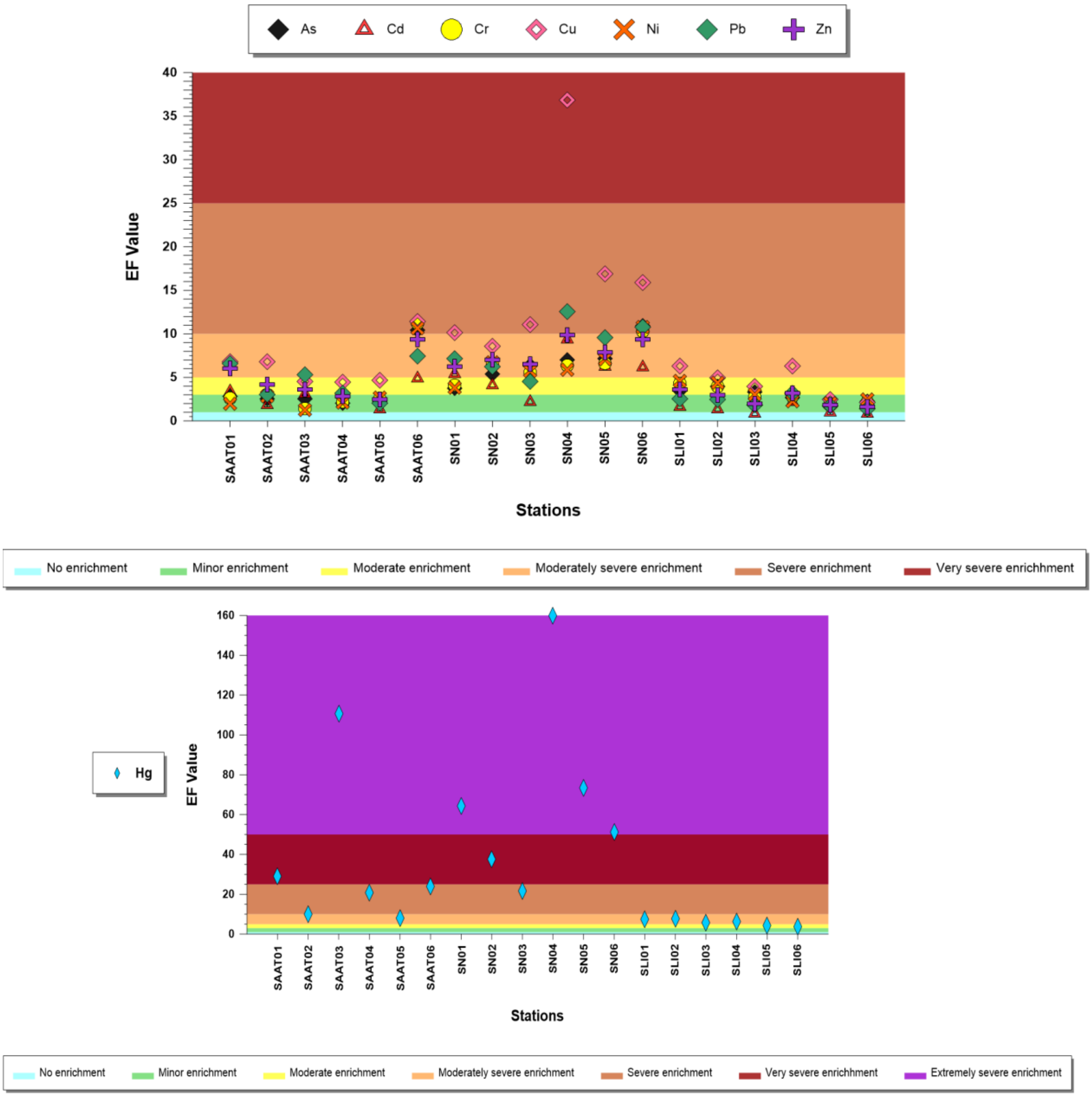


Figure 3.58 - Metal Enrichment Factors of Samsun Hot Spot Area (HS) sediments

The dominance of the EF values (75th percentiles) for the Samsun HS coastal area indicates “very severe enrichment” for the Hg and “severe enrichment” for the Cu metals. However, the dominance of the EF values indicates; “moderately severe enrichment” of As, Cd, Cr, Cu, Ni, Pb and Zn for the Samsun HS coastal area.

Conclusions

Metal concentrations measured in all surface seawater samples of the Samsun Hot Spot coastal area (in July 2019 and January 2020) were found below the MAC-EQS values identified as Priority Substances (EU-2013/39) and Specific Pollutants (TR-2016/08) under the WFD (Water Framework Directive). Generally, a decreasing gradient from coast industrialized area (eastern part of the HS) and WWT discharge (middle part of the HS area) to open area was noticed for most analysed metals, reflecting metal industry influence upon receiving zone. The seasonal difference was observed in Samsun HS water samples in terms of higher metal contents in summer sampling with minimum dilution effect of rivers and precipitation.

In the sediment matrix, higher concentrations (above ERL and ERM) of the metals were measured with dominance at the stations close to the industrial and WWTP area implying the impact of various anthropogenic inputs. The mean Ni and Hg concentrations of Samsun HS sediment samples are higher than and about the ERM values respectively. The mean As, Cr and Cu contents of Samsun HS sediment samples are higher than and similar to the ERL value. Furthermore, for the region affected by the Samsun Hot Spot, the data obtained in this study are generally higher than those reported (2017-2018) for Black Sea sediments. Especially the high difference in mercury (Hg) concentrations is striking. Similarly, the high EF values of Hg calculated in this study indicates the "extremely severe enrichment" (EF>50) of the sediments.

Organic pollutants in sediments

Organic carbon is one of the main parameters showing organic matter pollution in sediments. Organic matter entering the marine environment or naturally occurring (production) decomposes as long as it remains in the water column. In this process, the oxygen of the water column is used as a result of biochemical reactions in the environment. Depending on its residence time in the water column, either before it reaches the sediment, it is completely decomposed or accumulates in the sediment. The content of sedimentary organic carbon is related to the sediment grain size. Higher content of organic carbon correlates with increasing clay-silt contents due to an increased surface area (Tyson, 1995). Wind-driven currents and waves also influence the spatial distribution and transport of sediments and organic matter (Magni et al., 2002). An area with low hydrodynamic energy will favour the accumulation of fine sediments due to enhanced settlement of silt-clay particles. By contrast, areas exposed to higher hydrodynamic energy levels will be characterized by coarser sediments (Ergin & Bodur, 1999). Since the depth of the stations where sediment samples are taken is a factor affecting the organic carbon contents (due to residence time) in oxic conditions, it should also be taken into consideration when interpreting the carbon values. The contents of total organic carbon (TOC) (Figure 3.59) range from 0.2 % to 1.3 % (mean 0.7 %) in Samsun Port and WWTP - sea impact areas. Maximum value occurred in SN04 and SLI02 stations.

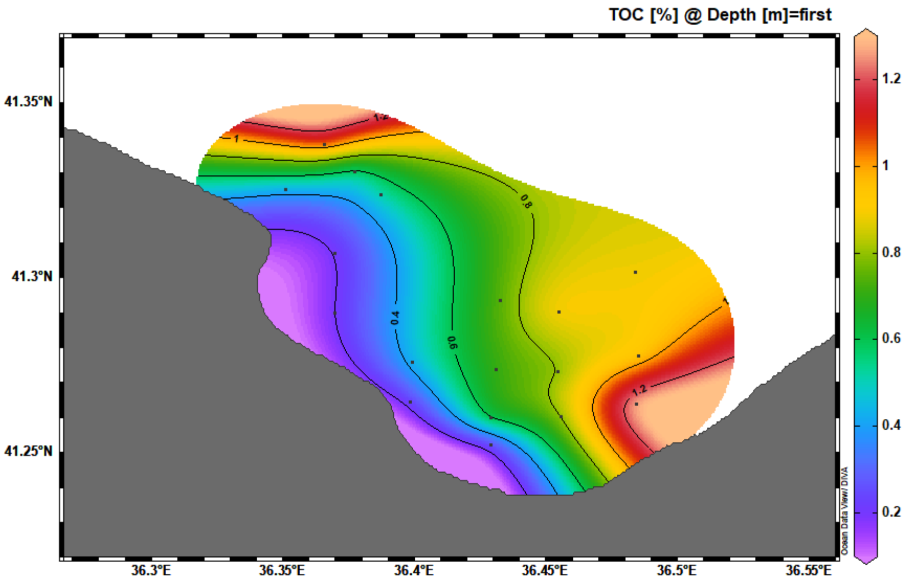


Figure 3.59 - Spatial distribution of the Total Organic Carbon in Samsun Port and WWTP impact areas

TPHs concentration in sediment varied from 4.5 µg/g dw to 27.2 µg/g dw in Samsun Port and WWTP. Total PAHs concentrations varied between 64.6-223.1 ng/g in sediments affected by Samsun Port and WWTP. Total PAHs levels remained far lower than the NOAA residue quality guideline value for the Low Effect Range (ERL) of 4000 ng/g (Long et al., 1990; Long et al., 1995). PAH components concentrations in the Samsun Port and WWTP-influenced sediments are shown in Figure 3.60.

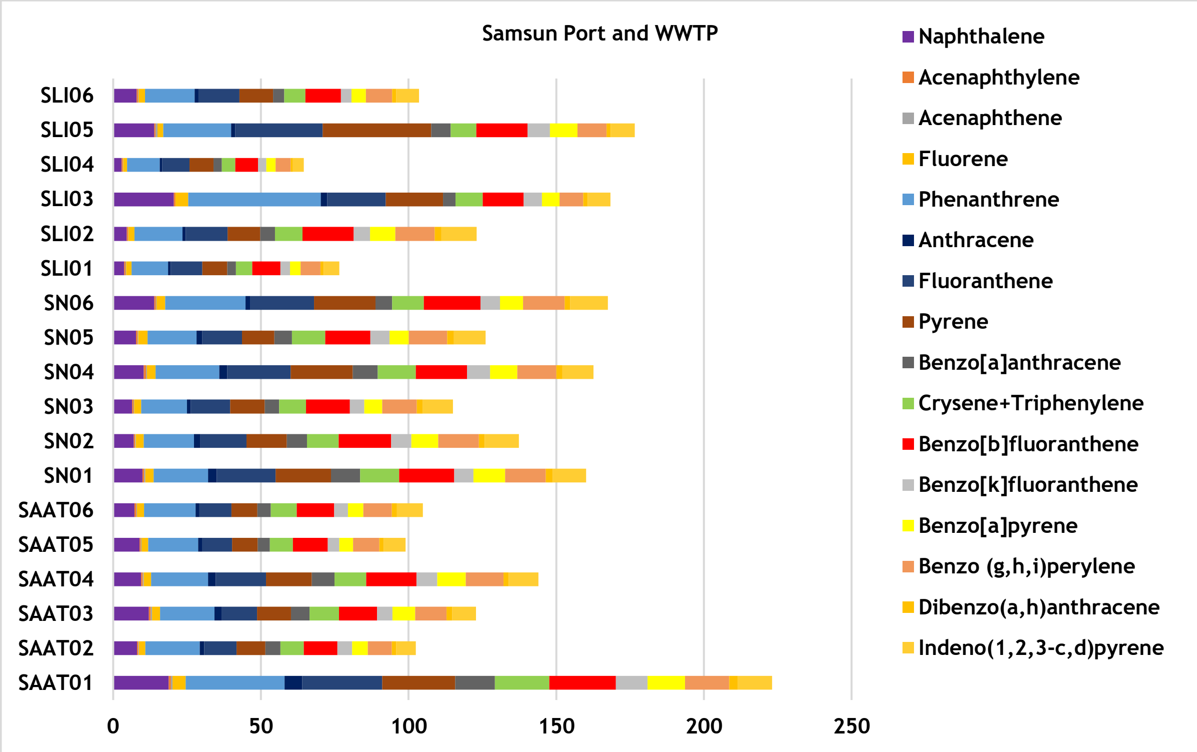


Figure 3.60 - Distribution of PAH components in sediments affected by Samsun Port and WWTP (July 2019)

α-HCH, lindane, heptachlor, aldrin, dieldrin, endrin p,p' DDT components the median concentrations were at detection limit (Annex C).

In sediment, the sum of the DDT's including metabolites (DDE+DDD+DDT) exceeded the threshold values (1.58 ng/g) in approximately 38.9 % of the Samsun Port and WWTP samples (Figure 3.61). Concentrations of other organochlorinated pesticides and polychlorinated biphenyls were below the threshold values in all stations.

The average values of DDT and its metabolites detected in Samsun Port and WWTP sediment samples indicated pp'-DDT 48.5 % > pp'-DDE 28.8 % > pp'-DDD 22.7 %. The distribution of DDT and its metabolites (%) in sediment are shown in Figure 3.62. This means that DDTs are caused by historical degradation (Figure 3.63). DDT can biodegradable to DDE under aerobic conditions and to DDD under anaerobic conditions (Da et al., 2013).

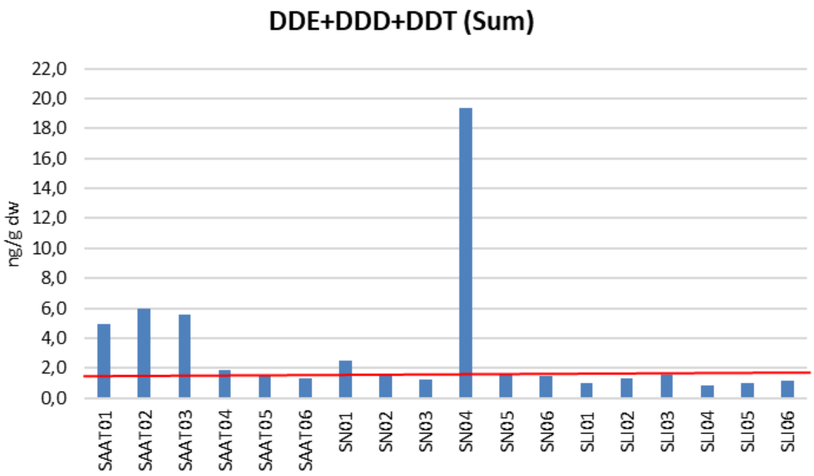


Figure 3.61 - Concentrations of DDD+DDE+DDT in surface sediments of the marine area under the influence of Samsun Port and WWTP compared with the proposed value to define good environmental status, July 2019

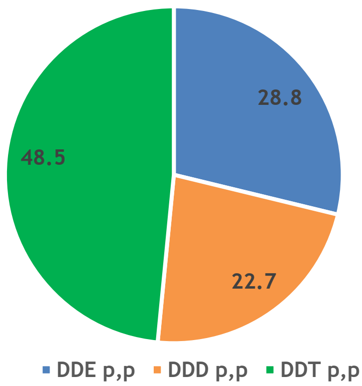


Figure 3.62 - Distribution of DDT and its metabolites (%) in sediment

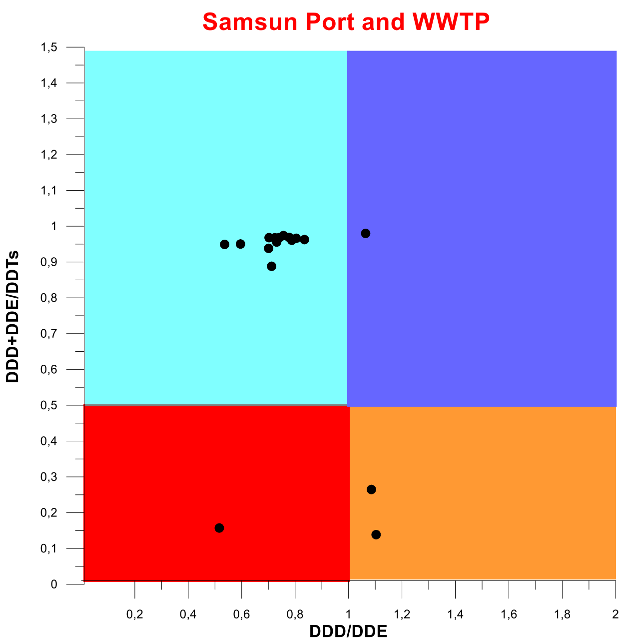


Figure 3.63 - Relationship between (DDD+DDE)/DDTs and DDD/DDE in surface sediments

β-HCH concentration in sediment varied from 0.07 ng/g dw to 0.33 ng/g dw in Samsun Port and WWTP. Lindane concentration in the sediment varied from <0.05 ng/g dw to 0.38 ng/g dw. Pesticide derivatives (α-HCH, heptachlor, aldrin, dieldrin, and endrin) were measured at trace quantity or below the detection limit.

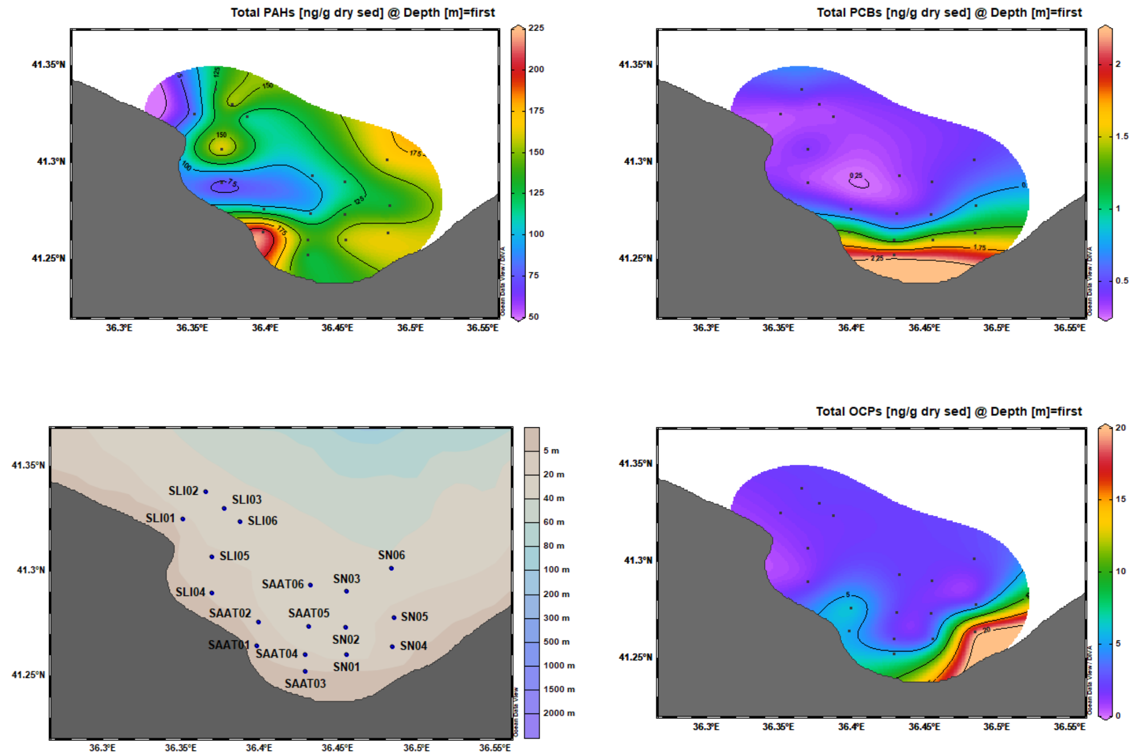


Figure 3.64 - Spatial distribution of organic pollutants concentrations in sediment in the marine area under the influence of Samsun Port and WWTP, July 2019

In July 2019, the majority of DDT and its metabolites concentrations in surface sediments presented an increasing tendency in the east of the Samsun WWTP (Figure 3.63).

Conclusions

In sediment, the sum of the DDT's including metabolites (DDE+DDD+DDT) exceeded the threshold values (1.58 ng/g) in approximately 38.9 % of the Samsun Port and WWTP samples. The average values of DDT and its metabolites detected in Samsun Port and WWTP sediment samples indicated pp'- DDT 48.5 % > pp'- DDE 28.8 % > pp'- DDD 22.7 %. Most of the DDTs detected at stations are caused by historical degradation. DDT can biodegradable to DDE under aerobic conditions and to DDD under anaerobic conditions. Concentrations of other organochlorinated pesticides, polychlorinated biphenyls (PCBs) and Polyaromatic hydrocarbons (PAHs) were below the threshold values in all stations.

4 Integrated assessments – TRIX, BEAST, CHASE, NEAT

4.1 TRIX

A universal method for assessing the level of the marine waters' eutrophication and generally accepted manuals for practical assessment does not exist to date. For each study on this problem, a subjective author's approach prevails, which usually determines the choice of indicators and their number when calculating various environmental indices. Usually, the proposed assessment methods are limited with the number of measured hydrochemical and biological parameters and indicators of the marine environment. The most frequently recommended for scientific research and use in monitoring programs for the state of the natural marine environment is the calculated E-TRIX index, which has been widely used in recent years. E-TRIX is an integral indicator related to the characteristics of the primary production of phytoplankton and nutritional factors. The calculation formula of the index E-TRIX is composed of the following indicators of the ecosystem: the concentration of chlorophyll *a* which replaces the index of phytoplankton autotrophic biomass; the deviation of oxygen saturation from 100 % – an indicator of the primary production intensity of the system, which covers the phase of active photosynthesis and the phase of respiration predominance; the concentration of total phosphorus and mineral nitrogen-indicators of the presence of the nutrients (Vollenveider, 1998).

E-TRIX is calculated by the formula:

$$TRIX = [log(Ch \cdot D\%O \cdot N \cdot P) + 1.5]/1.2$$

where Ch – chlorophyll a concentration, µg/L;

D%O – deviation in absolute values of dissolved oxygen from 100 % saturation;

N - concentration of the sum of mineral nitrogen dissolved forms, µg/L;

P – concentration of total phosphorus, µg/L.

The E-TRIX index changes according to the conditions of water trophic status in the range from 0 to 10, and the assessment of the category of trophic level and the state of water quality is carried out according to the index value (Table 4.1).

Table 4.1 Characteristics of water quality according to E-TRIX

MSFD	Water quality	Value of E-TRIX	Trophic level	Characteristics of water
GES*	High	≥0 - ≤4	Low	High transparency of water, lack of colour anomalies of water, lack of satiety and lack of saturation of dissolved oxygen
	Good	>4 - ≤5	Moderate	Occasional cases of reducing the transparency of water, lack of watercolour anomalies, hypoxic bottom waters.
Non-GES	Moderate	>5 - ≤6	High	Low water transparency, watercolour anomalies, hypoxia of bottom waters, and occasional cases of anoxia.
	Bad	>6 - ≤10	Very high	High water turbidity, large areas of colour anomalies of water, regular hypoxia over a large area and frequent anoxia of bottom waters, death of benthic organisms

Methodological aspects in determining the E-TRIX index by the averaged data of individual measurements, and by calculation for the initial data and subsequent averaging of index values, were discussed in (Ukrainsky, 2010). In the calculation, the formula uses standard and most frequently measured hydrochemical and hydrobiological characteristics of marine waters, the number of parameters does not change, which makes it possible to compare the values of E-TRIX for different areas of the sea and oceans.

For the assessment of trophic status and water quality with the E-TRIX in the hot spots area, we use the data collected in the Ukrainian part of the Black Sea shelf: Place of discharge from WWTP Odessa "South" and Place of discharge from WWTP city and port Chornomorsk, samples were taken in September 2019.

In general, based on the results of the E-TRIX assessment, the quality of the Black Sea waters in the study areas was assessed as GES for surface water.

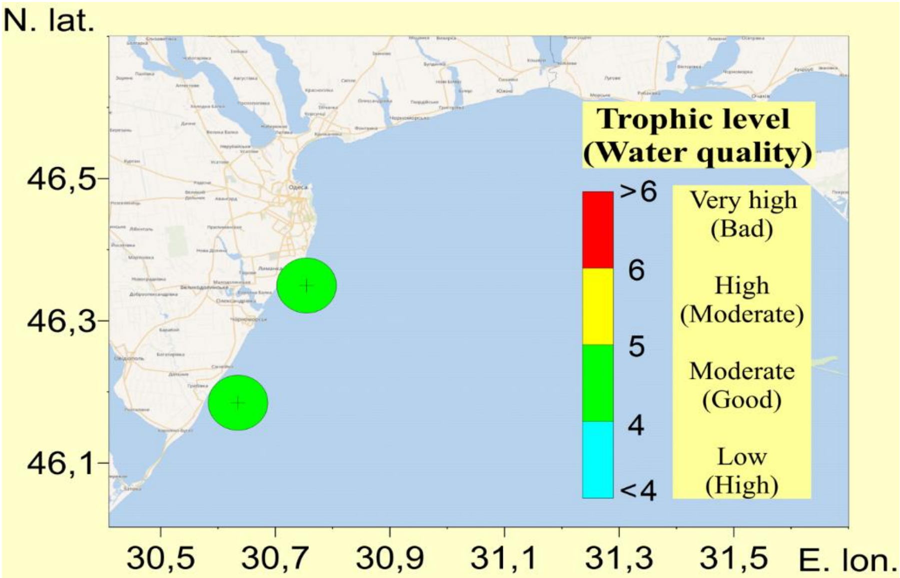


Figure 4.1 - Assessment of the trophic status and surface water quality with the E-TRIX in the hot spots area, September 2019

E-TRIX values were 4.04 and 4.3, which corresponds to “Moderate” trophic level and “Good” water quality. At these stations, the concentration of total phosphorus was 21.06 – 21.99 µg/L and, of mineral nitrogen is very low 2.38 µg/L and 2.66 µg/L, chlorophyll *a* concentration was 9.22 µg/L and 14.43 µg/L, oxygen saturation was also low (94.38 % and 95.34 %).

4.2 BEAST

BEAST (Black Sea Eutrophication ASsessment Tool) is an integrative tool for the eutrophication assessment proposed by the Black Sea Commission through the Baltic2Black project, and similar to HEAT (HELCOM, xxx) which runs on MS Excel. The eutrophication assessment of the Black Sea in respect to the descriptor's 5 (MSFD) and BEAST (Black Sea Eutrophication ASsessment Tool) requirements uses a core set of indicators (Lazar et al., 2016)) (Table 4.2).

BEAST categories have three criteria:

C1 - causes of eutrophication,

C2 - direct effects and

C3 - indirect effects, indicating the main cause-effect relationships in the eutrophication development.

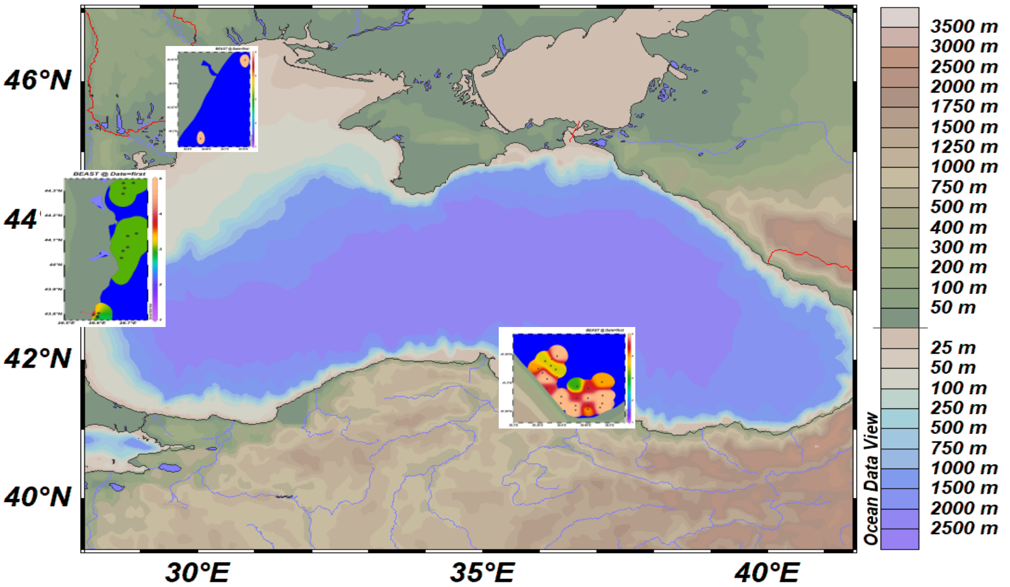
Each criterion could have a set of indicators (based on availability and expert's choice). Within the criteria, BEAST takes a weighted mean (according to the significance of the parameter or the data quality), evenly distributed. The result of each indicator status is the EUT_Ratio. Simultaneously, between the categories, the One-Out-All-Out-principle (OOAO) is applied (the worst assessment of a quality element determines the overall assessment result). The result is qualitative, the "Final eutrophication status": high, good, moderate, poor, and bad. With the scope of data visualization, we assigned a value to each qualitative result – 1-High (blue), 2-Good (green), 3-Moderate (yellow), 4-Poor (orange), 5-Bad (red).

For this assessment, we used as core indicators (due to their availability, reference conditions availability and relevance) as follows:

C1 - causative factors - surface nutrients concentrations - comprises ten nutrient indicators, though they are not used together in any assessment units.

C2 - direct effects - phytoplankton blooms - surface chlorophyll a (as an estimate of the Total biomass) or the total phytoplankton biomass (UA), and Secchi depth.

C3 - indirect effects - bottom dissolved oxygen (%) (effective only for coastal and shelf waters up to 50m bottom depth due to the natural features of the Black Sea).



BEAST (N=56) showed that all hotspots are triggering eutrophication. The status was "moderate", "poor", and "bad" either because of nutrients enrichment or their direct effect expressed as chlorophyll *a* levels (Table 4.2).

The results agree with each area assessment and confirm the influence of the point sources of jor pollution, the "Hot Spots". The risk of not achieving GES under descriptor 5 is major. Their monitoring needs an increased effort and measures for the nutrients input reduction. It is essential to assess all activities and their pressures but also the cumulative effect.

Table 4.2 Eutrophication status (BEAST) in the hot spots area

Station	Country	Causes	Direct effects	Indirect effects	BEAST
ST 4	Ukraine	1	5	2	Bad
ST 5	Ukraine	1	5	3	Bad
Midia Port (A)	Romania	3	2	2	Moderate
Midia Port (B)	Romania	3	2	2	Moderate
Midia Port (C)	Romania	3	2	2	Moderate
Constanta A	Romania	3	1	2	Moderate
Constanta B	Romania	3	1	2	Moderate
Constanta C	Romania	3	1	2	Moderate
Eforie	Romania	3	1	2	Moderate
Mangalia A	Romania	5	5	2	Bad
Mangalia B	Romania	2	1	2	Good
Mangalia C	Romania	3	1	2	Moderate
SAAT01	Turkey	5	5	1	Bad
SAAT02	Turkey	5	5	1	Bad
SAAT03	Turkey	5	5	2	Bad
SAAT04	Turkey	5	5	2	Bad
SAAT05	Turkey	5	4	1	Bad
SAAT06	Turkey	5	5	1	Bad
SLI01	Turkey	4	5	1	Bad
SLI02	Turkey	3	2	1	Moderate
SLI03	Turkey	3	2	1	Moderate
SLI04	Turkey	5	3	1	Bad
SLI05	Turkey	3	5	1	Bad
SLI06	Turkey	3	1	1	Moderate
SN01	Turkey	5	5	1	Bad
SN02	Turkey	5	3	1	Bad
SN03	Turkey	5	5	1	Bad
SN04	Turkey	5	5	1	Bad
SN05	Turkey	5	3	1	Bad
SN06	Turkey	3	2	2	Moderate
TRK34Y	Turkey	3	5	1	Bad
TRK35	Turkey	3	5	2	Bad
TRKSK1	Turkey	5	5	2	Bad
TRKSK2	Turkey	5	5	2	Bad
SAAT01	Turkey	5	4	1	Bad
SAAT02	Turkey	5	3	1	Bad
SAAT03	Turkey	5	4	1	Bad
SAAT04	Turkey	4	4	1	Poor
SAAT05	Turkey	3	3	1	Moderate
SAAT06	Turkey	2	3	2	Moderate
SLI01	Turkey	3	4	1	Poor
SLI02	Turkey	2	4	1	Poor
SLI03	Turkey	2	4	1	Poor
SLI04	Turkey	3	5	1	Bad
SLI05	Turkey	3	4	1	Poor
SLI06	Turkey	2	4	1	Poor
SN01	Turkey	5	4	2	Bad
SN02	Turkey	2	4	2	Poor
SN03	Turkey	5	4	2	Bad
SN04	Turkey	5	4	2	Bad
SN05	Turkey	5	5	2	Bad
SN06	Turkey	5	5	2	Bad
TRK34Y	Turkey	3	5	1	Bad
TRK35	Turkey	2	3	1	Moderate
TRKSK1	Turkey	5	2	2	Bad
TRKSK2	Turkey	5	4	2	Bad

4.3 CHASE

A good ecological and environmental status has as a prerequisite condition a good chemical condition. This is one of the most topical challenges facing policymakers, water managers, and scientists (Laane et al., 2012). Indicators are generally accepted as tools for evaluating the status of marine environments in relation to management targets or thresholds. Application of the widely used ''one out – all out'' principle could easily result in a fully negative overall evaluation for all objectives. A drawback of this approach is that a few strongly negative indicator values could shadow the potentially generally positive state of a given ecological objective. This would make any progress towards improving the environmental status invisible, as long as at least one indicator is showing the poor performance (Ojaveer & Eero, 2011).

To avoid misleading conclusions, the assessment of hot spot pollution sources impacts on the Black Sea coastal environmental status was done by using an integrated hazardous substances assessment tool (CHASE), as a common approach for the Black Sea region. To assess the river impacts on the Black Sea coastal environmental status, pollutants concentrations were evaluated against threshold values that define good environmental status in each region using the HELCOM integrated hazardous substances assessment tool (CHASE) developed by NIVA Denmark (Andersen et al., 2016). This tool integrates data on hazardous substances in different matrices as well as bio-effect indicators, if available and is based on a substance- or bio-effect-specific calculation of a 'contamination ratio' being the ratio between an observed concentration and a threshold value. Values <1.0 indicate areas potentially 'unaffected', while values >1.0 indicate areas potentially 'affected'. These ratios are combined within matrices, i.e., for water, sediment, biota and biological effects. The integrated assessment provides a final status for an assessment unit, placing it in one of five classes: bad, poor, moderate, good, and high. Thus, this classification system is essentially binomial (unaffected vs. affected) and is distinguished by a threshold value. The other classes are based on defined deviations from the unaffected/affected boundary. While the threshold between the good and moderate status equals 1.0 (reflecting the use of contamination ratios), the high-good threshold is 0.5, the moderate-poor threshold is 5.0 and the poor-bad threshold is 10.0. The overall assessment uses a "one-out, all-out principle" regarding each matrix (Andersen et al., 2016). To have a better view of the environmental status in each region the graphic representation was done using the program Ocean Data View, so for each status class, it has assigned a value, from 1 – "High" to 5 – "Bad".

The results were compared with the assessment done using the method in place, in each region, to figure out the benefit of using the CHASE tool.

In Ukraine, the national methodology to assess the ecological state is by calculation of a pollution factor, Kz which reflects the concentration of all pollutants of the same type in a certain period in each area. This factor represents the sum of the ratios of the concentration of each pollutant to its maximum permissible concentration, under the EU Directive 2013/39 (MAC-EQS) for water, even the implementation of MSFD is not obligatory or the maximum permissible concentration according to Ukrainian legislation for sediment, to the number of measurements performed for a certain timeframe. Like CHASE, there are five quality classes ("very good", "good", "satisfactory", "bad", and "very bad") and the overall assessment of the ecological condition of water or bottom sediments in the study area is determined by the worst assessment of the group of pollutants.

In Romania, the status of the Black Sea ecosystem in respect to MSFD is assessed by evaluating the 75th percentile of the data in the assessment unit in a given time against threshold values that define good environmental status (MAC-EQS) following European legislation (EU Directive 2013/39) in water or ERL and EAC values (Effect Range Low and Environmental Assessment Criteria) developed by US EPA and OSPAR for assessing the ecological significance of sediment concentrations (OSPAR, 2008; UNEP MAP, 2011; US EPA, 1998; Long et al., 1998). As a result, a "Good" or "Bad" status for each substance is obtained and the result of each matrix and the overall result is given by the worst-case using the "one-out, all-out principle" (Boicenco et al., 2018).

In Turkey, the implementation of MSFD is not obligatory yet. However, assessment of the contaminant levels in the sediment matrix is carried out under the national monitoring program using ERL (Effects Range Low) as the threshold value. Some pilot studies are carried out to assess contamination in the water matrix according to the WFD (EU Directive 2000/60), using Max-EQS (EU Directive 2013/39). To decide the chemical status of each station "one out all-out principle" is applied for both matrices (except heptachlor which has an EQS below the detection limit) and for overall assessment.

In the Ukrainian area, influenced by the wastewater treatment plant of the city of Odessa and the port of Chernomorsk, the overall assessment conducted to a similar result. In water, the results obtained for heavy metals correspond to a "very good" and "satisfactory" status on heavy metals pollution. High levels of individual PCBs and organochlorine pesticides were recorded. As follows, the ecological status of seawater corresponded to the quality class – "very bad" (Table 4.3). In sediment, was observed an increased content of organochlorine pesticides and polyaromatic hydrocarbons. Heavy metals status was "very good". As a result, the overall quality class was assessed as "very bad" in station 5 (Table 4.3).

The evaluation done using the integrated hazardous substances assessment tool (CHASE) in each station pointed out states of the chemical status "Bad" in sediment and water (Table 4.3) and the overall assessment was "Bad" in all stations. Thus, the results are the same in water and sediment matrices. The two approaches are the same using five quality classes, even if their definition is slightly different. As an overall result, the two assessments concluded the same quality for the area.

Table 4.3 - Seawater and sediment status according to CHASE and national methodology assessment – Ukraine

Station	Matrix	CHASE status	National methodology evaluation status
ST 4	Water	5-Bad	Very bad
ST 5	Water	5-Bad	Very bad
ST 5	Sediment	5-Bad	Very bad

The results from the Romanian area influenced by hot spot pollution sources (Midia, Constanta and Mangalia harbours and Eforie wastewater treatment plant) revealed some exceeding of the threshold values that define good environmental status.

Cyclodiene pesticides (aldrin, dieldrin, endrin), the sum of DDTs (DDT and metabolites), HCB, lindane and anthracene exceeded the threshold values proposed for water to define good ecological status (according to Directive 2013_39_EU) in 48 % to 70 % of the samples in the area influenced by hot spot pollution sources. The other organic pollutants were in "good" status in water, according to the methodology developed in Romania to assess the status of the Black Sea ecosystem in respect to MSFD (Boicenco et al., 2018). As for heavy metals, no element in surface waters surpassed recommended environment quality standards (EQS).

In sediment, only benzo (g,h,i)perylene and total PAHs concentrations surpassed recommended values in 17 %, respectively 8 % of the samples for organic pollutants. Also, 4 % of copper concentrations and 27 % of nickel concentrations in surface sediments surpassed recommended values (EQS), whereas the other investigated elements had levels below EQS (ERLs). As a result, nickel was the only pollutants in "bad" status, whereas the other contaminants had levels below thresholds that define good ecological status.

Based on the "one-out – all-out" principle the status was evaluated as "Bad" in 50 % of the stations in sediment and 92 % of the stations in water (Table 4.4, Table 4.5) and consequently, the overall status was evaluated as "Bad" in 92 % of the stations.

The evaluation done using the integrated hazardous substances assessment tool (CHASE) in each station, pointed out states of the chemical status from moderate to good in sediment, bad in water (Table 4.4, Table 4.5) and the overall assessment was bad in all stations.

The evaluations results are similar in water in most of the stations and some differences are noted for sediment. These differences are the result of the different approach: two quality classes of local methodology and five for the integrated tool. As an overall result, with one exception, the two assessments concluded the same quality for the area.

Table 4.4 - Sediment status according to CHASE and national methodology assessment – Romania

Station	Matrix	CHASE status	National methodology evaluation status
MD_M	Sediment	2-Good	Good
MD_A	Sediment	3-Moderate	Bad
MD_B	Sediment	3-Moderate	Bad
MD_C	Sediment	2-Good	Good
CT_M	Sediment	3-Moderate	Bad
CT_A	Sediment	3-Moderate	Bad
CT_B	Sediment	3-Moderate	Bad
CT_C	Sediment	2-Good	Good
EF_GD	Sediment	2-Good	Bad
MG_B	Sediment	3-Moderate	Bad
MG_C	Sediment	2-Good	Good

Table 4.5 - Seawater status according to CHASE and national methodology assessment – Romania

Station	Matrix	CHASE score/status	National methodology evaluation status
MD_M	Water	5-Bad	Bad
MD_A	Water	5-Bad	Bad
MD_B	Water	5-Bad	Bad
MD_C	Water	5-Bad	Bad
CT_M	Water	5-Bad	Bad
CT_A	Water	5-Bad	Bad
CT_B	Water	5-Bad	Bad
CT_C	Water	5-Bad	Bad
EF_GD	Water	5-Bad	Bad
MG_M	Water	5-Bad	Bad
MG_A	Water	5-Bad	Good
MG_B	Water	5-Bad	Bad
MG_C	Water	5-Bad	Bad

Measurement results of the organic compounds such as PAHs, PCBs and OCPs in water and sediment matrices indicate relatively less contamination of the Turkish coastal areas under the influence of hot spot pollution sources.

In water, all pollutants' concentrations were below thresholds values except heptachlor that has a detection limit higher than the threshold value.

In sediment, p,p' DDE and p,p' DDT exceeded the threshold values in 6 %, respectively 17 % of the stations. The concentrations of the other organic compounds were below the threshold values in all stations of the study sites. Most of the heavy metals were in "bad" status as they surpassed the threshold values in 27 % to 100 % of the samples. Cadmium was the only heavy metal that had concentrations below maximum admissible levels in all samples.

The assessment made for water using national assessment shows that all stations have "good" water quality (Table 4.6). For sediments, the national assessment concluded that all stations are in "bad" status (Table 4.7).

According to the CHASE results, the assessment made for the water matrix shows that all stations are in "Moderate" status (Table 4.6) and for sediments, most stations (62 %) are in "Moderate" status and the others in "Poor" (16 %) and "Bad" (22 %) status (Table 4.7).

Table 4.6 - Seawater status according to CHASE and national methodology assessment – Turkey

Station	Matrix	CHASE status	National methodology evaluation status
SAAT01	Water	3-Moderate	Good
SAAT02	Water	3-Moderate	Good
SAAT03	Water	3-Moderate	Good
SAAT04	Water	3-Moderate	Good
SAAT06	Water	3-Moderate	Good
SLI01	Water	3-Moderate	Good
SLI04	Water	3-Moderate	Good
SLI05	Water	3-Moderate	Good
SLI06	Water	3-Moderate	Good
SN01	Water	3-Moderate	Good
SN02	Water	3-Moderate	Good
SN04	Water	3-Moderate	Good
TRKSK1	Water	3-Moderate	Good
TRKSK2	Water	3-Moderate	Good
SAAT01	Water	3-Moderate	Good

Table 4.7 - Sediment status according to CHASE and national methodology assessment – Turkey

Station	Matrix	CHASE status	National methodology evaluation status
SAAT01	Sediment	4-Poor	Bad
SAAT02	Sediment	4-Poor	Bad
SAAT03	Sediment	5-Bad	Bad
SAAT04	Sediment	4-Poor	Bad
SAAT05	Sediment	4-Poor	Bad
SAAT06	Sediment	4-Poor	Bad
SLI01	Sediment	3-Moderate	Bad
SLI02	Sediment	4-Poor	Bad
SLI03	Sediment	4-Poor	Bad
SLI04	Sediment	3-Moderate	Bad
SLI05	Sediment	3-Moderate	Bad
SLI06	Sediment	4-Poor	Bad
SN01	Sediment	5-Bad	Bad
SN02	Sediment	4-Poor	Bad
SN03	Sediment	4-Poor	Bad
SN04	Sediment	5-Bad	Bad
SN05	Sediment	5-Bad	Bad
SN06	Sediment	4-Poor	Bad

Based on these assessments, we can say that the use of the CHASE tool makes a better separation in the chemical status. National classification based on the “one-out, all-out” principle can only create two categories that may not be useful for coastal managers.

As the overall assessment, CHASE uses the ‘one-out, all-out principle’, so the global status was evaluated to “Bad” for the north-western and western part of the Black Sea, whereas the southern area was evaluated from “Moderate” to “Bad” (Figure 4.2), even if in water the evaluation concluded a better quality than in the water in the north-western and western area (Figure 4.3, Figure 4.4).

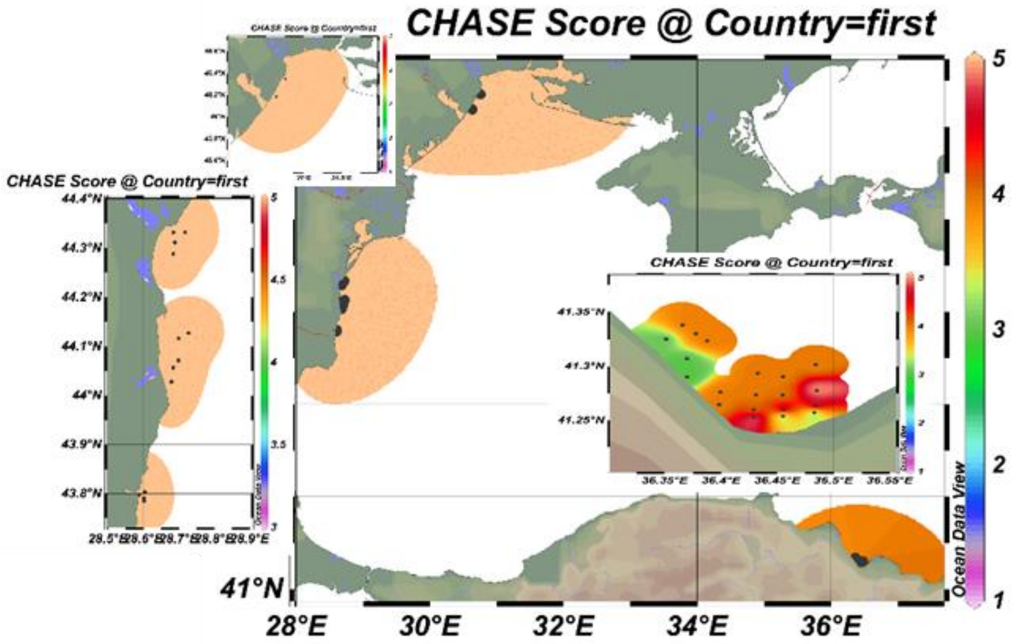


Figure 4.2 - CHASE in the areas influenced by hot spot pollution sources in the north-western, western, and southern part of the Black Sea – seawater and sediments

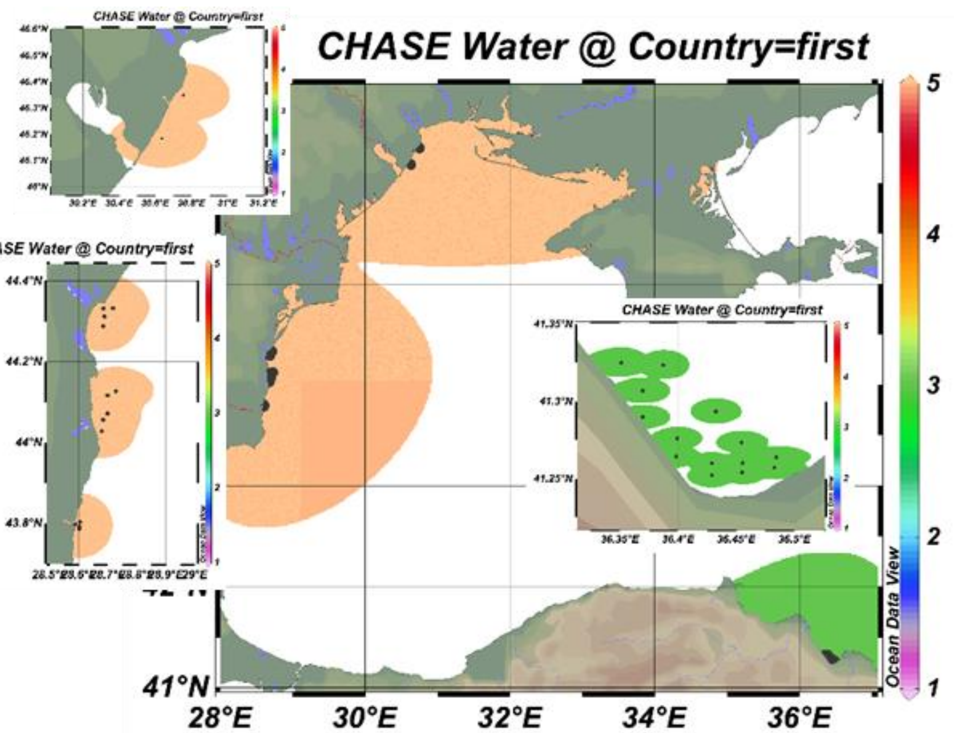


Figure 4.3 - CHASE in the areas influenced by hot spot pollution sources in the north-western, western, and southern part of the Black Sea – seawater

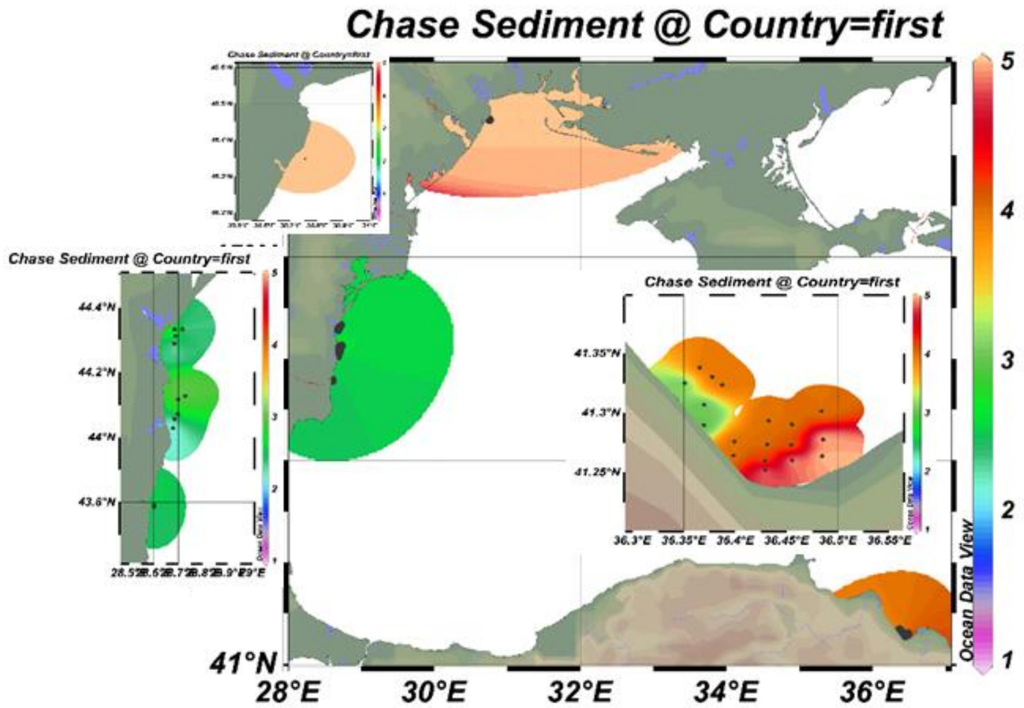


Figure 4.4 - CHASE results in the areas influenced by hot spot pollution sources in the north-western, western, and southern part of the Black Sea – sediments

The CHASE results give a warning about the general status in the assessment area: if a chemical is in bad status, you must take measures to protect the ecosystem against its effects. Still, the five quality classes allow for prioritization between different areas as some of them are more affected than others (even if we are talking about the levels of pollutants or the number of pollutants exceeding the thresholds). Any classification below good status requires adequate measures to reduce pollution.

Conclusions

The integrated assessment tools CHASE makes a clearer image of the pollution level, being more useful for the coastal managers. Even though there are many differences between areas regarding indicator substances or threshold values used in assessment, the Black Sea quality is better in the southern part where the status was mostly “poor” to “moderate” compared with the other areas, which were in “bad” status. A commonly agreed set of indicators and threshold will give a better understanding of the pressures of the Black Sea.

4.4 NEAT

Human-induced pressures on the marine environment may also affect human well-being and economic services, such as food production and nutrient cycling (Costanza et al., 1997; Pavlidou et al., 2019). Ecosystem-Based Management (EBM) framework for human activities in the marine environment, such as Marine Strategy Framework Directive (MSFD) and as adopted by the Regional Seas Conventions, provide a coherent approach for use and management of marine and coastal resources (Pavlidou et al., 2019). This policy aims to implement an integrated approach to manage pressure activities and to achieve Good Environmental Status (GES) in the marine environment.

Lately, there are few methods efficiently used to assess environmental status in an integrative way. Assessment tools such as Ocean Health Index (OHI; Halpern et al., 2012), HELCOM Eutrophication Assessment Tool (HEAT; HELCOM, 2014), Black Sea Eutrophication Assessment Tool (BEAST; Baltic2Black Project, 2010), and an innovative method, recently developed, is the Nested Environmental Status Assessment Tool (NEAT): (Borja et al., 2016).

The NEAT software is a flexible and user-friendly desktop application implementing the biodiversity assessment tool developed as an output of the DEVOTES project[4] (NEAT User Manual, Vers. 1.4). The used method is hierarchical consisting of a nested structure of spatial assessment units and habitats. It runs several steps to make an ecosystem-based assessment. These are:

- The order of these hierarchies is such that the assessment begins with the nested SAUs. (e.g. a regional sea or an individual bay)
- Assign habitats and ecosystem components that are associated with indicators.
- Select indicators. Each indicator requires a bad, high and a target value. Also, reference values should be entered in five quality classes (high, good, moderate, poor and bad).
- Weighting procedure can be applied to ensure no individual branch (SAUs, habitats, etc.) dominates the quality of the others
- NEAT value is the weighted average of all indicators belonging to a specific group with an uncertainty propagation

In this study, we have applied NEAT to coastal areas for assessing the environmental status of five Black Sea spatial assessment units (SAU) (Figure 4.5) and test the tool's performance. Coastal areas were identified as spatial units of 0-30 m depth interval by Romania, Bulgaria and Ukraine whereas it was identified as 0 – 40 m by Turkey.

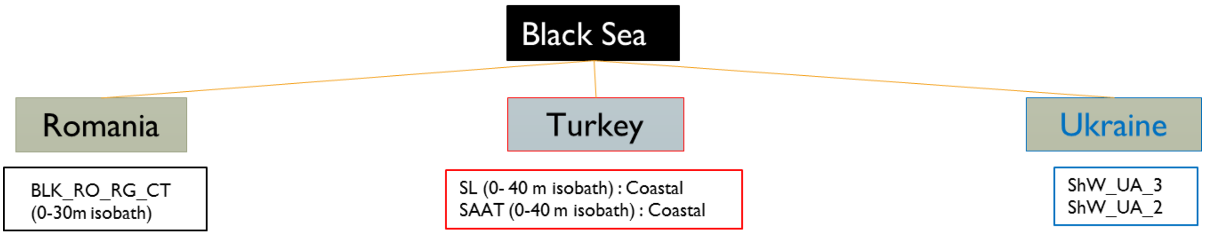


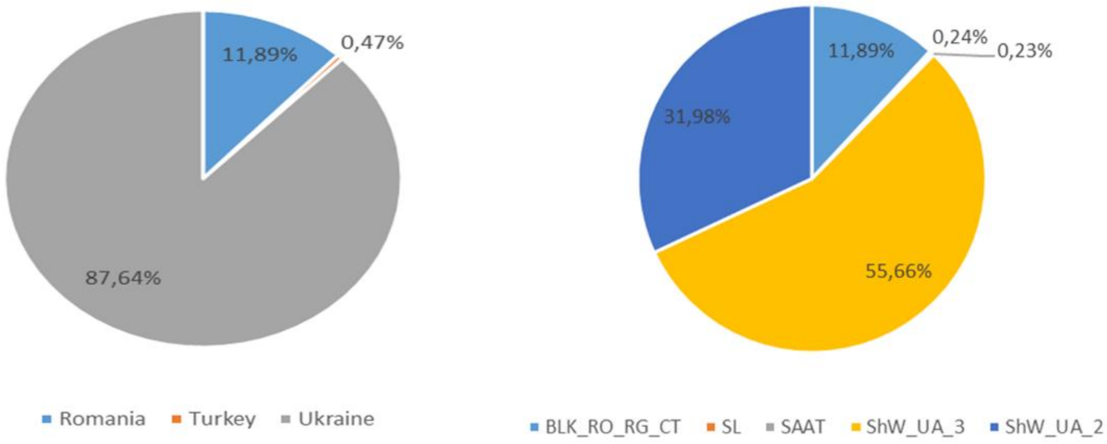
Figure 4.5 - Spatial Assessment Units identified by Romania, Turkey and Ukraine

Spatial units of Ukraine were the largest having 88 % of all, others shared the rest 12 %. Turkish SAUs were the smallest having both coastal environment (Table 4.8, Figure 4.6).

Table 4.8 - Areal distribution of SAUs of RO, TR, UA assigned in ANEMONE

Spatial Assessment Unit (SAU)	Area (km^2)
BLK_RO_RG_CT (0-30m isobath)	1041.00
SL (0- 40 m isobath) : Coastal	20.47
SAAT (0-40 m isobath) : Coastal	19.52
ShW_UA_3	4871.00
ShW_UA_2	2799.00

[4] http://www.devotes-project.eu



(a) *(b)*

Figure 4.6 - Coastal SAU distributions (%) (a) by country, (b) by area.

In the NEAT software, after the identification of SAUs and the assignment of their related habitats and ecosystem elements, indicators have to be selected. In this respect, three major habitats; rocky and sedimentary for benthic habitats and pelagic habitats were included in the ANEMONE's NEAT test. Rocky habitats were split into two groups whereas sedimentary had six sub-groups. Ecosystem components were defined in five major groups; benthos and contaminants as the major components were grouped in three sub-classification (Figure 4.7).

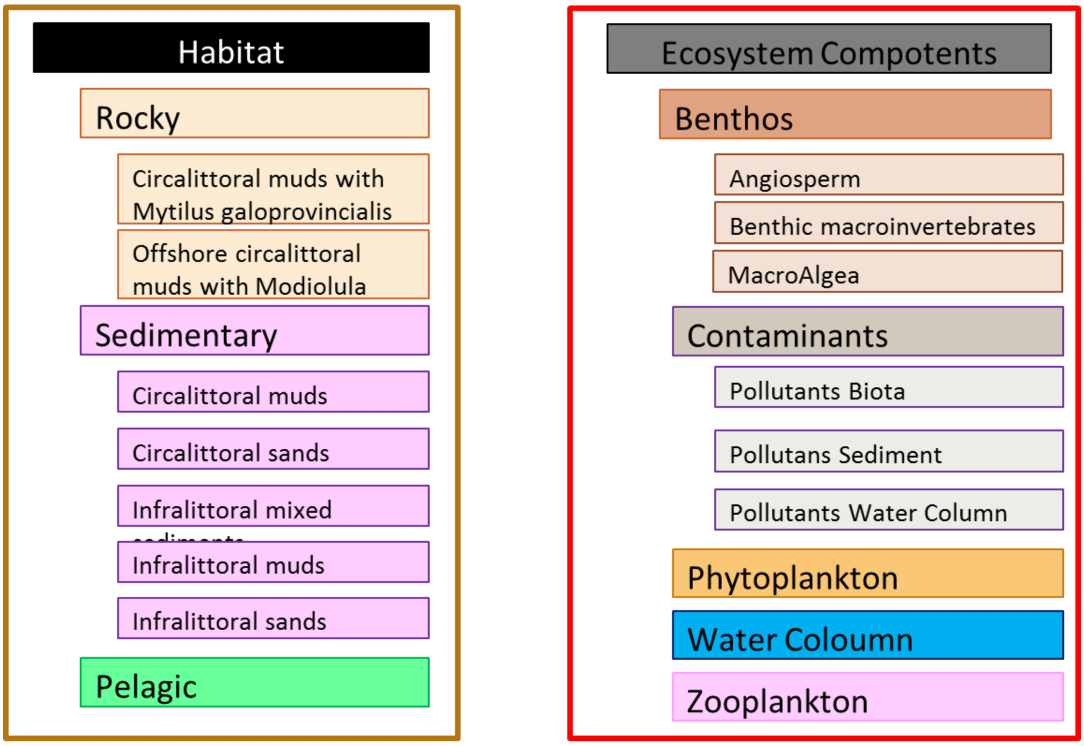


Figure 4.7 - Major and sub-grouping of habitats and ecosystem components used in ANEMONE's NEAT test

Figure 4.8 shows a possible set of indicators (as measured variables or calculated values and indices) referred by each country, including sampling periods and ecosystem components. While putting the identified indicators into the NEAT software it is also necessary to put boundary values of high, moderate and bad status for each.

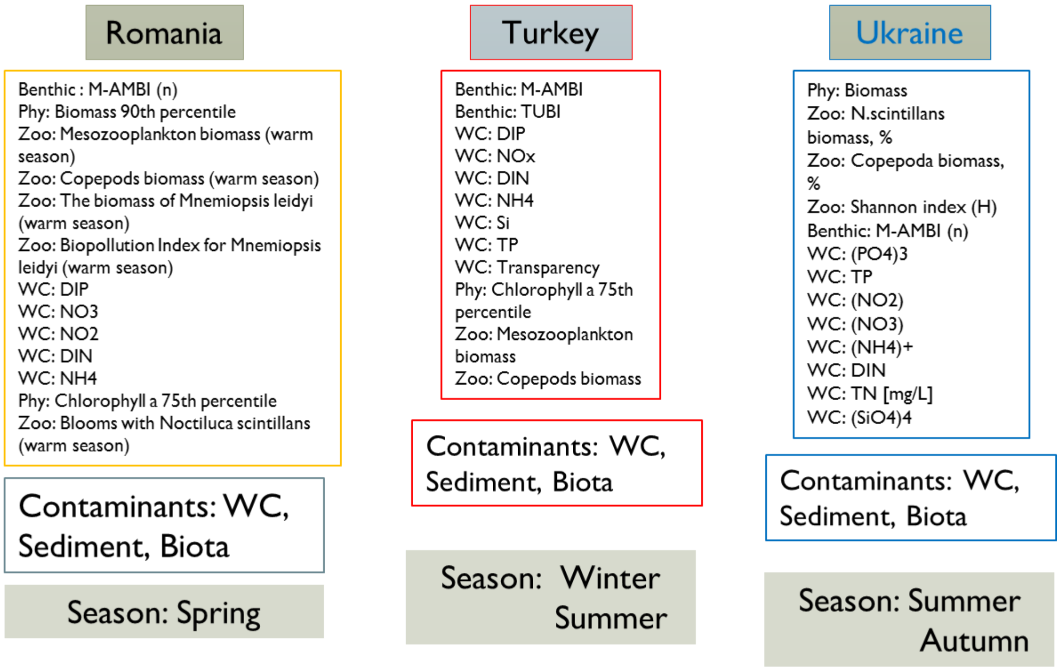


Figure 4.8 - Measured variables/assigned indicators, sampling periods and ecosystem components referred by each country (Phy: Phytoplankton, Zoo: Zooplankton, WC: Water Column)

The NEAT final assessment is done in 5-classes as presented in Table 4.9 (Torsten et al., 2019). In the final assessment, it is possible to choose a weighted/not-weighted approach for different scales of SAUs or even independent of the SAU size, to include different MSFD GES descriptors and the required habitat types (Torsten et al., 2019).

Table 4.9 - NEAT Classification scale

Boundary values	Colour code
0.8-1.0	High
0.6-0.8	Good
0.4-0.6	Moderate
0.2-0.4	Poor
0.0-0.2	Bad

In this study, all parameters' data for all season's scenario was tested. If it was required to work only with common parameters, it would ultimately be a eutrophication assessment which was not aimed in the scope of this study.

NEAT analysis was performed both with weighted and not-weighted approaches for SAUs. Mostly the results were obtained as good/high in both scenario (Table 4.10 - Table 4.11) where there were no distinct differences in the NEAT values. This might be mainly related to the good/high results obtained for all components of the contaminants.

When the analysis is only focused on eutrophication indicators, then the status of SAUs of Turkey and Ukraine declines to "moderate". However, the overall NEAT score was still good since no matter weighted or not weighted by SAUs. This is because Ukraine's SAUs area is much bigger than the others (Table 4.8).

Table 4.10 - NEAT results of all indicators & all sampling period with weighting according to SAUs

SAU	NEAT value	Confidence	WC	Phyto	Zoo	Pollutant WC	Pollutants Sed.	Pollutants Biota	MacroAlgea	Anigosperm	Benthic macroinvertebrates
DT2.1_Coastal_BS	0.770	100	0.834	0.504	0.904	0.812	0.693	0.742	0.450	0.647	0.674
Romania	0.698	100	0.352	0.502	0.848	0.724	0.825	0.864	0.464	0.647	0.709
BLK_RO_RG_CT	0.698	100	0.352	0.502	0.848	0.724	0.825	0.864	0.464	0.647	0.709
Turkey	0.692	100	0.745	0.560	0.602	0.945	0.798		0.255		0.480
SL	0.754	100	0.825	0.633	0.653	0.979	0.799		0.496		0.513
SAAT	0.626	91,3	0.658	0.482	0.546	0.911	0.797		0.001		0.446
Ukraine	0.780	100	0.858		0.923	0.823	0.684	0.724			0.629
ShW_UA_3	0.718	100	0.720		0.923	0.852	0.541	0.724			0.629
ShW_UA_2	0.888	63,4	0.921			0.771	1000				

Table 4.11 - NEAT results of all indicators & all sampling period with no weighted approach.

SAU	NEAT value	Confidence	WC	Phyto	Zoo	Pollutant WC	Pollutants Sed.	Pollutants Biota	MacroAlgea	Anigosperm	Benthic macroinvertebrates
DT2.1_Coastal_BS	0.730	100	0.751	0.533	0.791	0.812	0.780	0.806	0.325	0.647	0.580
Romania	0.698	100	0.352	0.502	0.848	0.724	0.825	0.864	0.464	0.647	0.709
BLK_RO_RG_CT	0.698	100	0.352	0.502	0.848	0.724	0.825	0.864	0.464	0.647	0.709
Turkey	0.690	100	0.743	0.558	0.600	0.944	0.798		0.249		0.479
SL	0.754	100	0.825	0.633	0.653	0.979	0.799		0.496		0.513
SAAT	0.626	91,4	0.658	0.482	0.546	0.911	0.797		0.001		0.446
Ukraine	0.803	89,3	0.879		0.923	0.812	0.743	0.724			0.629
ShW_UA_3	0.718	100	0.720		0.923	0.852	0.541	0.724			0.629
ShW_UA_2	0.888	63	0.921			0.771	1000				

In this study, two scenarios were tested. The final assessment results of NEAT for two scenarios are given in Table 4.12. The NEAT results showed that if one area is much larger than the others, the larger areas' parameters are weighted more to the final results. In addition, when some of the selected indicators are in good and very good status, it raises NEAT results to a higher quality class than they should be. Thus, these effects were hidden from the true NEAT results.

Table 4.12 - Assessment of both scenario

SAU	WSAU	DNWSAU
	S1	S1
DT2.1_Coastal_BS	0.770	0.730
Romania	0.698	0.698
BLK_RO_RG_CT	0.698	0.698
Turkey	0.692	0.690
SL	0.754	0.754
SAAT	0.626	0.626
Ukraine	0.780	0.803
ShW_UA_3	0.718	0.718
ShW_UA_2	0.888	0.888

The existing practice showed us that NEAT is a strong ecosystem assessment tool. However, the assessment units, habitats and indicators including the sampling seasons need to be designed from the beginning for more reliable NEAT results. For example, the SAUs could be comparable in the area (km^2) and the same indicators even with a larger number could be used for the same periods. It could also be suggested that, especially for the large assessment units, a pressure analysis can be made and sub-assessment units might be identified.

5 Conclusions

The monitoring and assessment of the sea and its coast, and their interactions, based on scientific knowledge, is the indispensable basis for the management of human activities, for promoting their sustainable use and conserving the marine ecosystems. As part of the ANEMONE's aims, we brought in this deliverable through collaborative efforts among partners, the results of common monitoring of the land-based sources of pollution, so-called "Hot Spots".

We took into account the existing regional (BSIMAP) and national monitoring programs, the best practices of other Regional Sea Conventions, and last, but not least, the Marine Strategy Framework Directive (MSFD) principles, aiming to contribute to the harmonization of methodologies and filling of knowledge gaps identified in the region. We collected quality controlled and comparable data sets for the Black Sea environmental status assessment, via conducting case studies in selected study areas for the response of coastal ecosystems under the influence of human pressures

Data and information gathered in this study contribute to the improvement and upgrading of the existing Black Sea database, and a better understanding of the human-induced changes.

The case studies contribute also to enhance the cross-border contacts within the Black Sea Basin scientists to enhance knowledge and skills by using new tools for the integrated assessments; to exchange experience, good practices and harmonized methodologies.

Generally, through monitoring and integrated assessment tools, we found local but very significant pressures, as the introduction of non-indigenous species, nutrients and contaminants. The impact was observed in both pelagic and benthic habitats.
Thus, the highest phytoplankton diversity was found in the less polluted areas, while some of the dominant species, with maximum development in the central part of harbours, are listed as harmful in IOC-UNESCO Taxonomic Reference List of Harmful Micro Algae (Moestrup et al., 2009) or are recorded as eutrophication indicators (Dorgham et al., 1987).
The study has emphasised the presence of 7 species of tintinnids newly introduced in the Black Sea basin and the tendency to enrich the microzooplankton component from the last decades with new non-indigene species.

Mitigating negative port impacts is essential for the long-term survival of ports and port cities. Even if ports generate large local economic benefits, building on competitive strengths in services, industrial development or consumer-driven port-related waterfront development, they will not have sustainable future perspectives if they do not mitigate negative impacts related to their development. These negative impacts can be considerable, as illustrated in this deliverable, and can relate to the environmental impacts – such as pollution of air, water and soil – land use, traffic congestion and risks related to climate change and security.

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7 ANNEXES

ANNEX A CRUISES – STUDIED AREAS

Ukraine

To assess the anthropogenic impact on the Black Sea in the areas of influence of "Hot Spots", water and bottom sediment samples were taken on the traverse of discharges from the wastewater treatment plants (WWTP) of the city of Odessa (WWTP "South"), the city and port of Chernomorsk (Figure 7.1, stations 4 and 5, and Table 7.1).

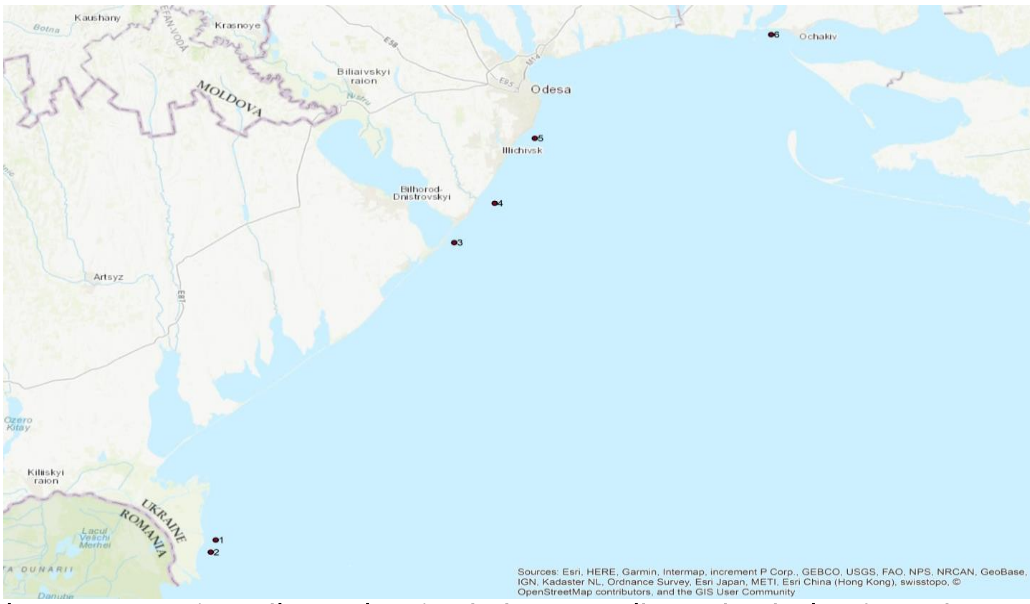

Figure 7.1- Map of sampling stations for the hot-spots pilot study, Ukraine, September 2019

Table 7.1- "Hot Spots" sampling stations coordinates

Station	Station position	Bottom Depth (m)	Longitude	Latitude
ST 4	Place of discharge from WWTP city and port Chernomorsk	10.0	30.6347	46.1846
ST5	Place of discharge from WWTP Odessa "South"	18.5	30.7548	46.3493

Romania

The study areas were as follows: Midia, Constanta and Mangalia harbour basins (stations MD_A, CT_A and MG_A) and surrounding area, and the marine area in front of the Eforie South WWTP discharge (Figure 7.2).

- 3 were established as control stations being disposed of the north of the three harbours (Midia M, Constanta M and Mangalia M),
- 3 stations were disposed of within the harbours (Midia A, Constanta A, Mangalia A)
- 6 stations were disposed south of the harbours, outside their basins (Midia B, C; Constanța B, C și Mangalia B, C),
- 1 station at the end of the wastewater discharge pipeline from Eforie. For the Eforie station, the Constanta C station will be considered as control.

A total of 30 samples have been collected from the surface with a bucket. Samples from different depths (5-24 m) were collected with 5 L Nansen bottles. The sampling depths were selected according to the CTD profile and the in-situ readings: surface, temperature/salinity gradient (thermocline) and 1 m above the station depth.

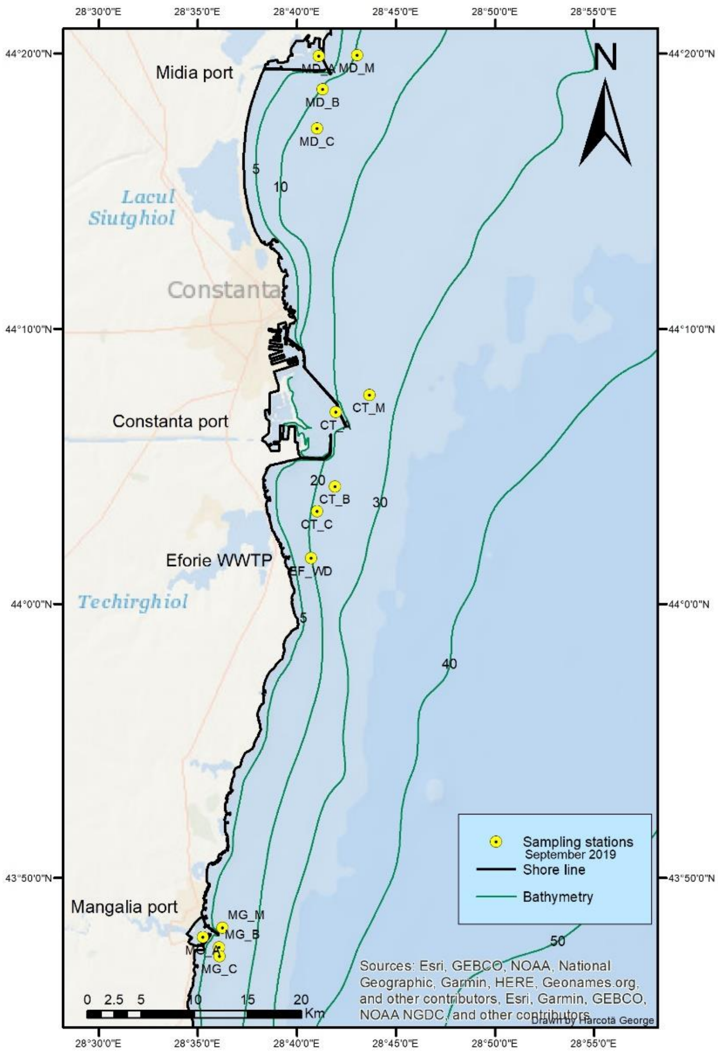

Figure 7.2 - Map of sampling stations for hot-spots pilot study, Romania, September 2019

Table 7.2 - Sampling stations for hot-spots pilot study, Romania, September 2019

Station	Code	Longitude	Latitude	Station Depth (m)	Sample Depth (m)
Midia Control	MD_M	28.7174	44.3326	8	0
Midia St. A (Harbour)	MD_A	28.6849	44.3320	7	0, 6
Midia St. B	MD_B	28.6884	44.3118	6	0, 5
Midia St. C	MD_C	28.6837	44.2882	8.5	0, 8
Constanta Control	CT_M	28.7276	44.1270	25	0, 10, 24
Constanta St. A (Harbour)	CT_A	28.6993	44.1165	20	0, 10, 19
Constanta St. B	CT_B	28.6988	44.0714	21	0, 10, 20
Constanta St. C	CT_C/EF_M	28.6837	44.0563	21	0, 10, 20
Gura deversare Eforie	EF_WD	28.6786	44.0279	22	0, 10, 21
Mangalia Control	MG_M	28.6039	43.8032	7.5	0, 7
Mangalia St. A (Harbour)	MG_A	28.5876	43.7974	6	0, 5
Mangalia St. B	MG_B	28.6011	43.7911	7	0, 6
Mangalia St. C	MG_C	28.6015	43.7858	8	0, 7

Turkey

The national expedition activities were conducted in July 2019 and January 2020 onboard R/V *TÜBİTAK Marmara*. The positions of the stations discussed in this study are shown in Figure 7.3. Seawater sampling was carried out in both periods, while sediment sampling was performed only in July 2019.

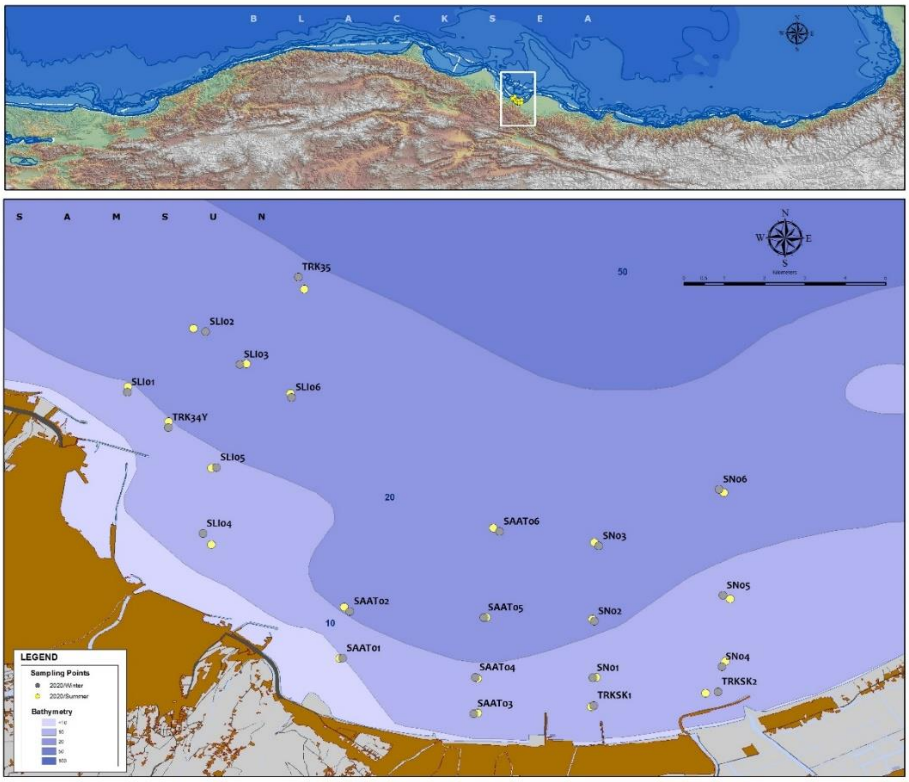

Figure 7.3 - Map of sampling stations for Samsun port and WWTP (Hot Spot), July 2019 and January 2020

Table 7.3 - Coordinates and sampling depths of stations in Samsun port-WWTP sampling stations in July 2019 and January 2020

Station code	Longitude	Latitude	Sampling depth (m)
SN01	36.4554	41.2598	18
SN02	36.4556	41.2729	20
SN03	36.4553	41.2902	18
SLI05	36.3691	41.3071	14
SLI06	36.3880	41.3246	16

ANNEX B METHODS

Biology

Phytoplankton

Ukraine

Phytoplankton samples were collected using 5L Niskis bottles, attached to CTD rosette system. Each sample consisted of 1-2 L of water, fixed with 40 % buffered formaldehyde up to the final concentration of 2 % in a sample and carried to the laboratory. Then phytoplankton cells were allowed to settle for 2 weeks and after that, the samples were slowly decanted to 30–40 ml.

Identification of species and counting of cells was carried out under a light microscope LOMO (Russia) with magnifications of 600x in the drop with the volume of 0.05 ml. The wet biomass was calculated by the method of geometric similarity, equating shapes of cells to corresponding geometrical shapes and assuming that the cell density is equal to 1.

For species identification there were used the appropriate key-books: Schiller (1937), Kiselew (1950), Proshkina-Lavrenko (1955), Tsarenko (1990), Carmelo (1997), Steidinger and Tangen (1997), Cronberg and Annadotter (2006), Krakhmalny (2011), and the taxonomic nomenclature is according to the on-line database of World Register of Marine Species (WORMS).

Romania

Taxonomic composition and cell counts were done under inverted microscope connected to a video-interactive image analysis system at 400x magnification by the Utermöhl (1958) method and counting chambers (Utermöhl chambers). The individual cell biovolume (V, μm^3) was derived by measurements through the approximation of the cell shape of each species to the most similar regular solid, calculated by the respective formulas used routinely in the lab. Cell biovolume was converted to weight (W, ng) following Hatchinson (1967).

Species identification was mainly after Schiller (1937), Kisselew (1950), Proshkina-Lavrenko (1955), Carmelo (1997), Fukuyo (2000) and the taxonomic nomenclature according to the on-line database of World Register of Marine Species (WoRMS). Each harbour was described based on the qualitative and quantitative analysis of the phytoplankton. Then, the Stations outside harbours (B and C) were compared with the Stations inside harbours (A) and with the Control Station. The shade plots were performed in PRIMER 7 (Clarke et al., 2014) for the visual representation of the dominant species which contributed with over 2% in minimum one station.

Turkey

A total of 53 samples have been collected during July 2019 and January 2020 periods along 13 stations distributed over the river impact and hotspot (Sakarya River, Yeşilırmak River and Samsun Port) areas.

Samples were collected by 5l Teflon Niskin bottles attached to CTD - SBE 25 - Rosette System equipped with in situ fluorometer (Chelsea Minitraca). The sampling depths were selected according to the CTD profile and the in situ fluorometer readings: surface, temperature/salinity gradient (thermocline), fluorescence max (deep sea chlorophyll) and 1 m above the station depth. Lugol (2ml/L) was used for fixation of water samples.

A Sedwick-Rafter counting chamber was used for phytoplankton species. Cell numbers were counted under Zeiss Axiovert A1 inverted microscope at various magnifications. For estimation of biomass, the diameter, length and width of each cell was measured under a microscope equipped with Zeiss automatic computer system.

Zooplankton

Ukraine

Zooplankton was collected with Juday plankton net (0.1 m2 opening, 150 µm mesh size). In the shallow area samples were taken from the bottom to the surface and in deeper places, samples were collected from the upper mixed layer, thermocline layer and under the thermocline. Zooplankton samples were preserved using 4% formaldehyde buffered to pH 8-8.2 with borax ($Na_2B_4O_3 \cdot 10\ H_2O$) formalin solution (1 part 40 % formaldehyde solution and 9 parts water - sample) and stored in plastic containers. In the laboratory, the samples were concentrated to 100-200 ml and processed samples according to standard methodology (Alexandrov, 2016). A Bogorov's chamber was used for quantitative assessment (abundance and biomass calculation, using species individual weight) and qualitative (taxonomic structure) processing of samples. For species identification there were used the appropriate key-books: Mordukhai – Boltovskoy (1968), Mordukhai – Boltovskoy (1969), Mordukhai – Boltovskoy (1972), Murina V.V. (2005), Alekseeva V.R., Tsalokhina S.Ya. (2010), and the taxonomic nomenclature is according to the online database of the World Register of Marine Species (WORMS). The biomass was calculated according to standard weights and according to the allometric equation of length (Alimov, 1989).

Romania

To analyze the microzooplankton component, particularly the loricate ciliate community, the samples were taken from the 0 m and 10 m layers from the Southern area of the Romanian Black Sea coast (Mangalia, Eforie, Constanta and Midia profile). Samples were collected in 500 ml labelled plastic containers, from Niskin bottles and preserved with formalin 4%. In the laboratory, the samples were concentrated to a final volume of 10 ml by repeated sedimentation. The final volume was analyzed by the inverted microscope (Olympus XI 51) with magnification factors of 200× and 400×. The taxonomic identification of tintinnids was made according to the shape and dimensions of the lorica, indicated by literature. For qualitative and quantitative analysis, both empty tintinnids and those with protoplasm were considered because mechanical and chemical disturbances associated with collection and fixation procedures have been demonstrated to cause cell detachment (Thompson & Alder, 2005). The density of organisms was expressed as individual species/litre (ind/L). The lorica volume was calculated according to the total length and aboral diameter of the lorica, and to the geometric form assumed for each species, respectively. Biomass was expressed as carbon biomass (µgC/L) using the specific biovolume conversion formula for formalin conserved biological material (Verity & Langdon, 1984).

We collected 13 mesozooplankton samples from the port areas of the Romanian Black Sea coast in September 2019. Collecting of mesozooplankton samples was performed using a Juday net (0.1 m^2 mouth opening area, 150 µm mesh size) by vertical hauls. The samples were stored in 500 ml plastic jars and preserved with 4 % buffered formaldehyde solution and were further analysed under the binocular magnifying glass.

According to the methodology, the sample was homogenised, and quantitative and qualitative processing was performed in the Bogorov chamber. In the subsample(s) all plankters were counted until each of the three dominant taxonomic groups reached 100 individuals. For estimation of large animals' numbers, the whole sample was observed. All species were identified taxonomically to the species level except for the meroplankton larvae. The number of individuals and mean individual weights were used for estimating the density as ind./$m^{3,}$ respectively the biomasses as mg/m^3 wet weight (Alexandrov et al., 2011).

Turkey

The sampling of zooplankton was carried out in July 2019 and January 2020 at five stations in Samsun port-WWTP sampling stations. Zooplankton samples were collected vertically tows using UNESCO WP2 net (mesh size: 200 µm, mouth diameter: 57 cm) from bottom to surface. After collection, the zooplankton samples were immediately fixed in a 4% formalin-seawater solution for quantitative and qualitative taxonomic analyses. In the laboratory, two subsamples were taken from a container of known volume using a Stempel pipette (1 ml). Samples were analysed under a stereomicroscope with a zooplankton counting apparatus. Finally, the whole sample was examined for rare organisms and large organisms which were counted and recorded (Postel et al. 2000). The biomass transformations were based on individual wet weights according to Petipa (1957) and Niermann et al. (1995). The abundance and biomass results were given in ind./m^3 and mg/m^3, respectively. The mean abundance and biomass of the species/groups of mesozooplankton are presented as mean ± standard error of the mean (SE). Taxa of Cladocera, Copepoda, Appendicularia and Chaetognatha were identified at the species level. All other taxa were identified to the phylum, class, or order levels. The main references used to identify the major zooplanktonic groups were Bradford-Grieve et al. (1999) and Conway et al. (2003). Systematic classification and the nomenclature of zooplankton species was done according to WoRMS (2020).

To interpret the mesozooplankton quantitative data, the Shannon–Weaver diversity index (H′) and the number of species were applied to the species abundance data using PRIMER 5 software.

Zoobenthos

Ukraine

Assessment of macrozoobenthic communities on the North-western part of the Black Sea (Ukrainian part) was done based on eight samples (total 14 subsamples) taken on one station (St 5 – in front of the WWTP Odessa "South"). The macrozoobenthos sampling followed the protocol described in Todorova & Konsulova, 2005. Thus, all samples have been collected with an "Ocean" Van Veen grab and square frames, washed through a 0.5 mm mesh size sieve, fixed with formaldehyde 4% buffered with seawater, and finally stored in plastic jars. In the laboratory, the organisms were identified to the lowest possible taxonomic level.

The ecological state of a particular station was assessed using M-AMBI*(n), a combined biotic index including diversity (H'), species richness (S), and AMBI (proportion of opportunistic to sensitive taxa), into a multivariate approach (Muxika et al., 2007). The ecological classes' boundaries were those given by Borja et al. (2007).

The assessment of benthic habitats' condition is one of the evaluation criteria both in the WFD (as the biological quality element) and in the MSFD descriptors (Benthic Habitat - D1, D4, D6). For describing the structure and functional conditions of the macrozoobenthos community under D4, the following classification of organisms was used (Macdonald et al. 2010). This classification includes the type of 1) Food source collecting type (EPibenthic, SUrface, SS-subsurface) and 2) Feed Mode (Deposit feeder (ingests sediment; De), Detritus feeder (ingests particular matter only, without sediment; Dt), Suspension/Filter feeder (strains particles from the water, Su), Predator (eats live animals only; Pr), Scavenger (carrion only; Sc), Suctorial parasite (Sp), Chemosynthetic (with symbiotic bacteria, Ch), Lignivorous (eats wood, Li), Grazer (feeds by scraping, either on algae or sessile animals, Gr), and Browsing (feeds by tearing or gathering particular items, Br)), 3) Food size (Macdonald et al. 2010)

For calculation of AMBI and m-AMBI*(n), we used the freeware software available on www.azti.es, for structural indexes (S, iChao1, H', IMg), PAST 3.14, and MS Excel.

Romania

Ecological assessments of the macrozoobenthic associations were done based on 34 samples taken from 13 stations. All macrozoobenthos samples were collected using a Van Veen grab with a surface of 0.1 m^2. At each station, three replicates were collected, except for Mangalia B (1 sample) and Mangalia Martor (no sample). Despite the effort made to take three replicates, in these two stations was impossible due to the hard substrate.

A pre-washing of the samples through 0.5 mm mesh size sieves for sediments excess removal was performed onboard (Figure 7.4). A macro-visual description of each sample was done before preserving. The preservation was done with formaldehyde 4% buffered with seawater and the samples were stored in labelled plastic containers until their subsequent examination in the laboratory. After sieving through 1mm and 0.5 mm mesh sieve, in the laboratory, all organisms were identified to the lowest possible taxonomic level.

Figure 7.4 - Benthos samples collected from Midia Harbour

Turkey

Macrozoobenthos sampling was performed at 4 stations (Table 7.3) in July 2019 and January 2020 in front of Samsun Port and Wastewater Treatment Plant to determine macrozoobenthic species diversity and their abundance and ecological quality of the area. Soft-bottom samples were collected by a Van Veen Grab (sampling an area of 0.1 m^2) with three replicates. Benthic samples were sieved with a 0.5 mm mesh and the retained fauna were put in jars containing 4% seawater–formalin solution. The samples brought to the laboratory were washed through 1 mm and 0.5 mm sieve mesh sizes (Figure 7.5). The material obtained was examined under a stereo binocular dissecting microscope and zoobenthic organisms were sorted into higher systematic groups. These samples were delivered to the concerned specialists for taxonomic identifications.

Figure 7.5 - Wet sieving and sorting of benthic samples in the laboratory

Chemistry - Water

Ukraine

Analytical methods for trace metals

Surface water samples collected for metals analysis were filtered through the membrane with pore size 0.45 µm. Metals dissolved have been determined in seawater samples, acidified up to pH=2 with Ultrapure HNO_3.

Instrumental analysis and quantification: metals were analysed by electrothermal furnace atomic absorption spectrometry (AAS-ET Analytik Jena AG ZEENIT 650P). The concentration of metals calibration was performed with working standards for each element, starting from stock solutions of 1000 µg/L (Sigma-Aldrich). At least 3 instrumental readings have been performed for each sample, with an average value reported. The work domains are as follows: water Cd 0-1 µg/L; other metals 0-40 µg/L; sediment Cd 0-2 µg/L; other metals 0-80 µg/L.

Analytical methods for organic pollutants

Water samples were taken from the surface layer (0.01 m below the surface) from 10 L Niskin bottles of the Rosette system. For the determination of organic pollutants, 5 L of seawater were poured into a polypropylene tank, which was sent to the laboratory for analysis. Internal standards PCB29 and Phenanthrene-d10 were added to the water sample before extraction. Extraction was carried out with hexane using a high-speed stirrer; the organic phase was separated from water in a separatory funnel. The extraction was followed by concentration in a turbo evaporator under nitrogen flow.

The concentration of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) was determined on gas chromatograph 7890B (Agilent, USA) with electron capture detector (15 millicuries of nickel 63 G2397A ECD) equipped with splitless injector and capillary column HP-5 (30 m 0.32mm 0.25 µm). The carrier gas was helium at a flow rate of 2 ml/min, ECD gas was nitrogen at a flow rate of 30 ml/min.

The concentration of PAHs was determined by gas chromatography-mass spectrometry on gas chromatograph 7890A (Agilent, USA) with mass-detector 5975C equipped with PTV injection and capillary column DB-5MS (30 m 0.25mm 0.25 µm). The carrier gas was helium at a flow rate of 1.2 ml/min. Injector starting temperature was 50 ^{0}C, ventilation of the solvent during 1 minute, the volume of the sample was 15 µL, the final temperature of injector was 300 ^{0}C, rate of temperature elevation was 600 ^{0}C; onset temperature of the incinerator was 60 ^{0}C, hold up time 7 minutes, temperature rise to 200 ^{0}C at the rate of 10 ^{0}C/min, hold on during 1 minute, temperature rise to

310 ^{0}C at the rate of 7 ^{0}C/min, hold on during 5 minutes. The mass detector in the mode SIM (search for target weight), temperature MS Source 230 ^{0}C, MS Quad 150 ^{0}C. Analytical standards of naphthalene, anthracene, fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, benzo(b)fluoranthene, phenanthrene, benzo(a)anthracene, chrysene, fluorene, acenaphthene, pyrene (Supelco, USA), indeno(1,2,3cd)pyrene and dibenzo(a,h)anthracene (ULTRA Scientific, USA) were used for calibration. ChemStation (Agilent, USA) and AMDIS software were used for data analysis.

Romania

Water samples were collected from the surface layer (1 m below the surface) from the 5 L Niskin bottles of the Rosette System. Nutrients were quantified by spectrophotometric analytical methods validated into the laboratory and having reference manual "Methods of Seawater Analysis" (Grasshoff, 1999) with the following detection limits and extended relative uncertainties, coverage factor, 95.45%:

Parameter	Unit	Limit of detection (µM)	Extended relative uncertainty, U(c), k=2, coverage factor 95.45%
$(NO_3)^-$	µM	0.12	c x 0.08 µM
$(NO_2)^-$	µM	0.03	c x 0.06 µM
$(NH_4)^+$	µM	0.12	c x 0.10 µM
$(PO_4)^{-3}$	µM	0.01	c x 0.12 µM

It was used a Shimadzu UV-VIS spectrophotometer, 0-1000 nm. Salinity was measured with CTD and dissolved oxygen using the Winkler method.

Total metals (dissolved and acid-soluble suspended forms) have been determined in unfiltered seawater samples, acidified up to pH=2 with Ultrapure HNO_3. Metals were analysed by graphite furnace – atomic absorption spectrometry (GF – AAS).

Water samples for organic pollutants were collected from the surface layer (1 m below the surface) from the 5 L Niskin bottles of the Rosette System. About 1 L of seawater was transferred into glass bottles, which were stored at refrigerator temperature until their subsequent analysis in the laboratory. After extraction with hexane/dichloromethane (3/1) mixture in separating funnel, purification on florisil column for organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), respectively silica/alumina column for polyaromatic hydrocarbons (PAHs,) concentration using the Kuderna-Denish concentrator and nitrogen flow, samples were analysed by gas chromatography. GC-ECD method was used for OCPs and PCBs and GC-MS method for PAHs. The total petroleum hydrocarbons (TPHs) were analysed by the fluorescence method.

Turkey

The water samples for metal analysis were collected from the surface layer (1 m below the surface) from the 5 L Niskin bottles of the Rosette System. The collected samples were stored in plastic bottles (250 mL). Total metals (dissolved and acid-soluble suspended forms) have been determined in unfiltered seawater samples, acidified up to pH=2 with Ultrapure HNO_3. The analytical determination of the trace elements (such as copper, cadmium, lead, nickel, and chromium) was carried out by inductively Coupled Plasma Mass Spectroscopy (ICP-MS) (Perkin Elmer- Neixon300x model).

Seawater samples taken for PAH, PCB and pesticide were extracted on board with twister using methanol and internal standard (stir bar sorptive extraction method). Before extraction, each water sample (100 mL) was filtered through a glass fibre filter (1.2 µm). The sample was then placed in an Erlenmeyer flask which had been rinsed prior to use with Milli-Q water and methanol and then dried in an oven at 110 °C. Next, 10 mL of methanol was added to prevent the adhesion of compounds to the Erlenmeyer flask glass wall. Before use, all Twisters were conditioned overnight at 280 °C in a thermal desorption system (TDS) using a Gerstel Tube Conditioner with 200 mL/min nitrogen flow. A 100 µL aliquot of internal standard mixture was added to all prepared flasks. For sample extraction, a Twister with dimensions of 1.0 mm (thickness) × 20 mm (length) was used. The sample was stirred at 850 rpm for 2 h with the Gerstel stirrer at room temperature. After the extraction was completed and stored in the refrigerator. Twister bars were taken from the glassware, rinsed with Milli-Q water, dried with lint-free paper and inserted into thermal desorption unit (TDU) liners for GC injection. Calibration injection sets were prepared in the same manner as the sample extraction procedure. An Agilent 7890B gas-chromatograph coupled with a 7000D triple quadrupole detector was used. The system was equipped with a CIS-4 Cooled Injection System with a programmable temperature vaporizing inlet (PTV), on a Thermal Desorption Unit (TDU), and autosampler (MultiPurpose Sampler -MPS) to introduce Twister bars into the system. The triple quadrupole was operated in electron ionization (EI) mode, 300 °C temperature ion source, 150 °C for both quadrupoles, with acquisition mode set to dMRM (dynamic multiple reaction monitoring). An HP-5ms UI 30 m× 0.25 mm× 0.25 μm) column was used as the analytical column, and a 0.7m× 0.25mm column was used as the backflush column. TDU / GC-MSMS method was used for OCPs and PCBs and PAHs.

The seawater sample for TPH was extracted with hexane on board. The extract was stored in the refrigerator. The total petroleum hydrocarbons (TPHs) were analysed by the fluorescence method.

Chemistry - Sediments

Ukraine

Analytical methods for trace metals

Sediment samples were collected using a Van Veen boden-greifer, freeze-dried, homogenized. Further processing of samples consisted of treatment with ultrapure acids HNO_3, HCl, after which HF was added. Instrumental analysis and quantification: metals were analyzed by electrothermal furnace atomic absorption spectrometry (AAS-ET Analytik Jena AG ZEENIT 650P).

Analytical methods for organic pollutants

Sediment samples were collected using a Van Veen boden-greifer, freeze-dried, homogenized. For organic pollutants, extraction was carried out on an accelerated pressure extraction unit (PLE) with a hexane/dichloromethane/methanol mixture (60 % / 20 % / 20 %). Internal standards PCB29 and Phenanthrene-d10 were added to the bottom sediment sample before extraction. Extraction was followed by purification on a silica gel column and concentration in a turbo evaporator under nitrogen flow.

Persistent organic pollutants were analyzed by gas chromatography. GC-ECD (Agilent 7890B) was used for OCPs and PCBs, and GC-MS (Agilent 7890A with MS 5975C) was used for PAHs.

Romania

Sediments samples were collected with a Van Veen boden-greifer. Sediments were freeze-dried and then well homogenized, and 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. At the end of mineralization, the samples were resumed in the 100 ml flask, with deionized water. The analytical determination of the copper, cadmium, lead, nickel, and chromium was carried out by graphite furnace – atomic absorption spectrometry method (GF-AAS).

Further processing of samples consisted of microwave extraction with a mixture of hexane/acetone (1:/1). The extraction was followed by purification on florisil column for organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), respectively silica/alumina column for polyaromatic hydrocarbons (PAHs) and concentration using the Kuderna-Denish concentrator and nitrogen flow. Identification and quantification of organic compounds were done by gas chromatography. GC-ECD method was used for OCPs and PCBs and GC-MS method for PAHs. The total petroleum hydrocarbons (TPHs) were analyzed by the fluorescence method.

Turkey

The modified EPA-3052 method was used for the preparation of the metal analysis. About 0.1 g of the homogenized sediment samples were put into a closed Teflon vessel with 4 mL of HNO3 (Merck), 2 mL of HCl (Merck) and 1 mL of HF acids (Merck) for the complete digestion of the metal samples. A microwave acid digestion system (Milestone Ultrawave) was used for the digestion at 120 ◦C for 35 min. Teflon vessels were left to cool, and 0.3 g boric acid was added to permit the complexation of fluoride to protect the quartz plasma torch from excess hydrofluoric acid. Then the same microwave digestion procedure was reapplied. After cooling, the vessel contents were filtered and then diluted to 50 mL with deionized water. The diluted samples were preserved in polyethylene bottles for analysis. Sample solutions and blanks were analysed for the metals (Al, Fe, As, Cu, Cr, Cd, Ni, Pb, Zn) using the ICPMS instrument (Perkin Elmer Nexion 3000x) utilizing a Kinetic Energy Discrimination (KED) mode. The mercury (Hg) content of the samples was determined using the Milestone DMA-80 Direct Mercury Analyzer.

The total organic carbon (TOC) content of the samples was determined according to the High-Temperature Combustion Method (Thermo Finnigan Flash EA 1112 Series - CHNS analyzer) after removal of inorganic carbon. Grain size analysis of sediment samples was carried out using standard sieves (granulometric method). Results were assessed according to the procedure outlined by Folk (1974).

For POPs in sediment samples, the extraction was conducted using a microwave oven. Approximately 5 g portion of freeze-dried sediment samples was put in the teflon tube (PTFE) of the reactor with 30 ml hexane: acetone (1:1 v/v). Various internal standards were added to the sediment for quantifying the overall recovery of the analytical procedures: Chrysene-d12, Acenapthene-d10, Napthhalene-d8, Perylene-d12 and Phenathrene-d10 for the aromatic hydrocarbon fraction; PCB29 and PCB198 for the organochlorine compounds. The extraction was carried out at 120 °C for 35 min. Sulphur was removed used activated elemental copper. The extracts were concentrated using a rotary evaporator. Extraction was followed by purification on florisil column for organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), respectively silica column for polyaromatic hydrocarbons (PAHs) and concentration using the rotary evaporator and nitrogen flow.

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbon (PAHs) were analysed by gas chromatography (GC-MS MS). The total petroleum hydrocarbons (TPHs) were analysed by fluorescence method.

Table 7.4 - Organic pollutants analysis methods in sediment

Matrix	Parameter	Method	Device	Reference	Unit
Sediment	OCPs and PCBs	Microwave Extraction (Acetone-hexane) Removal of sulfur by copper Clean up technique: Florisil column (three fractions)	GC/MS MS	UNEP/IOC/IAEA EPA 8081 B EPA 8121 EPA 8270 C EPA 3545 A	ng/g
	PAH	Microwave Extraction (Acetone-hexane) Removal of sulfur by copper Clean up technique: Florisil column (two fractions)	GC/MS MS	UNEP/IOC/IAEA No:20; 1992 EPA 3630C Silica Gel Cleanup	ng/g
	TPH	Ultrasonic Extraction (with THF)	Luminisans Spectrofluorometer	According to Chrysene Ex: 310nm ve Em: 360 nm	µg/L
	TOC	High-Temperature Combustion Method (TOC)	CHNS Analyzer	In-House Method	%

ANNEX C SPECIES LISTS

Table 7.5 - List of phytoplankton taxa identified during hot spot cruises

Species / Group	UA	RO	TR
Bacillariophyceae			
Amphora sp. C.G. Ehrenberg ex F.T. Kützing, 1844		+	
Aulacoseira granulata (Ehrenberg) Simonsen, 1979		+	
Cerataulina bergonii Ostenfeld, 1903		+	
Ceratoneis fasciola Ehrenberg, 1839			+
Chaetoceros affinis Lauder, 1864			+
Chaetoceros compressus Lauder, 1864			+
Chaetoceros curvisetus Hustedt in Schmidt, 1920	+	+	+
Chaetoceros danicus Cleve, 1889			+
Chaetoceros decipiens Cleve, 1873			+
Chaetoceros peruvianus Brightwell, 1856			+
Chaetoceros similis Cleve, 1896			+
Chaetoceros *socialis* H.S.Lauder, 1864		+	
Cocconeis scutellum (Grunow in Van Heurck) P.T. Cleve, 1896	+		
Coscinodiscus angustelineatus Schmidt in Schmidt et al., 1878			+
Coscinodiscus centralis Ehrenberg, 1844			+
Coscinodiscus granii Gough, 1905			+
Coscinodiscus perforatus Ehrenberg, 1844			+
Coscinodiscus radiatus J.W. Bailey, 1842		+	
Cyclotella choctawhatcheeana Grunow, 1878		+	
Cyclotella meneghiniana Kützing, 1844		+	
Cylindrotheca closterium (Ehrenberg) Reimann & J.C.Lewin, 1964			+
Ditylum brightwellii (T.West) Grunow, 1885	+		+
Gaillonella sulcata Ehrenberg, 1838		+	
Lennoxia faveolata H.A.Thomsen & K.R.Buck, 1993		+	
Leptocylindrus minimus Gran, 1915		+	
Melosira moniliformis (O.F. Müller) C. Agardh, 1824	+		
Navicula sp. J.B.M. Bory de Saint-Vincent, 1822		+	
Navicula palpebralis de Brébisson, 1853	+		
Navicula pennata A. Schmidt, 1876	+		
Nitzschia sp.	+		
Nitzschia acicularis Frenguelli, 1923		+	
Nitzschia closterium Eulenstein, 1868		+	
Nitzschia delicatissima Cleve, 1897	+	+	+
Nitzschia longissima (Brébisson in Kützing) Ralfs in Pritchard, 1861	+		
Nitzschia tenuirostris Manguin in Bourrelly & Manguin, 1952		+	
Pleurosigma angulatum (Queckett) W.Smith, 1852		+	
Pleurosigma elongatum Auerswald in litt. ed sched. Rabenhorst, 1863		+	+
Proboscia alata (Brightwell) Sundström, 1986	+		+
Pseudosolenia calcar-avis (Schultze) B.G.Sundström, 1986	+	+	+
Rhizosolenia fragilissima f. fragilissima Bergon, 1903			+
Rhizosolenia setigera Brightwell, 1858			+
Rhizosolenia styliformis T.Brightwell, 1858			+
Skeletonema costatum (Greville) Cleve, 1873		+	+
Stephanodiscus hantzschii Grunow, 1880	+		
Synedra nitzschioides f. nitzschioides Grunow, 1862	+	+	+
Thalassiosira aestivalis Gran, 1931		+	
Thalassiosira eccentrica (Ehrenberg) Cleve, 1904			+
Thalassiosira minima Mertz, 1966		+	
Thalassiosira parva Proschkina-Lavrenko, 1955		+	
Thalassiosira subsalina Proshkina-Lavrenko, 1955		+	
Dinophyceae			
Akashiwo sanguinea (K.Hirasaka) Gert Hansen & Moestrup, 2000			+
Alexandrium sp. Halim, 1960		+	
Alexandrium catenella (Whedon & Kofoid) Balech, 1985			+
Archaeperidinium minutum (Kofoid) Jørgensen, 1912		+	
Dinoflagellate cyst Ehrenberg, 1830		+	
Dinophyceae	+		

Species / Group	UA	RO	TR
Dinophysis acuminata Claparède & Lachmann, 1859			+
Dinophysis caudata Saville-Kent, 1881			+
Dinophysis fortii Pavillard, 1924			+
Dinophysis hastata F.Stein, 1883			+
Dinophysis sacculus F.Stein, 1883		+	+
Diplopsalis lenticula Bergh, 1881	+	+	+
Durinskia agilis (Kofoid & Swezy) Saburova, Chomérat & Hoppenrath, 2012	+		
Glenodinium sp. Ehrenberg, 1836			+
Glenodinium minutum Skvortzov, 1946		+	
Glenodinium paululum Lindemann, 1928	+	+	
Glenodinium pilula (Ostenfeld) Schiller, 1935	+	+	
Gonyaulax ceratocoroides Kofoid, 1910		+	+
Gonyaulax minima Matzenauer, 1933	+	+	
Gymnodinium sp. F. Stein, 1878	+	+	
Gymnodinium agiliforme Schiller, 1928		+	
Gymnodinium najadeum J.Schiller, 1928	+	+	
Gymnodinium simplex (Lohmann, 1911) Koifoid , Swezy, 1921	+		
Gymnodinium wulffii J.Schiller, 1933	+	+	
Gyrodinium sp. Kofoid & Swezy, 1921		+	
Gyrodinium fusiforme Kofoid & Swezy, 1921		+	+
Gyrodinium helveticum (Penard) Y.Takano & T.Horiguchi, 2004		+	
Gyrodinium lachryma (Meunier) Kofoid & Swezy			+
Gyrodinium pingue (Schütt) Kofoid & Swezy, 1921	+	+	
Heterocapsa rotundata (Lohmann) Gert Hansen, 1995		+	+
Kryptoperidinium triquetrum (Ehrenberg) U.Tillmann, M. Gottschling, M.Elbrächter, W.-H.Kusber & M.Hoppenrath, 2019	+	+	
Lessardia elongata Saldarriaga & F.J.R.Taylor, 2003		+	
Lingulodinium polyedra (F.Stein) J.D.Dodge, 1989	+	+	+
Margalefidinium citron (Kofoid & Swezy) F.Gómez, Richlen & D.M.Anderson, 2017		+	
Mesoporos perforatus (Gran) Lillick, 1937		+	
Oblea rotunda (Lebour) Balech ex Sournia, 1973		+	
Oxytoxum variabile Schiller, 1937		+	
Peridinium quadridentatum (F.Stein) Gert Hansen, 1995		+	
Peridinium volzii Lemmermann, 1906		+	
Phalacroma rotundatum (Claparéde & Lachmann) Kofoid & J.R.Michener, 1911		+	+
Polykrikos schwartzii Bütschli, 1873			+
Preperidinium meunieri (Pavillard) Elbrächter, 1993		+	
Pronoctiluca pelagica Fabre-Domergue, 1889			+
Prorocentrum compressum (Bailey) T.H.Abé ex J.D.Dodge, 1975	+		+
Prorocentrum cordatum (Ostenfeld) J.D.Dodge, 1975	+	+	+
Prorocentrum gracile F.Schütt, 1895			+
Prorocentrum micans Ehrenberg, 1822	+	+	+
Prorocentrum scutellum Schröder, 1900		+	+
Protoperidinium bipes (Paulsen, 1904) Balech, 1974	+	+	+
Protoperidinium brevipes (Paulsen, 1908) Balech, 1974		+	+
Protoperidinium bulla (Meunier, 1910) Balech, 1974		+	
Protoperidinium claudicans (Paulsen, 1907) Balech, 1974			+
Protoperidinium conicum (Gran) Balech, 1974		+	+
Protoperidinium crassipes (Kofoid, 1907) Balech, 1974			+
Protoperidinium curtipes (Jørgensen, 1912) Balech, 1974			+
Protoperidinium depressum (Bailey, 1854) Balech, 1974		+	+
Protoperidinium divergens (Ehrenberg) Balech, 1974	+	+	+
Protoperidinium grande Kofoid, 1907) Balech, 1974			+
Protoperidinium granii (Ostenfeld) Balech, 1974		+	+
Protoperidinium oblongum (Aurivillius) Parke & Dodge, 1976			+
Protoperidinium pellucidum Bergh, 1881			+
Protoperidinium steinii (Jørgensen, 1899) Balech, 1974	+	+	+
Pyrophacus horologium F.Stein, 1883			+
Scrippsiella acuminata (Ehrenberg) Kretschmann, Elbrächter, Zinssmeister, S.Soehner, Kirsch, Kusber & Gottschling, 2015	+	+	+
Speroidium fungiforme (Anisimova) Moestrup & Calado, 2018	+		
Torodinium robustum Kofoid & Swezy, 1921		+	+

Species / Group	UA	RO	TR
Tripos furca (Ehrenberg) F.Gómez, 2013	+	+	+
Tripos fusus (Ehrenberg) F.Gómez, 2013	+	+	+
Tripos lineatus (Ehrenberg) F.Gómez, 2013			+
Tripos muelleri Bory de Saint-Vincent, 1827		+	+
Chlorophyceae			
Ankistrodesmus arcuatus Korshikov, 1953		+	
Ankistrodesmus falcatus (Corda) Ralfs, 1848	+		
Carteria sp. Diesing, 1866		+	
Chlamydomonas sp. Ehrenberg, 1833		+	
Chlorophyceae Pascher, 1914	+	+	
Desmodesmus communis (E.Hegewald) E.Hegewald, 2000		+	
Desmodesmus spinosus (Chodat) E.Hegewald, 2000		+	
Kirchneriella lunaris (Kirchner) K. Möbius, 1894	+		
Monoraphidium irregulare (G.M.Smith) Komárková-Legnerová, 1969		+	
Monoraphidium minutum (Nägeli) Komárková-legnerová, 1969		+	
Pseudopediastrum boryanum (Turpin) E.Hegewald, 2005		+	
Schroederia spiralis (Printz) Korshikov, 1953		+	
Tetraëdron minimum (A.Braun) Hansgirg, 1888		+	
Willea rectangularis (A.Braun) D.M.John, M.J.Wynne & P.M.Tsarenko, 2014		+	
Chlorodendrophyceae			
Pachysphaera sp. Ostenfeld, 1899		+	
Cryptophyceae			
Cryptomonas Ehrenberg, 1831		+	
Cryptophyceae	+		
Hillea fusiformis (J.Schiller) J.Schiller, 1925		+	+
Komma caudata (L.Geitler) D.R.A.Hill, 1991		+	
Plagioselmis sp.	+		
Small flagellates Cavalier-Smith, 1986		+	
Cyanophyceae			
Chroococcus minor (Kützing) Nägeli, 1849		+	
Cyanophyceae	+		
Jaaginema sp.	+		
Merismopedia tenuissima Lemmermann, 1898		+	
Microcystis aeruginosa (Kützing) Kützing, 1846		+	
Oscillatoria sp. Vaucher ex Gomont, 1892		+	
Phormidium hormoides Setchell & N.L.Gardner, 1918		+	
Pseudanabaena limnetica (Lemmermann) Komárek, 1974		+	
Snowella lacustris (Chodat) Komárek & Hindák, 1988		+	
Spirulina sp. Turpin ex Gomont, 1892		+	
Euglenoidea			
Eutreptia lanowii Steuer, 1904		+	
Lepocinclis acus (O.F.Müller) B.Marin & Melkonian, 2003		+	
Prymnesiophyceae			
Acanthoica quattrospina Lohmann, 1903		+	
Emiliania huxleyi (Lohmann) Hay, Mohler, 1967	+	+	+
Syracosphaera sp.	+		
Chrysophyceae			
Ollicola vangoorii Vørs, 1992	+		
Dictyochophyceae			
Apedinella radians (Lohmann) P.H.Campbell, 1973		+	
Dictyocha fibula Ehrenberg, 1839	+		
Octactis octonaria (Ehrenberg) Hovasse, 1946			+
Octactis speculum (Ehrenberg) F.H.Chang, J.M.Grieve & J.E.Sutherland, 2017			+
Ebriophyceae			
Ebria tripartita (J.Schumann) Lemmermann, 1899		+	+
Hermesinum adriaticum O.Zacharias, 1906		+	
Trebouxiophyceae			
Crucigenia tetrapedia (Kirchner) Kuntze, 1898		+	
Trochiscia sp. Kützing, 1834			+
Prasinophyceae			
Pterosperma cristatum Schiller, 1925		+	

Table 7.6 - List of zooplankton taxa identified during hot spot cruises

Species / Group	UA	RO	TR
Oligotrichea			
Tintinnopsis beroidea Stein, 1867		+	
Tintinnopsis campanula Ehrenberg, 1840		+	
Tintinnopsis minuta Wailes, 1925		+	
Tintinnopsis tocantinensis Kofoid & Campbell, 1929		+	
Tintinnopsis tocantinensis Kofoid & Campbell, 1929		+	
Tintinnopsis tubulosa Levander, 1900		+	
Favella ehrenbergii (Claparède & Lachmann, 1858) Jörgensen, 1924		+	
Amphorellopsis acuta Schmidt, 1902		+	
Eutintinnus lusus-undae Entz, 1885		+	
Eutintinnus pectinis (ofoid & Campbell, 1929		+	
Eutintinnus tubulosus (Ostenfeld, 1899) Kofoid & Campbell, 1939		+	
Salpingella decurtata Jörgensen, 1924		+	
*Tintinnidium mucicola (*Claparède & Lachmann, 1858*) Daday, 1887*		+	
Rhizodomus tagatzi Strelkow & Wirketis, 1950		+	
Appendicularia			
Oikopleura (Vexillaria) dioica Fol, 1872	+	+	+
Bivalvia			
Bivalvia Linnaeus, 1758	+	+	+
Branchiopoda			
Bosmina (Bosmina) longirostris O.F. Müller, 1785	+	+	
Evadne spinifera P.E.Müller, 1867	+	+	+
Penilia avirostris Dana,1849	+	+	+
Pleopis polyphemoides Leuckart, 1859	+	+	+
Pseudevadne tergestina Claus, 1877	+		
Dinophyceae			
Noctiluca scintillans (Macartney) Kofoid & Swezy, 1921		+	+
Gastropoda			
Gastropoda Cuvier, 1795	+	+	+
Hexanauplia			
Acartia (Acanthacartia) tonsa Dana, 1849	+	+	+
Acartia (Acartiura) clausi Giesbrecht, 1889			+
Acartia sp. Dana, 1846		+	+
Balanus Costa, 1778	+	+	+
Calanus euxinus Hulsemann, 1991		+	+
Centropages ponticus Karavaev, 1895	+		
Copepoda Milne Edwards, 1840	+	+	
Cyclops Müller O.F., 1785		+	+
Ectinosoma Boeck, 1865	+	+	+
Harpacticoida Sars M., 1903	+	+	+
Harpacticus Edwards H., 1840			+
Metis ignea Philippi, 1843			+
Oithona davisae Ferrari F.D. & Orsi, 1984	+	+	+
Oithona similis Claus, 1866	+		+
Paracalanus parvus parvus Claus, 1863	+		
Pseudocalanus elongatus Boeck, 1865	+		
Polychaeta			
Polychaeta Grube, 1850	+	+	+
Spionidae Grube, 1850	+		
Sagittoidea			
Parasagitta setosa J. Müller, 1847	+	+	+
Hydrozoa			
Hydrozoa Owen, 1743	+		
Nuda			
Beroe ovata Bruguière, 1789	+		
Rotatoria			
Rotatoria Cuvier, 1795	+		
Pisces			
Pisces (ova, larvae)			+

Table 7.7 - List of zoobenthos taxa identified during hot spot cruises

Species / Group	UA	RO	TR
Anthozoa			
Anthozoa sp. Ehrenberg, 1834			+
Diadumene lineata Verrill, 1869		+	
Sagartiogeton undatus Muller, 1778		+	
Nemertea			
Leucocephalonemertes aurantiaca Grube, 1855		+	
Nemertea sp. Schultze, 1851		+	+
Gastropoda			
Rapana venosa Valenciennes, 1846			+
Calyptraea chinensis Linnaeus, 1758			+
Retusa truncatula Bruguière, 1792			+
Tritia neritea Linnaeus, 1758		+	+
Bivalvia			
Abra alba W. Wood, 1802		+	+
Abra ct. *nitida (*Juvenile*)* O.F. Müller, 1776			+
Abra nitida O.F. Müller, 1776			+
Abra prismatica Montagu, 1808		+	
Abra sp.			+
Acanthocardia paucicostata G.B. Sowerby,1834		+	+
Anadara kagoshimensis Tokunaga, 1906		+	
Chamelea gallina Linnaeus, 1758		+	+
Gouldia minima Montagu, 1803			+
Lucinella divaricata Linnaeus, 1758			+
Macomangulus tenuis da Costa, 1778		+	
Mytilus galloprovincialis Lamarck, 1819	+		+
Papillicardium papillosum Poli, 1791			+
Parvicarium exiguum Gmelin, 1791		+	
Pitar rudis Poli, 1795		+	+
Polititapes aureus Gmelin, 1791		+	
Spisula cf. *subtruncata* da Costa, 1778			+
Spisula subtruncata da Costa, 1778			+
Arcuatula senhousia Benson, 1842			+
Clitellata			
Oligochaeta sp. Grube, 1850			+
Polychaeta			
Alitta succinea Leuckart, 1847	+	+	
Aonides paucibranchiata Southern, 1914	+		
Aricidea (Acmira) catherinae Laubier, 1967			+
Aricidea (Strelzovia) claudiae Laubier, 1967			+
Capitella capitata Fabricius, 1780	+	+	
Capitella minima Langerhans, 1880		+	
Eunereis longissima Johnston, 1840			+
Harmothoe sp. Kinberg, 1856			+
Heteromastus filiformis Claparede, 1864		+	+
Lagis koreni Malmgren, 1866		+	
Lentidium mediterraneum O. G. Costa, 1830		+	
Lindrilus flavocapitatus Uljanin, 1877		+	
Melinna palmata Grube, 1870		+	+
Micronephthys longicornis Perejaslavtseva, 1891			+
Mysta picta Quatrefages, 1865		+	
Nephtys hombergii Savigny in Lamarck, 1818	+	+	+
Nereis zonata Malmgren, 1867		+	
Paradoneis sp. Hartman, 1965			+
Pholoe inornata Johnston, 1839			+
Phyllodoce mucosa Örsted, 1843			+
Polydora cornuta Bosc, 1802		+	
Polydora limicola Annenkova, 1934	+		
Prionospio cirrifera Wirén, 1883	+	+	
Prionospio maciolekae Dagli & Çinar, 2011			+
Pygospio elegans Claparede, 1863		+	

Species / Group	UA	RO	TR
Saccocirrus papillocercus Bobretzky, 1872		+	
Salvatoria clavata Claparede, 1863		+	
Scolelepis (Scolelepis) squamata O.F. Muller, 1806		+	
Sigambra tentaculata Treadwell, 1941			+
Sphaerosyllis bulbosa Southern, 1914		+	
Spio decoratus Bobretzky, 1870			+
Spio filicornis Muller, 1776	+	+	
Spionidae sp.		+	
Streblospio sp.		+	
Terebellides stroemii M. Sars, 1835			+
Briozoa			
Briozoa sp.		+	
Thecostraca			
Amphibalanus improvisus Darwin, 1854		+	
Balanus sp. Costa, 1778			+
Malacostraca			
Ampelisca diadema Costa, 1853		+	+
Ampelisca sarsi Chevreux, 1888		+	
Ampelisca pseudosarsi Bellan-Santini & Kaim-Malka, 1977			+
Ampelisca pseudospinimana Bellan-Santini & Kaim-Malka, 1977			+
Ampelisca sp.			+
Amphipoda sp. Latreille, 1816			+
Brachynotus sexdentatus Risso, 1827			+
Diogenes pugilator Roux, 1829		+	+
Gastrosaccus sp. Norman, 1868			+
Gilvossius candidus Olivi, 1792			+
Iphinoe elisae Băcescu, 1950			+
Iphinoe serrata Norman, 1867			+
Iphinoe maeotica Sowinskyi, 1893		+	
Iphinoe sp. Bate, 1856			+
Iphinoe trispinosa Goodsir, 1843			+
Medicorophium runcicorne Della Valle, 1893			+
Monocorophium acherusicum Costa, 1853		+	
Microdeutopus gryllotalpa Costa, 1853		+	
Nototropis guttatus Costa, 1853		+	
Palaemon elegans Rathke, 1837	+		
Perioculodes longimanus Spence Bate & Westwood, 1868			+
Perioculodes sp. G.O. Sars, 1892			+
Phtisica marina Slabber, 1769			+
Phtisica sp.			+
Pseudocuma (Pseudocuma) longicorne Bate, 1858			+
Synchelidium maculatum Stebbing, 1906			+
Upogebia pusilla Petagna, 1792		+	+
Upogebia tipica Nardo, 1869			+
Larve zoe		+	
Holothuroidea			
Holothuroidea sp. Blainville, 1834			+
Phoronida			
Phoronis sp. Wright, 1856			+
Tunicata			
Tunicata sp. Lamarck, 1816			+
Rhabditophora			
Stylostomum ellipse Dalyell, 1853	+		
Hydrozoa			
Hydrozoa sp.			+

ANNEX D DESCRIPTIVE STATISTICS - CHEMISTRY

Table 7.8 - Descriptive statistics for physical-chemical parameters and nutrients in seawater

	N	Mean	Median	Min.	Max.	Lower Quartile	Upper Quartile	Percentile 10^{th}	Percentile 90^{th}	Std. Dev.
Ukraine										
T [°C]	4	21.33	22.25	17.30	23.50					2.75
S [PSU]	4	17.38	17.19	17.14	18.01					0.42
O_2 [µM]	4	208.7	230.00	141.6	233.1					44.82
O_2 [%]	4	84.0	94.2	52.5	95.1					21.0
pH	4	8.25	8.32	8.01	8.37					0.16
$(PO_4)^{3-}$ [µM]	4	0.22	0.14	0.10	0.50					0.19
TP, [µM]	4	0.64	0.67	0.52	0.71					0.08
$(SiO_4)^{4-}$[µM]	4	7.3	5.3	3.5	15.1					5.4
TNOx [µM]	4	0.63	0.18	0.15	2.00					0.92
$(NH_4)^+$ [µM]	4	0.04	0.04	0.04	0.04					0.00
TSS [mg/L]	4	3.97	3.95	0.54	7.43					3.90
Romania										
T [°C]	31	22.06	22.11	20.96	22.49	22.00	22.20	21.56	22.41	1.21
S [PSU]	31	16.76	16.93	15.81	17.31	16.38	16.98	16.27	17.06	0.38
O_2 [µM]	31	250.6	250.5	216.6	293.9	236.7	265.3	221.5	271.5	18.8
O_2 [%]	31	101.1	102.0	87.5	115.9	96.1	106.6	90.0	109.6	7.3
pH	31	8.66	8.66	8.44	8.72	8.64	8.70	8.60	8.71	0.05
$(PO_4)^{3-}$ [µM]	31	0.48	0.40	0.29	1.59	0.35	0.49	0.32	0.70	0.25
TP, [µM]	31	0.71	0.64	0.45	2.17	0.52	0.75	0.49	0.88	0.31
$(SiO_4)^{4-}$[µM]	31	7.1	6.2	4.6	17.9	5.8	6.9	5.5	8.7	2.8
TNOx [µM]	31	4.66	3.39	2.08	16.98	2.48	6.45	2.21	8.48	3.19
$(NH_4)^+$ [µM]	31	7.30	5.87	3.97	23.27	4.82	8.61	4.25	11.27	3.84
DIN [µM]	31	11.96	10.49	6.52	33.08	7.78	14.10	6.55	15.91	5.95
TSS [mg/L]	13	13.63	12.80	0.60	32.80	11.60	14.00	11.20	16.00	6.87
Turkey										
T [°C]	127	17.06	11.73	8.80	26.65	11.16	25.65	10.91	26.09	7.01
S [PSU]	127	18.19	18.16	17.86	19.05	18.08	18.27	18.04	18.43	0.16
O_2 [µM]	127	347.1	354.2	238.4	442.0	302.5	389.4	283.9	406.3	46.8
O_2 [%]	127	126.8	127.1	96.5	195.0	118.4	132.2	113.5	136.6	13.2
pH	127	8.35	8.35	8.17	8.78	8.33	8.37	8.29	8.39	0.07
$(PO_4)^{3-}$ [µM]	127	0.78	0.08	0.02	12.33	0.02	0.39	0.02	2.71	1.83
TP, [µM]	127	1.13	0.39	0.08	13.63	0.18	0.72	0.13	3.41	2.23

$(SiO_4)^{4-}$[µM]	126	2.76	2.78	0.06	9.92	1.39	3.77	0.98	5.13	1.66
TNOx [µM]	126	0.45	0.29	0.05	2.21	0.05	0.72	0.05	1.06	0.48
$(NH_4)^+$ [µM]	126	0.92	0.13	0.04	25.27	0.05	0.58	0.04	2.04	2.80
TSS [mg/L]	43	1.86	1.76	0.20	5.30	0.80	2.70	0.56	3.31	1.12

Table 7.9- Descriptive statistics for heavy metals in seawater

	N	Mean	Median	Min.	Max.	Lower Quartile	Upper Quartile	Percentile 10^{th}	Percentile 90^{th}	Std. Dev.
Ukraine										
Cu [µg/L]	4	51.26	51.73	0.57	101.00					57.44
Cd [µg/L]	4	0.42	0.43	0.07	0.74					0.34
Pb [µg/L]	4	26.48	1.90	1.14	101.00					49.68
Ni [µg/L]	4	ND*	ND	ND	ND					
Cr [µg/L]	4	ND	ND	ND	ND					
As [µg/L]	4	ND	ND	ND	ND					
Hg [µg/L]	4	0.16	0.02	0.01	0.57					0.28
Zn [µg/L]	4	16.07	15.85	10.70	21.90					4.58
Fe [mg/L]	4	30.50	24.50	23.00	50.00					13.03
Co [µg/L]	4	ND	ND	ND	ND					
Romania										
Cu [µg/L]	13	8.45	8.48	4.95	13.01	7.74	9.65	5.12	10.56	2.22
Cd [µg/L]	13	0.08	0.06	0.03	0.20	0.05	0.07	0.04	0.18	0.05
Pb [µg/L]	13	1.57	0.79	0.09	5.48	0.60	2.07	0.39	4.38	1.64
Ni [µg/L]	13	3.29	3.06	1.56	6.36	2.91	3.54	1.95	4.56	1.19
Cr [µg/L]	13	1.68	1.63	0.72	4.78	1.05	1.85	0.85	2.11	1.03
Turkey										
Cu [µg/L]	14	1.08	1.38	0.32	1.87	0.43	1.61	0.38	1.68	0.62
Cd [µg/L]	14	0.20	0.04	0.02	1.33	0.02	0.11	0.02	0.84	0.39
Pb [µg/L]	14	0.49	0.27	0.03	2.31	0.07	0.52	0.04	1.54	0.66
Ni [µg/L]	14	0.86	0.86	0.57	1.21	0.73	1.00	0.63	1.02	0.18
Cr [µg/L]	14	0.34	0.34	0.22	0.59	0.25	0.36	0.24	0.49	0.10

***ND-not detected**

Table 7.10 Descriptive statistics for chlorinated compounds concentrations in water samples

	N	Mean	Median	Min.	Max.	Lower Quartile	Upper Quartile	Percentile 10th	Percentile 90th	Std. Dev.
Ukraine										
HCB [µg/L]	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
a-HCH [ng/L]	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
ß-HCH [ng/L]	4	1.560	1.555	1.020	2.110	1.210	1.910	1.020	2.110	0.463
Lindane [µg/L]	4	0.093	0.080	0.060	0.150	0.065	0.120	0.060	0.150	0.040
Heptachlor [µg/L]	4	2.950	0.050	0.050	11.650	0.050	5.850	0.050	11.650	5.800
Aldrin [µg/L]	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dieldrin [µg/L]	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p'DDE [µg/L]	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p'DDD [µg/L]	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p'DDT [µg/L]	4	4.403	4.430	3.960	4.790	4.125	4.680	3.960	4.790	0.359
Atrazine [ng/L]	4	0.635	0.760	0.050	0.970	0.335	0.935	0.050	0.970	0.418
Dursban [ng/L]	4	1.008	1.110	0.500	1.310	0.755	1.260	0.500	1.310	0.361
AR-1254 [ng/L]	4	10.120	8.835	7.910	14.900	8.005	12.235	7.910	14.900	3.272
AR-1260 [ng/L]	4	0.193	0.175	0.140	0.280	0.140	0.245	0.140	0.280	0.067
Romania										
HCB [µg/L]	13	2.111	2.293	0.004	5.958	0.004	3.477	0.004	4.126	1.917
Lindane [µg/L]	13	4.968	0.003	0.003	32.407	0.003	3.875	0.003	19.897	10.038
Heptachlor [µg/L]	13	0.632	0.003	0.003	8.185	0.003	0.003	0.003	0.003	2.269
Aldrin [µg/L]	13	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dieldrin [µg/L]	13	2.000	0.002	0.002	11.889	0.002	2.523	0.002	6.253	3.687
Endrin [µg/L]	13	2.430	0.003	0.003	31.548	0.003	0.003	0.003	0.003	8.749
p,p'DDE [µg/L]	13	2.354	0.002	0.002	10.699	0.002	4.807	0.002	6.936	3.580
p,p'DDD [µg/L]	13	0.221	0.002	0.002	2.846	0.002	0.002	0.002	0.002	0.789
p,p'DDT [µg/L]	13	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.000
Turkey										
HCB [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND
Lindane [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aldrin [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dieldrin [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endrin [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p'DDE [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p'DDD [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p'DDT [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 7.11 Polyaromatic hydrocarbons concentrations in seawater

	N	Mean	Median	Min.	Max.	Lower Quartile	Upper Quartile	Percentile 10th	Percentile 90th	Std. Dev.
Ukraine										
Naphthalene [µg/L]	4	0.845	0.860	0.670	0.990	0.730	0.960	0.670	0.990	0.144
Acenaphthylene [µg/L]	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthene [µg/L]	4	0.065	0.050	0.050	0.110	0.050	0.080	0.050	0.110	0.030
Fluorene [µg/L]	4	0.073	0.050	0.050	0.140	0.050	0.095	0.050	0.140	0.045
Phenanthrene [µg/L]	4	6.527	6.730	5.200	7.450	5.650	7.405	5.200	7.450	1.078
Anthracene [µg/L]	4	0.070	0.050	0.050	0.130	0.050	0.090	0.050	0.130	0.040
Fluoranthene [µg/L]	4	0.867	0.815	0.420	1.420	0.475	1.260	0.420	1.420	0.474
Pyrene [µg/L]	4	0.318	0.310	0.160	0.490	0.175	0.460	0.160	0.490	0.167
Benzo[a]anthracene [µg/L]	4	0.792	0.765	0.430	1.210	0.445	1.140	0.430	1.210	0.405
Crysene [µg/L]	4	0.695	0.685	0.190	1.220	0.275	1.115	0.190	1.220	0.497
Benzo[b]fluoranthene [µg/L]	4	2.133	1.810	0.810	4.100	0.820	3.445	0.810	4.100	1.607
Benzo[k]fluoranthene [µg/L]	4	1.705	1.450	0.680	3.240	0.690	2.720	0.680	3.240	1.247
Benzo[a]pyrene [µg/L]	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo [g,h,i]perylene [µg/L]	4	1.018	0.860	0.390	1.960	0.430	1.605	0.390	1.960	0.738
Dibenzo[a,h]anthracene [µg/L]	4	2.565	2.185	0.600	5.290	0.775	4.355	0.600	5.290	2.208
Indeno[1,2,3-c,d]pyrene [µg/L]	4	4.872	3.680	0.950	11.180	1.475	8.270	0.950	11.180	4.606
Romania										
Naphthalene [µg/L]	13	0.288	0.223	0.044	1.071	0.176	0.252	0.135	0.484	0.258
Acenaphthylene [µg/L]	13	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthene [µg/L]	13	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fluorene [µg/L]	13	ND	ND	ND	ND	ND	ND	ND	ND	ND
Phenanthrene [µg/L]	13	0.029	0.011	0.000	0.121	0.000	0.045	0.000	0.074	0.039
Anthracene [µg/L]	13	0.343	0.207	0.000	1.719	0.051	0.361	0.032	0.766	0.482
Fluoranthene [µg/L]	13	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pyrene [µg/L]	13	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[a]anthracene [µg/L]	13	ND	ND	ND	ND	ND	ND	ND	ND	ND
Crysene [µg/L]	13	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[b]fluoranthene [µg/L]	13	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[k]fluoranthene [µg/L]	13	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[a]pyrene [µg/L]	13	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo [g,h,i]perylene [µg/L]	13	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibenzo[a,h]anthracene [µg/L]	13	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-c,d]pyrene [µg/L]	13	0.125	0.180	0.000	0.189	0.000	0.186	0.000	0.188	0.087
Turkey										
Naphthalene [µg/L]	28	0.014	0.000	0.000	0.133	0.000	0.000	0.000	0.119	0.040
Acenaphthylene [µg/L]	28	0.001	0.000	0.000	0.015	0.000	0.000	0.000	0.000	0.003

Acenaphthene [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fluorene [µg/L]	28	0.003	0.000	0.000	0.028	0.000	0.000	0.000	0.015	0.007
Phenanthrene [µg/L]	28	0.004	0.002	0.002	0.015	0.002	0.002	0.002	0.012	0.004
Anthracene [µg/L]	28	0.014	0.006	0.001	0.050	0.001	0.024	0.001	0.036	0.015
Fluoranthene [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pyrene [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[a]anthracene [µg/L]	28	0.015	0.000	0.000	0.174	0.000	0.000	0.000	0.050	0.040
Crysene [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[b]fluoranthene [µg/L]	28	0.026	0.000	0.000	0.322	0.000	0.000	0.000	0.131	0.070
Benzo[k]fluoranthene [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[a]pyrene [µg/L]	28	0.034	0.006	0.006	0.305	0.006	0.019	0.006	0.125	0.067
Benzo [g,h,i]perylene [µg/L]	28	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000
Dibenzo[a,h]anthracene [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-c,d]pyrene [µg/L]	28	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 7.12 - Descriptive statistics for heavy metals in sediments

	N	Mean	Median	Min.	Max.	Lower Quartile	Upper Quartile	Percentile 10^{th}	Percentile 90^{th}	Std. Dev.
Ukraine										
Cu [µg/g]	1	25.50								
Cd [µg/g]	1	0.23								
Pb [µg/g]	1	17.70								
Ni [µg/g]	1	22.20								
Cr [µg/g]	1	50.40								
Zn [µg/g]	1	71.80								
Mn [µg/g]	1	327.00								
Co [µg/g]	1	6.87								
As [µg/g]	1	7.37								
Al [µg/g]	1	88800.00								
Hg [µg/g]	1	0.20								
Fe[µg/g]	1	22100.00								
Romania										
Cu [µg/g]	11	11.28	4.80	1.36	31.77	3.21	15.12	2.65	31.60	11.15
Cd [µg/g]	11	0.02	0.01	0.00	0.07	0.00	0.05	0.00	0.06	0.03
Pb [µg/g]	11	16.01	6.89	3.92	50.05	4.71	31.86	4.57	32.20	15.61
Ni [µg/g]	11	34.60	31.75	9.01	68.87	20.12	50.08	13.93	57.84	18.39
Cr [µg/g]	11	30.25	24.21	5.65	69.23	13.43	45.67	9.89	55.06	20.58
Turkey										
Cu [µg/g]	18	150.25	132.57	78.63	464.33	105.57	159.92	83.59	207.84	85.74
Cd [µg/g]	18	0.32	0.27	0.15	0.71	0.20	0.41	0.17	0.59	0.16
Pb [µg/g]	18	34.66	28.49	18.34	66.59	22.48	47.19	19.26	63.30	15.05
Ni [µg/g]	18	120.91	132.92	55.53	158.07	102.59	148.19	60.03	157.28	33.68
Cr [µg/g]	18	150.01	159.15	86.24	207.08	135.58	172.21	87.08	178.37	32.98
Zn [µg/g]	18	154.10	154.92	87.07	223.40	115.47	187.14	103.88	205.43	39.89
Mn [µg/g]	18	870.72	866.31	652.03	1031.02	820.17	944.27	697.99	1007.15	110.10
V [µg/g]	18	147.27	143.06	134.37	174.81	137.96	154.03	134.62	173.49	12.33
Co [µg/g]	18	24.08	24.51	18.54	26.88	23.74	25.47	19.17	26.76	2.40
As [µg/g]	18	15.20	15.68	8.23	20.45	12.56	17.95	10.54	20.38	3.67
Al [µg/g]	18	39378.72	34191.81	15781.41	74220.83	23173.67	57490.14	17041.51	62801.14	17676.07
Hg [µg/g]	18	3.85	1.85	0.57	20.75	1.00	3.95	0.79	12.07	5.10
Fe[µg/g]	18	43456.64	44940.70	34013.94	51524.33	37975.77	47450.30	36225.08	50318.64	5439.05

Table 7.13 - Descriptive statistics for chlorinated compounds concentrations in sediments

	N	Mean	Median	Min.	Max.	Lower Quartile	Upper Quartile	Percentile 10th	Percentile 90th	Std. Dev.
Ukraine										
HCB [ng/g dry sed]	1	ND								
a-HCH [µg/kg]	1	ND								
ß-HCH [µg/kg]	1	ND								
Lindane [ng/g dry sed]	1	10.40								
Heptachlor [ng/g dry sed]	1	19.30								
Aldrin [ng/g dry sed]	1	ND								
Dieldrin [ng/g dry sed]	1	12.20								
p,p'DDE [ng/g dry sed]	1	258.00								
p,p'DDD [ng/g dry sed]	1	543.00								
p,p'DDT [ng/g dry sed]	1	288.00								
Romania										
HCB [ng/g dry sed]	11	ND	ND	ND	ND	ND	ND	ND	ND	ND
Lindane [ng/g dry sed]	11	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor [ng/g dry sed]	11	0.164	0.200	0.000	0.200	0.200	0.200	0.000	0.200	0.081
Aldrin [ng/g dry sed]	11	0.036	0.000	0.000	0.200	0.000	0.000	0.000	0.200	0.081
Dieldrin [ng/g dry sed]	11	0.073	0.000	0.000	0.200	0.000	0.200	0.000	0.200	0.101
Endrin [ng/g dry sed]	11	0.164	0.300	0.000	0.300	0.000	0.300	0.000	0.300	0.157
p,p'DDE [ng/g dry sed]	11	0.164	0.200	0.000	0.200	0.200	0.200	0.000	0.200	0.081
p,p'DDD [ng/g dry sed]	11	0.109	0.200	0.000	0.200	0.000	0.200	0.000	0.200	0.104
p,p'DDT [ng/g dry sed]	11	ND	ND	ND	ND	ND	ND	ND	ND	ND
Turkey										
a-HCH [µg/kg]	18	0.053	0.050	0.050	0.103	0.050	0.050	0.050	0.052	0.013
ß-HCH [µg/kg]	18	0.219	0.226	0.074	0.335	0.165	0.266	0.123	0.318	0.069
Lindane [ng/g dry sed]	18	0.153	0.050	0.050	0.384	0.050	0.276	0.050	0.378	0.127
Heptachlor [ng/g dry sed]	18	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aldrin [ng/g dry sed]	18	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dieldrin [ng/g dry sed]	18	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endrin [ng/g dry sed]	18	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p'DDE [ng/g dry sed]	18	0.894	0.769	0.446	2.554	0.624	0.890	0.598	1.279	0.465
p,p'DDD [ng/g dry sed]	18	0.706	0.627	0.312	1.818	0.456	0.766	0.321	1.411	0.403
p,p'DDT [ng/g dry sed]	18	0.580	0.050	0.050	5.055	0.050	0.050	0.050	4.087	1.466

Table 7.14 - Polyaromatic hydrocarbons concentrations in sediments

	N	Mean	Median	Min.	Max.	Lower Quartile	Upper Quartile	Percentile 10th	Percentile 90th	Std. Dev.
Ukraine										
Naphthalene [ng/g dry sed]	1			39.7						
Acenaphthylene [ng/g dry sed]	1			361.0						
Acenaphthene [ng/g dry sed]	1			366.0						
Fluorene [ng/g dry sed]	1			6900.0						
Phenanthrene [ng/g dry sed]	1			9050.0						
Anthracene [ng/g dry sed]	1			486.0						
Fluoranthene [ng/g dry sed]	1			516.0						
Pyrene [ng/g dry sed]	1			521.0						
Benzo[a]anthracene [ng/g dry sed]	1			232.0						
Crysene [ng/g dry sed]	1			331.0						
Benzo[b]fluoranthene [ng/g dry sed]	1			366.0						
Benzo[k]fluoranthene [ng/g dry sed]	1			195.0						
Benzo[a]pyrene [ng/g dry sed]	1			246.0						
Benzo [g,h,i]perylene [ng/g dry sed]	1			194.0						
Dibenzo[a,h]anthracene [ng/g dry sed]	1			106.0						
Indeno[1,2,3-c,d]pyrene [ng/g dry sed]	1			291.0						
Romania										
Naphthalene [ng/g dry sed]	11	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthylene [ng/g dry sed]	11	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthene [ng/g dry sed]	11	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fluorene [ng/g dry sed]	11	47.68	0.10	0.10	131.77	0.10	130.52	0.10	131.49	66.01
Phenanthrene [ng/g dry sed]	11	67.09	1.04	0.10	148.33	0.10	147.75	0.10	147.82	76.52
Anthracene [ng/g dry sed]	11	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.00
Fluoranthene [ng/g dry sed]	11	77.15	139.53	0.10	142.91	0.10	142.08	0.10	142.89	73.78
Pyrene [ng/g dry sed]	11	97.21	151.39	0.10	154.63	0.10	153.60	0.10	154.13	77.00
Benzo[a]anthracene [ng/g dry sed]	11	23.09	0.10	0.10	127.32	0.10	0.10	0.10	125.81	51.16
Crysene [ng/g dry sed]	11	9.30	0.10	0.10	101.32	0.10	0.10	0.10	0.10	30.52
Benzo[b]fluoranthene [ng/g dry sed]	11	25.98	0.10	0.00	144.74	0.10	0.10	0.10	140.19	57.60
Benzo[k]fluoranthene [ng/g dry sed]	11	22.31	0.10	0.00	124.59	0.10	0.10	0.10	120.00	49.45
Benzo[a]pyrene [ng/g dry sed]	11	78.10	121.79	0.10	123.80	0.10	123.19	0.10	123.78	61.84
Benzo [g,h,i]perylene [ng/g dry sed]	11	49.08	0.10	0.10	271.43	0.10	0.10	0.10	267.51	108.97
Dibenzo[a,h]anthracene [ng/g dry sed]	11	0.09	0.10	0.00	0.10	0.10	0.10	0.10	0.10	0.03
Indeno[1,2,3-c,d]pyrene [ng/g dry sed]	11	10.77	0.10	0.00	117.55	0.10	0.10	0.10	0.10	35.42
Turkey										
Naphthalene [ng/g dry sed]	18	9.63	8.49	2.88	20.51	6.94	12.13	3.78	18.76	4.75
Acenaphthylene [ng/g dry sed]	18	0.54	0.53	0.40	0.81	0.45	0.60	0.41	0.72	0.11

Acenaphthene [ng/g dry sed]	18	0.25	0.21	0.10	0.65	0.15	0.32	0.10	0.49	0.14
Fluorene [ng/g dry sed]	18	2.63	2.50	1.33	4.46	2.13	2.86	1.89	4.35	0.78
Phenanthrene [ng/g dry sed]	18	20.24	17.94	11.07	44.84	16.56	21.49	12.33	33.51	8.01
Anthracene [ng/g dry sed]	18	1.97	1.46	0.81	5.91	1.29	2.43	0.89	2.92	1.18
Fluoranthene [ng/g dry sed]	18	16.17	14.00	9.28	29.59	11.02	19.90	10.24	27.15	5.93
Pyrene [ng/g dry sed]	18	15.04	11.57	8.10	36.75	9.74	19.34	8.45	24.65	7.43
Benzo[a]anthracene [ng/g dry sed]	18	6.02	5.38	2.84	13.49	4.30	6.79	2.95	9.88	2.62
Crysene+Triphenylene [ng/g dry sed]	18	9.78	9.27	4.56	18.42	7.91	10.81	5.55	13.20	3.11
Benzo[b]fluoranthene [ng/g dry sed]	18	14.95	15.04	7.71	22.57	12.00	17.35	9.54	19.16	3.78
Benzo[k]fluoranthene [ng/g dry sed]	18	5.82	5.86	2.77	10.67	4.65	6.87	3.21	7.87	1.93
Benzo[a]pyrene [ng/g dry sed]	18	7.23	7.13	3.12	12.77	5.19	9.16	3.63	10.73	2.61
Benzo [g,h,i]perylene [ng/g dry sed]	18	10.93	11.16	5.08	14.95	8.86	13.41	6.69	14.05	2.88
Dibenzo[a,h]anthracene [ng/g dry sed]	18	1.77	1.81	0.83	2.75	1.47	2.07	1.04	2.38	0.49
Indeno[1,2,3-c,d]pyrene [ng/g dry sed]	18	9.13	9.47	3.69	12.77	7.70	11.27	5.38	11.96	2.49

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Project partner 2 - Mare Nostrum Non-Governmental Organization (Romania)

Project partner 3 - Institute of Oceanology - Bulgarian Academy of Sciences (IO-BAS) (Bulgaria)

Project partner 4 - Ukrainian Scientific Center of Ecology of Sea (UkrSCES) (Ukraine)

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Project partner 6 - Turkish Marine Research Foundation (TUDAV) (Turkey)

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TURKISH MARINE RESEARCH FOUNDATION

Project funded by EUROPEAN UNION

Joint Operational Programme Black Sea Basin 2014-2020
National Institute for Marine Research and Development “Grigore Antipa” (NIMRD) Constanta, Romania 2021
Joint Operational Programme Black Sea Basin 2014-2020 is co-financed by the European Union through the European Neighbourhood Instrument and by the participating countries: Armenia, Bulgaria, Georgia, Greece, Republic of Moldova, Romania, Turkey and Ukraine.
This publication has been produced with the financial assistance of the European Union.
The contents of this publication are the sole responsibility of NIMRD and can in no way be taken to reflect the views of the European Union.

Black Sea CROSS BORDER COOPERATION

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