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CURRENT LEVELS OF INORGANIC AND ORGANIC POLLUTANTS IN ROMANIAN MARINE WATERS: IMPLICATIONS FOR ECOSYSTEM HEALTH

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ABSTRACT

Human activities continue to impact the Romanian Black Sea, with implications for the marine ecosystem. This study presents new data (2023) on the spatial distribution of heavy metals, persistent organic pollutants, and nutrients in Romanian Black Sea waters. Our findings reveal the influence of various pollution sources, including the Danube River, municipal and industrial discharges, and maritime activities. Nutrient loads, primarily from the Danube and diffuse sources, exert pressure on the pelagic habitat. While there has been some improvement in nutrient conditions, the potential for increased eutrophication due to climate change remains a concern. Understanding the spatial distribution of pollutants and identifying their sources is crucial for developing effective management strategies to protect the marine environment.
Keywords: Black Sea, eutrophication, pollution, marine waters

INTRODUCTION

The Black Sea is a semi-enclosed marine basin characterized by unique hydrological features and significant freshwater input from major rivers such as the Danube, Dniester, and Dnieper. These rivers collectively discharge approximately 350 cubic kilometers of freshwater annually into the Black Sea, significantly influencing its ecosystem (Oğuz & Velikova, 2010). This input comes from a drainage basin that spans 17 countries and is home to over 170 million people (Llope *et al.*, 2010). The interaction between these freshwater inputs and the limited exchange of water with the Aegean Sea through the Bosphorus and Dardanelles straits results in a strong vertical stratification, leading to natural anoxia in 87% of the Black Sea's waters (Palazov *et al.*, 2019).

Over the past several decades, the Black Sea has experienced significant ecological changes driven by both natural processes and anthropogenic activities. One of the most pressing issues is eutrophication, primarily caused by the excessive input of nitrogen and phosphorus from agricultural runoff, sewage discharge, and industrial activities. Nutrient inputs from the Danube River alone have increased by over 30% since the 1960s, leading to the proliferation of algal blooms and subsequent hypoxia (Strokal & Kroeze, 2012). This eutrophication has resulted in a documented decline in oxygen saturation levels by over 20% in certain areas of the aerobic zone, exacerbating the release of organic contaminants from sediments (Granberg *et al.*, 2008; Vidnichuk & Konovalov, 2021).

The ecological disturbances in the Black Sea have led to significant biodiversity loss and habitat degradation. Invasive species such as the ctenophore *Mnemiopsis leidyi* have thrived under these altered conditions, contributing to the collapse of native fish populations, including commercially important species like anchovy and sprat (BSC, 2019). Habitat loss has been particularly severe in coastal areas, with a 50% reduction in seagrass beds reported over the past two decades, which has further contributed to the decline in marine biodiversity (Strokal & Kroeze, 2012). Eutrophication is a significant issue in both the Black Sea and the Mediterranean Sea, with both regions experiencing similar challenges due to their unique hydrological features. The Mediterranean Sea, like the Black Sea, is particularly sensitive to eutrophication, partly because of its long water residence time of 80 to 100 years, necessitating careful monitoring and management (Karydis & Kitsiou, 2011). Efforts to address this in the Mediterranean include evaluating trophic status through biochemical parameters (Tuğrul *et al.*, 2018) and tackling the threat of pollution, including microplastic, to which the region is especially vulnerable (Sharma *et al.*, 2021). Studies in areas like the Gulf of Gabès and Morocco's Nador lagoon have highlighted eutrophication risks and the need for improved management, mirroring concerns in the Black Sea (Annabi-Trabelsi, 2024; Quaranta *et al.*, 2021). Both seas face multiple anthropogenic stressors, including eutrophication, leading to biodiversity loss, habitat degradation, and invasive species (Mandić & Piraino, 2023).

In addition to eutrophication, the Black Sea faces significant challenges from various hazardous substances, including heavy metals, polycyclic aromatic hydrocarbons (PAHs), persistent organic pollutants (POPs), and emerging contaminants such as microplastics and pharmaceutical residues. These pollutants accumulate in the marine environment, particularly in sediments, and can bioaccumulate in marine organisms, posing serious risks to marine life and human health. For instance, concentrations of heavy metals such as lead and cadmium in sediments along the Romanian coast have been found to exceed safe thresholds by up to five times (Jitar *et al.*, 2015). The bioaccumulation of these contaminants in marine organisms, including fish and algae, reflects the widespread pollution in the region (Bat *et al.*, 2019; Cadar *et al.*, 2019). Both the Mediterranean and Black Seas face significant pollution challenges from heavy metals, persistent organic pollutants - POPs (organochlorine pesticides - OCPs, and polychlorinated biphenyls - PCBs), and polycyclic aromatic hydrocarbons (PAHs). Addressing these issues requires integrated monitoring, risk assessments, and management strategies to safeguard these vital marine ecosystems. Heavy metals such as Fe, Zn, Cu, Mn, Ni, Co, Pb, and Cd have been monitored in the Mediterranean using bivalves as bioindicators, revealing varying concentrations linked to sources like wastewater discharges and river inputs (El-Sikaily *et al.*, 2004; Rosa *et al.*, 2022; Ardila, 2024). Persistent organic pollutants (POPs) and PAHs are other major pollutants in the Mediterranean, with studies emphasizing their risks to marine organisms and ecosystems, necessitating continuous monitoring and risk assessments

(Impellitteri *et al.*, 2023; Amirgaliyev, 2023; Hassaan, 2024). The discharge of these pollutants from rivers further exacerbates the pollution load in the sea (Montuori *et al.*, 2020; Montuori *et al.*, 2013).

This study aims to evaluate the ecological status of the North-Western Black Sea waters, with a particular focus on key contaminants and their impacts on the marine ecosystem. The research seeks to provide a comprehensive understanding of the environmental challenges facing the Black Sea, supported by new datasets on the concentrations of both inorganic and organic pollutants in the Romanian marine waters. These datasets will be crucial for developing targeted mitigation strategies and informing policy decisions aimed at protecting and sustainably managing the Black Sea.

MATERIALS AND METHODS

Study area and sampling

Between October 4-13, 2023, an expedition was carried out with the research vessel "Steaua de Mare 1". Water samples were taken from a network of 26 stations covering the area from the Romanian Black Sea coast up to the isobath of 60m (Fig. 1). The stations are included within the marine reporting regions (MRUs) within the Marine Strategy Framework Directive (MSFD):

- BLK_RO_RG_TT03: Northern stations, under the Danube's direct influence, up to a 30 m depth isobath.
- BLK_RO_RG_CT: Stations in the coastal zone, neighboring harbor activities, shipping, tourism, wastewater discharges, up to a 20 m depth isobath.
- BLK_RO_RG_MT01: Stations in shelf waters, including maritime activities, vessel traffic, and industrial activities, from a 30 m depth to 200 m.

The data analyzed for contaminants are based on surface water samples (N=26) and nutrient samples (N=72) from the water column, from standard depths of 0 m, 10 m, 20m, 30m, 50m. Water samples were taken with Niskin bathometers and stored in labelled containers at 4^{o}C.

Analytical Methods

Heavy metals

Surface water samples collected for metal analysis were acidified to pH=2 with SUPRAPUR Nitric acid 65% (Merck). Heavy metal (HM) - copper (Cu), cadmium (Cd), lead (Pb), nickel (Ni), and chromium (Cr) determinations were performed using the graphite furnace atomic absorbtion spectrometry (GF AAS) method on a High-Resolution Continuum Source AAS (HR-CS ContrAA 800 G equipment, Analytik Jena, Jena, Germany).Calibration was performed with working standards prepared from Merck stock solutions for each element in the following ranges: 0–50 µg/L (Cu), 0–10 µg/L (Cd), 0–25 µg/L (Pb), 0–50 µg/L (Ni), 0–50 µg/L (Cr). Each sample was measured in three replicates, and the average value was reported. The method detection limits for HMs were, depending on the element, between 0.001 and 0.01 µg/L (Grasshoff, 1999; IAEA-MEL, 1999a).

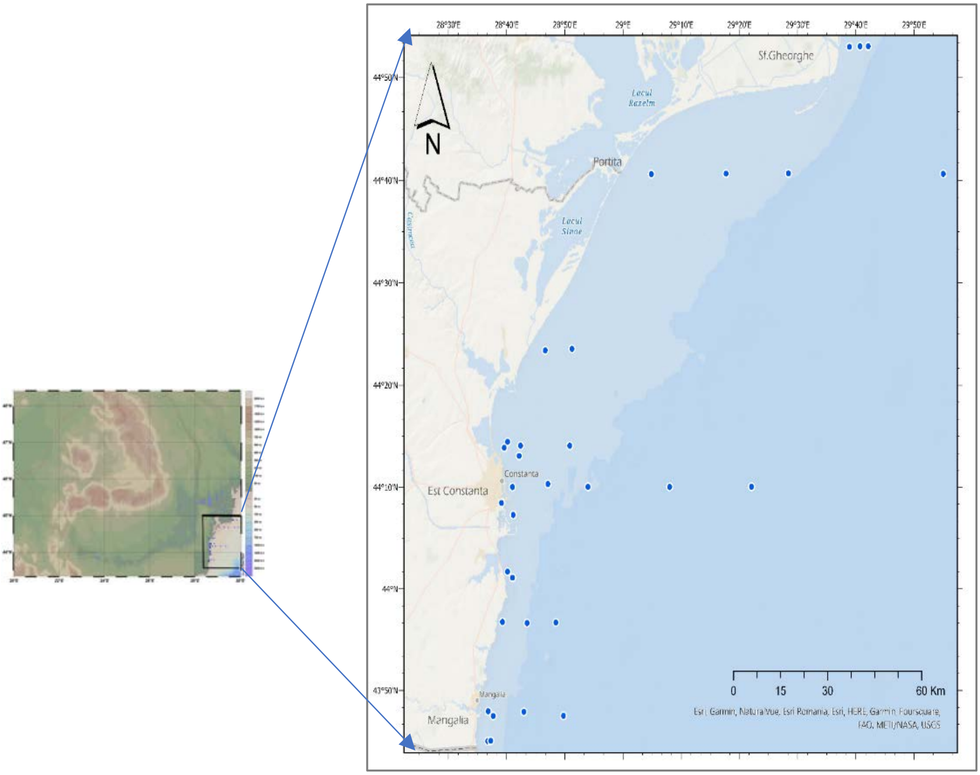


Fig. 1. Map of water sampling stations at the Romanian Black Sea coast, October 2023

Persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs)

Extraction of persistent organic pollutants from water samples was done with hexane/dichloromethane 3/1 mixture in separation funnel. Further sample processing went through the following steps: sample treatment with copper to remove sulfur compounds, fluorisil column separation, and sample concentration using Kuderna-Danish concentrator and nitrogen flow. The reagents used in this process were of gas chromatography grade purity and were sourced from established suppliers such as Merck.

The analytical determination of the content of persistent organic pollutants was done by gas chromatographic method with a Perkin Elmer (USA) gas chromatograph equipped with electron capture and mass spectrometry detectors, respectively. The POPs compounds analyzed were: HCB, lindane, heptachlor, aldrin, dieldrin, endrin, p,p'-DDE, p,p'-DDD, p,p'-DDT and polychlorinated biphenyls: PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, PCB 180. The PAHs compounds analyzed were: (naphthalene (Na), acenaphthylene (Ac), acenaphthene (Ace), fluorene (Flu), anthracene (An), phenanthrene (Ph), fluoranthene (Fln), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[g,h,i]perylene (BghiP),indeno [1,2,3-cd]pyrene (IP), and dibenzo[a,h]anthracene (DaA)) (IAEA-MEL, 1999b).

Nutrients

The nutrients dissolved in seawater have been quantified by spectrophotometric analytical methods, using a UV-VIS Spectrophotometer model UV-1900i (Shimadzu, Japan). Methods were validated in the NIMRD laboratory, having as reference the manual "Methods of Seawater Analysis" (Grasshoff, 1999). Detection limits and extended relative uncertainties, k=2, coverage factor, 95.45% are presented in Table 1.

Table 1. Detection limits and extended relative uncertainties

Parameter Measured	UM	Limit of detection (µmol/dm³)	Relative uncertainty, U (c) extended (%) k=2, coverage factor 95.45%
Nitrates, $(NO_3)^-$	µM	0.12	8.4
Nitrites, $(NO_2)^-$	µM	0.03	6.6
Ammonium, $(NH_4)^+$	µM	0.12	7.1
Phosphates, $(PO_4)^{3-}$	µM	0.01	14.0

The data were processed using MS Excel 365, Statistica (TIBCO Software Version 14.0.1.25), Ocean Data View (ODV) version 5.1.7., and ArcGIS Desktop 10.7 software. Distribution maps in ArcGIS were generated through inverse distance weighting (IDW) interpolation, a method that calculates cell values based on a weighted combination of nearby sampling points.

RESULTS AND DISCUSSION

The data resulted from the investigations carried out in 2023 on the levels of contaminants in the Romanian Black Sea waters are presented herein, structured within 5 tables and 16 figures (13 distribution maps, 5 box plots, 5 histograms and 2 scatter plots).

Heavy metals

The investigations carried out in 2023 on the levels of heavy metals in the surface marine waters of the Romanian seaside determined the following average concentrations and variation ranges: copper (Cu) 2,286 ± 1,724 (0,566 – 7,223) µg/L; cadmium (Cd) 0,051 ± 0,013 (0,031 – 0,091) µg/L; lead (Pb) 0,934 ± 1,314 (0,001 – 6,597) µg/L; nickel (Ni) 7,556 ± 19,592 (0,01 – 82,280) µg/L; chromium (Cr) 0,813 ± 0,268 (0,219 – 1,778) µg/L. Especially for nickel (Ni), but to some extent also copper (Cu) and lead (Pb), average annual values were higher than the median values, suggesting a highly (Ni), respectively slightly (Cu, Pb), right-skewed distribution, due to few extremely high concentration values (outliers) that are pulling the average up. Cadmium (Cd) and chromium (Cr) average and median values were very similar, suggesting a relatively normal distribution, with minimal outliers (Table 2). A cleared picture of the HMs concentrations distributions is provided in box plots and histograms depicted in Fig. 2-6, b), c). The 25th and 75th percentiles values can also help understand data distribution, identify outliers, and compare datasets. Furthermore, the 75th percentile of contaminant levels is a valuable metric for assessing ecological status in accordance with the Marine Strategy Framework Directive (MSFD) six-year reporting cycles (Boicenco *et al.*, 2018).

Table 2. Heavy metal concentrations determined in marine surface waters from the Romanian continental shelf in October 2023

	Average	Median	Minimum	Maxim	Percentile 25th	Percentile 75th	Std.Dev.	EQS
Cu (µg/L)	2.286	1.623	0.566	7.223	1.209	2.601	1.724	30
Cd (µg/L)	0.051	0.0503	0.031	0.091	0.041	0.059	0.013	1,50
Pb (µg/L)	0.934	0.463	0.001	6.597	0.138	1.202	1.314	14
Ni (µg/L)	7.556	0.411	0.010	82.280	0.010	2.582	19.592	34
Cr (µg/L)	0.813	0.839	0.219	1.778	0.757	0.839	0.268	100

The vast majority (about 62%) of copper concentrations determined in coastal and marine waters corresponding to the southern central zone of the coast are diminished, up to 2 µg / L. Slightly higher values were observed in the fluvial influence zone (transient waters) and marine waters (beyond the 30 m isobath) in the northern sector (Sf. Gheorghe and Portița transects), with possible anthropogenic influences (offshore platforms area) or from various diffuse sources from the north and northwest of the Black Sea region. Also, slightly higher values than average were measured in the central area of the coast in the stations near the discharges of the Constanta North and Constanta South treatment plants, as well as in the area near the port of Constanta (Fig. 2). It is noted that in 2023 there were no exceedances of the quality standard for the marine environment (30 µg/L Cu) (Ord. 161/2006).

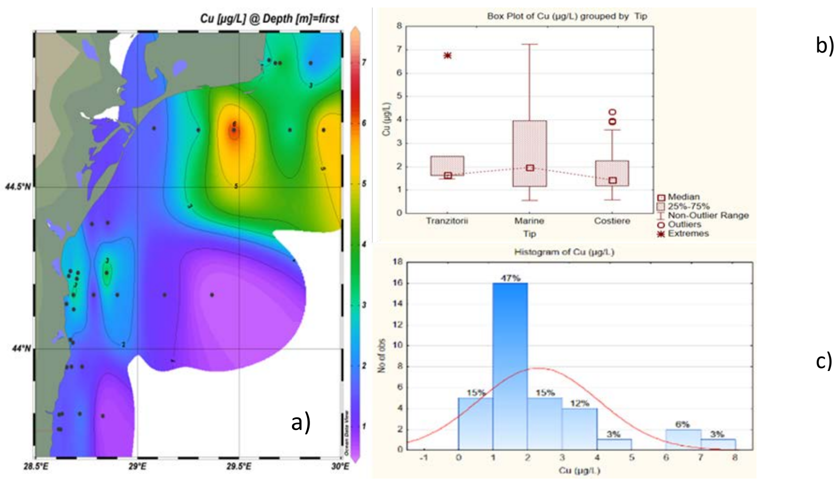


Fig. 2. Distribution of copper concentrations in Romanian Black Sea waters in 2023
a) distribution map (ODV 5.1.7); b) box plots and c) histogram (Statistica 14.0.1.25)

Cadmium concentrations were more evenly distributed, with most values (about 75%) below 0.06 µg/L. As in the case of copper, slightly higher values, in the range 0.06 – 0.09 µg/L, were observed in the fluvial influence zone (transitional waters) and marine waters (beyond the 30 m isobath) in the northern sector (Sf. Gheorghe and Portița transects), and also in the central-southern area of the coast in coastal waters near the discharges of the Constanta North, Constanta South and Eforie South wastewater treatment plants, as well as in the vicinity of Constanta port (Fig. 3). It is noted that in 2023 there were no exceedances of the quality standard for the marine environment (1,5 μg/L Cd) (Directive 39/2013/EU).

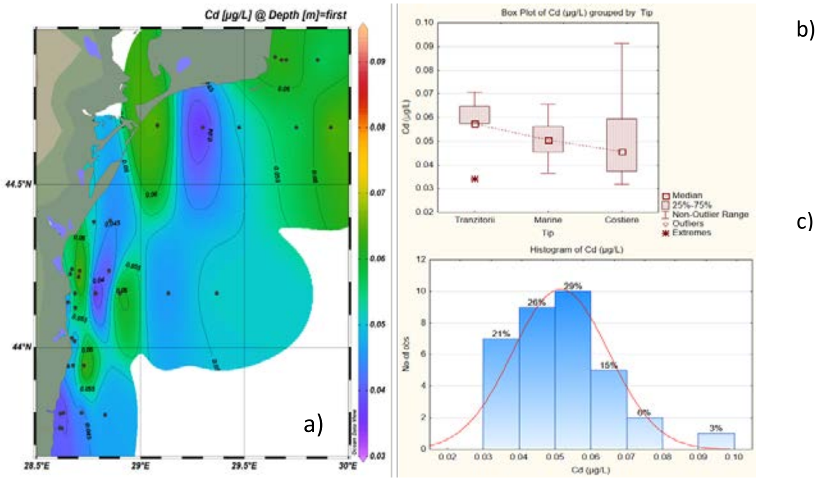


Fig. 3. Distribution of cadmium concentrations in Romanian Black Sea waters in 2023
a) distribution map (ODV 5.1.7); b) box plots and c) histogram (Statistica 14.0.1.25)

Lead had a relatively uniform distribution in marine waters, with most values (about 83%) below 2 μg/L. Slightly higher values, ranging from 2 to 6,59 μg/L, were observed in coastal waters in the central coastal area - Constanta North, Constanta South, as well as in the vicinity of Constanta port (roadstead area), probably in connection with the recent increase in naval traffic (Fig. 4). It is noted that in 2023 there were no exceedances of the quality standard for the marine environment (14 μg/L Pb) (Directive 39/2013/EU).

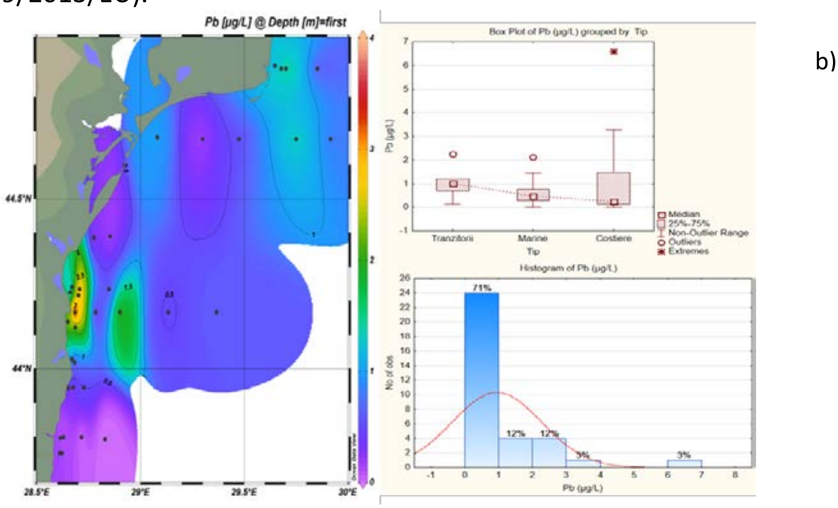
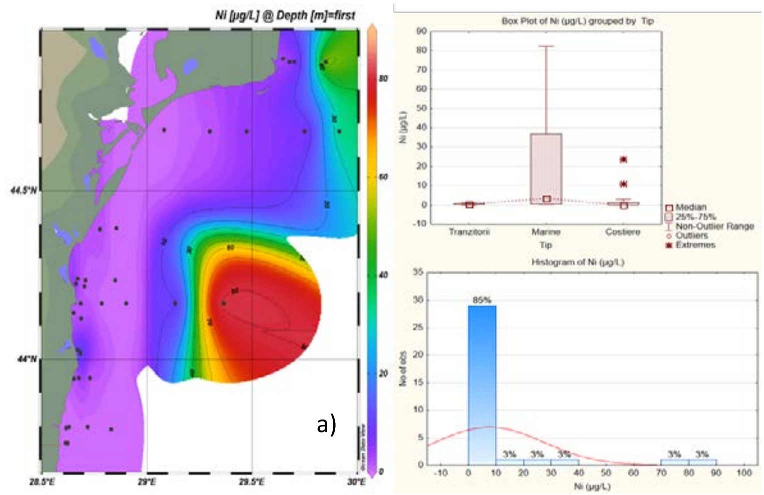


Fig. 4. Distribution of lead concentrations in Romanian Black Sea waters in 2023
a) distribution map (ODV 5.1.7); b) box plots and c) histogram (Statistica 14.0.1.25)

Nickel showed a different distribution from the other elements investigated, with lower concentrations in transient, coastal waters and part of marine waters (85% of samples had values below 10 µg/L). Higher values above 30 µg/L, have been observed in marine waters beyond the 40 and 60 m isobaths, probably in connection with diffuse sources from the north and northwest of the Black Sea region (Fig. 5). It is noted that in 2023 there were exceedances of the quality standard for the marine environment in 9% of seawater samples (34 µg/L Ni) (Directive 39/2013/EU).



b)

c)

Fig. 5. Distribution of nickel concentrations in Romanian Black Sea waters in 2023
a) distribution map (ODV 5.1.7); b) box plots and c) histogram (Statistica 14.0.1.25)

Chromium concentrations were evenly distributed in transient, coastal (southern sector) and marine waters, with the majority (89%) below 1 µg/L. Slightly higher values were observed in coastal waters in the central area of the coast - Constanta North, Constanta South (Fig. 6). It is noted that in 2023 there were no exceedances of the quality standard for the marine environment (100 µg/L Cr) (Ord. 161/2006).

Heavy metals, naturally occurring in the environment, can pose significant risks to both marine ecosystems and human health when their concentrations in the marine environment exceed safe levels. Human activities, such as mining, manufacturing, and industrial processes, can contribute to the elevated levels of heavy metals in the ocean.

Heavy metal contamination of the marine environment can be directly linked to urban or industrial sources, such as factories, thermal power plants, port facilities, wastewater treatment plants, offshore or coastal protection activities. (UNEP, 2002; UNEP, 2006). The influence of rivers can also be significant, constituting a major source of metals, especially in particulate forms, extreme hydrological events (floods) contributing to the intensification of this input. Atmospheric flows of metals, demonstrating both natural and anthropogenic influences, are also considered to have an important share, both in coastal areas and at basin level (Fashola *et al.*, 2016; Sakson *et al.*, 2018).

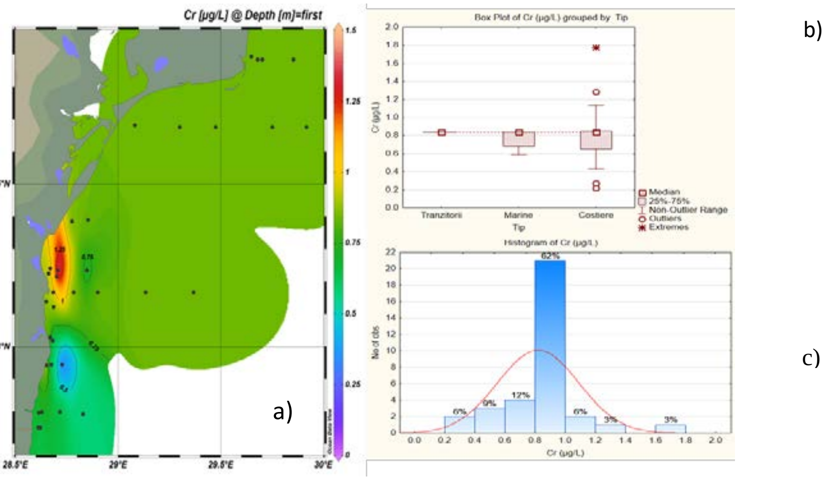


Fig. 6. Distribution of chromium concentrations in Romanian Black Sea waters in 2023
a) distribution map (ODV 5.1.7); b) box plots and c) histogram (Statistica 14.0.1.25)

Heavy metal pollution in seawater is a critical environmental issue due to its harmful effects on marine ecosystems and human health. Heavy metals such as lead (Pb), cadmium (Cd), copper (Cu), and zinc (Zn) often enter marine environments through human activities like industrial discharges, agricultural runoff, and urban wastewater (Rong *et al.*, 2022). The toxicity of heavy metals varies based on their concentration and type. High levels of metals like nickel, cobalt, and zinc are particularly toxic in industrially polluted waters (Abd-El-Haleem *et al.*, 2006). Heavy metals do not degrade but accumulate in sediments and marine organisms, causing long-term ecological damage and disrupting marine biogeochemical cycles (Lu *et al.*, 2022; Bharti, 2018). Beyond ecological damage, heavy metal pollution poses health risks to humans, especially through the consumption of contaminated seafood, such as shellfish (Lee *et al.*, 2022). Additionally, heavy metals can negatively impact marine hatcheries, especially during the vulnerable embryonic and larval stages (Hassan, 2023). Overall, the widespread introduction of heavy metals into seawater through human activities results in significant environmental and health challenges, necessitating effective monitoring and management to mitigate these impacts.

Heavy metals in seawater, especially lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As), present severe toxic effects on marine organisms and ecosystems. These metals are persistent in the environment and bioaccumulate in marine food webs, posing significant risks (Rong *et al.*, 2022; Singare *et al.*, 2012; Venkateswarlu & Venkatrayulu, 2019). Even at low concentrations, heavy metals like cadmium and lead can disrupt metabolic processes, impair growth, and affect the reproductive success of marine species. These metals induce oxidative stress and interfere with cellular functions in primary producers, like marine algae, which are vital to the marine food web (Caroppo *et al.*, 2006; Seo *et al.*, 2023; Jin *et al.*, 2021; Sun *et al.*, 2020).

Bioaccumulation and biomagnification further exacerbate the toxic effects of heavy metals as they concentrate in higher trophic levels, increasing exposure for larger predators. This is especially concerning for species consumed by humans, as heavy metal accumulation in seafood can lead to serious health issues, including neurological and developmental disorders (Danovaro, 2023; Mofarrah & Husain, 2011; Singare *et al.*, 2012; Rabaoui *et al.*, 2013). Beyond individual organisms, heavy metal pollution impacts entire ecosystems by reducing biodiversity and altering community structures. Sensitive species may decline, causing shifts in predator-prey dynamics and species competition, which destabilizes marine ecosystems (Jarwar *et al.*, 2023; Faiz, 2024; Sun *et al.*, 2020; Fu *et al.*, 2014). In summary, heavy metals in seawater have complex and far-reaching toxic effects, impacting marine life and posing serious health risks to humans through seafood consumption. Addressing this pollution is critical for maintaining ecological and public health.

Many studies conducted in the past on biogeochemical processes and distribution of heavy metals in the NW of the Black Sea have demonstrated the importance of metal input from the Danube and other localized sources, along with the influence of redox cycles of manganese (Mn) and iron (Fe) complexes. For example, higher concentrations of copper (Cu) and nickel (Ni) were found in the Black Sea continental shelf compared to the surface layer of the deep-sea basin, reflecting the significant impact of fluvial and anthropogenic inputs on this semi-enclosed sea. The data obtained confirmed that the distribution of concentrations of most elements has a pronounced gradient in the north-south direction, demonstrating the importance of the Danube's contribution. However, high concentrations of dissolved lead observed in offshore surface waters have been attributed to atmospheric inputs combined with less efficient metal capture in these particulate-poor waters (Tankere S.P.C., 2001).

Data obtained between 2012-2017 in Black Sea Romanian waters confirm that the distribution of concentrations of most elements in marine waters shows a pronounced gradient in the north-south direction, confirming the importance of the Danube's input. Also, most metals (Pb, Ni, Cr) showed a certain degree of enrichment around port areas (Constanta, Mangalia), suggesting the impact of local activities (treatment plants, port activities, naval traffic). In relation to the EQS, exceedances of the maximum allowable values for certain elements, such as cadmium, lead, or copper, have been recorded over time, supporting the need for further monitoring as well as for extending the range of elements investigated (Oros, 2019).

Persistent organic pollutants

Persistent organic pollutants (POPs) are a diverse group of organic substances, which are not found in the natural environment, but are synthetic chemicals released as a result of anthropogenic activities.

The category of persistent organic pollutants includes organochlorine pesticides and polychlorinated biphenyls, chemicals with toxic properties (carcinogenic, neurotoxic, affecting the functioning of different systems of organisms, so that over a certain dose they become lethal) and which, unlike other pollutants, resist degradation. The half-life in soil of these compounds can reach up to 10-15 years (endrin, DDT), and some of them even longer (between 3 and 22 years for HCB) (Association of Environmental Experts, 2003). They accumulate in living organisms, propagate through air, water, and migratory species, and accumulate in terrestrial and aquatic ecosystems.

Persistent organic pollutants have been extensively studied over the past 30 years, given their bioaccumulation, persistence and impact on both ecosystems and human health (Ritter *et al.*, 1995; Xing *et al.* 2005), as well as their capacity for long-distance transport in the environment. The transport and circulation of persistent organic pollutants depend on temperature: these chemicals circulate over the entire surface of our planet, evaporating in warm regions, then being carried by wind with dust particles, again settling in cold regions of the Earth. The volatilization and condensation sequence may repeat frequently and, consequently, POPs are detected in regions far from their place of origin (Ashraf, 2017). This is why pollution caused by persistent organic pollutants is a transboundary problem (UNEP, 2005). Over the past decade, persistent organic pollutants have often been detected in the Black Sea basin (Boicenco *et al.*, 2018; Denga *et al.*, 2017; Nicolaev *et al.*, 2019; Anemone Deliverable 2.1. and 2.3, 2021). Although the Convention on Persistent Organic Pollutants, adopted in Stockholm on 22 May 2001 (Law 261/2004) has been ratified in Romania, severely restricting the use of DDT and banning a number of highly polluting chemicals, such as aldrin, chlordane, dieldrin, endrin, heptachlorine, hexachlorobenzene, mirex, toxafen, and polychlorinated biphenyls (PCBs), the presence of these compounds in the components of the marine ecosystem in the Romanian Black Sea area continues to be evinced, sometimes in significant quantities.

Data obtained in October 2023 on the distribution of persistent organic pollutants in marine surface waters from the Romanian coast revealed a large variability in concentrations of these compounds, with average values of organochlorine pesticides ranging from 0,004 ±0,00 µg/L and 3,62±5,68 µg/L (Table 3) and between 0,004 ±0,00 µg/L and 0,11±0,30 µg/L in the case of polychlorinated biphenyls (Table 4).

The dominant compounds were organochlorine pesticides, with most compounds in this class having concentrations higher than quality standards for the marine environment (Directive 39/2013/EU), except hexachlorobenzene, dieldrin and endrin which had 75 % of their values below the limit of analytical determination.

The highest concentrations were recorded for heptachlor and p,p' DDT both in the northern area under fluvial influence and in the central and southern areas subject to anthropogenic pressures (discharges of treatment plants Constanta North, Constanta South and Eforie South, port activities in Constanta and Mangalia areas) (Fig. 7).

This distribution does not highlight a direct correlation with point sources from the Romanian seaside, but suggests pollution from diffuse sources, such as, for example, air pollution. It is worth noting that most of the values of polychlorinated biphenyls are below the detection limit, so although no quality standards are provided, we can say that marine water in the Romanian seaside area has a good quality in terms of these compounds. Concentrations higher than the detection limit were measured for PCB 52, in the central coastal area, in stations located on the 20m, 30m and 50m isobaths on the Transects Casino Mamaia, East Constanta and Constanta South (Fig. 8).

Table 3. Descriptive statistics of organochlorine pesticides in Romanian waters of the Black Sea, October 2023

	Average	Median	Minimum*	Maximum	Percentile 25th	Percentile 75th	Std. Dev.
HCB (µg/L)	0.004	0.004	0.004	0.004	0.004	0.004	-
Lindan (µg/L)	0.581	0.003	0.003	3.510	0.003	1.055	1.020
Heptaclor (µg/L)	1.985	0.675	0.003	6.616	0.247	4.000	2.187
Aldrin (µg/L)	0.151	0.003	0.003	1.050	0.003	0.085	0.307
p,p'DDE (µg/L)	0.349	0.002	0.002	5.335	0.002	0.358	1.040
Dieldrin (µg/L)	0.115	0.003	0.003	1.692	0.003	0.003	0.353
Endrin (µg/L)	0.153	0.002	0.002	2.223	0.002	0.002	0.507
p,p'DDD (µg/L)	0.447	0.002	0.002	2.487	0.002	0.636	0.826
p,p'DDT (µg/L)	3.624	0.144	0.002	16.330	0.002	7.080	5.680

*Limit of detection

Table 4. Descriptive statistics of polychlorinated biphenyls in Romanian waters of the Black Sea, October 2023

	N	Average	Median	Minimum*	Maximum	Percentile 25th	Percentile 75th	Std. Dev.
PCB28 (µg/L)	26	0.004	0.004	0.004	0.004	0.004	0.004	0.000
PCB52 (µg/L)	26	0.110	0.006	0.006	1.403	0.006	0.006	0.301
PCB101 (µg/L)	26	0.051	0.006	0.006	1.184	0.006	0.006	0.231
PCB118 (µg/L)	26	0.016	0.004	0.004	0.282	0.004	0.004	0.055
PCB153 (µg/L)	26	0.012	0.009	0.009	0.087	0.009	0.009	0.015
PCB138 (µg/L)	26	0.011	0.007	0.007	0.104	0.007	0.007	0.019
PCB180 (µg/L)	26	0.005	0.003	0.003	0.045	0.003	0.003	0.008

*Limit of detection

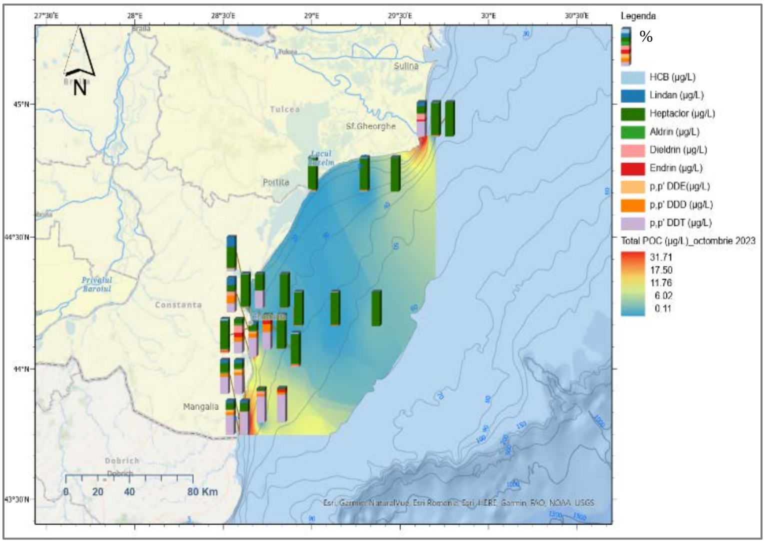


Fig. 7. Spatial distribution of organochlorine pesticide concentrations (µg/L) and the percentage contribution of each compound to the total (%) in Romanian waters of the Black Sea, October 2023 (ArcGIS Desktop 10.7)

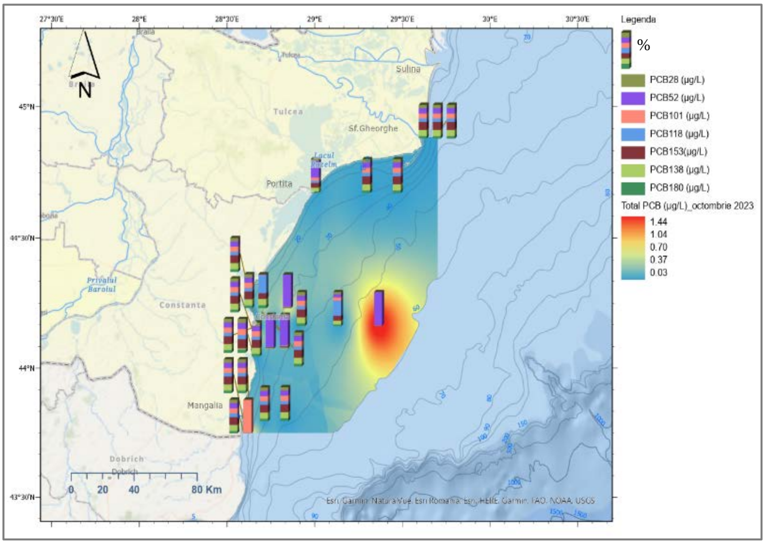


Fig. 8. Spatial distribution of polychlorinated biphenyls concentrations (µg/L) and the percentage contribution of each compound to the total (%) in Romanian waters of the Black Sea, October 2023 (ArcGIS Desktop 10.7)

Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) result from combustion processes involving C- and H-containing materials (coal, petroleum, fuel, wood). Emissions from anthropogenic activities are prevalent in the environment, but small amounts of PAHs also come from natural sources, such as forest fires (Baek *et al.*, 1991), biogenic sources (plants, phytoplankton, and microorganisms) and diagenesis processes. PAHs are found naturally in crude oil and constitute a significant component of petroleum products such as some paints, creosote (used in wood preservation) and asphalt, and can therefore be considered both as intentionally used substances and as by-products introduced into the environment unintentionally. PAHs are relatively reactive in the atmosphere but can persist long enough to be transported over long distances to areas far from the source (Daisey *et al.*, 1981; Gagosian *et al.*, 1981).

Both pyrolytic and petrogenic PAHs are present in the Black Sea basin. Petroleum-derived PAHs are dominant in the northeastern part (Sochi), pyrolytic sources are predominant in the Bosphorus region, and mixed pollution, both pyrogenic and petrogenic, in the other regions (ANEMONE Deliverable 2.3, 2021; Readman *et al.*, 2002).

Total concentrations of PAHs are comparable to relatively unpolluted areas in the Mediterranean and much lower than the levels reported for polluted North Sea and Irish Sea estuaries of the Mersey, Tyne, Thames rivers. The absence of a correlation between total hydrocarbons and PAHs indicates different primary sources for them (Readman *et al.*, 2002). Polycyclic aromatic hydrocarbons have started to be monitored at the Romanian seaside in the last 20 years, often observing concentrations that can affect the ecological status of the ecosystem, especially for fluorene, phenanthrene, anthracene, benzo(a)perylene, benzo(a)pyrene, benzo(g,h,i)perylene and dibenzo(a,h)anthracene (ANEMONE Deliverable 2.3. și 2.1, 2021; Nicolaev *et al.*, 2019).

According to research in the last decade, polycyclic aromatic hydrocarbons have a constant presence in the Black Sea ecosystem (Denga *et al.*, 2017), benzo(a)pyrene, as an indicator of PAHs from oil spills resulting from naval traffic or offshore activities, being often quantified in concentrations above the maximum permissible value (0.05 µg/L, Directive 39/2013/EU).

Data on the distribution of polyaromatic hydrocarbons obtained in October 2023 in marine surface waters from the Romanian coast revealed a great variability in concentrations of these compounds, with average values between the limit of detection (0,0001 µg/L) and 4,0085±7,462 µg/L (Table 5). It is noted that in 2023, except for benzo(g,h,i)perylene, in the Romanian waters of the Black Sea there were no exceedances of the quality standard for the marine environment (Directive 39/2013/EU).

The fluvial contribution to the mixture of polyaromatic hydrocarbons in the Black Sea waters is predominant by naphthalene and phenanthrene in the northern area (Portița and Sfântu Gheorghe profiles) up to the 30m isobath.

The total content of polyaromatic hydrocarbons in the Romanian waters of the Black Sea varied between 0.2756 and 98.6627 µg/L. Higher concentrations were measured in the central-southern area of the coast, in stations located on the 10m, 40m and 50m isobaths on the East Constanta and Eforie South transects (Fig. 9).

Polynuclear aromatic hydrocarbons (PAHs) registered heterogeneous values that highlighted the contribution of river intake in the northern waters as well as the influence of anthropogenic pressures in the central-southern area of the Romanian Black Sea coast (Fig. 10).

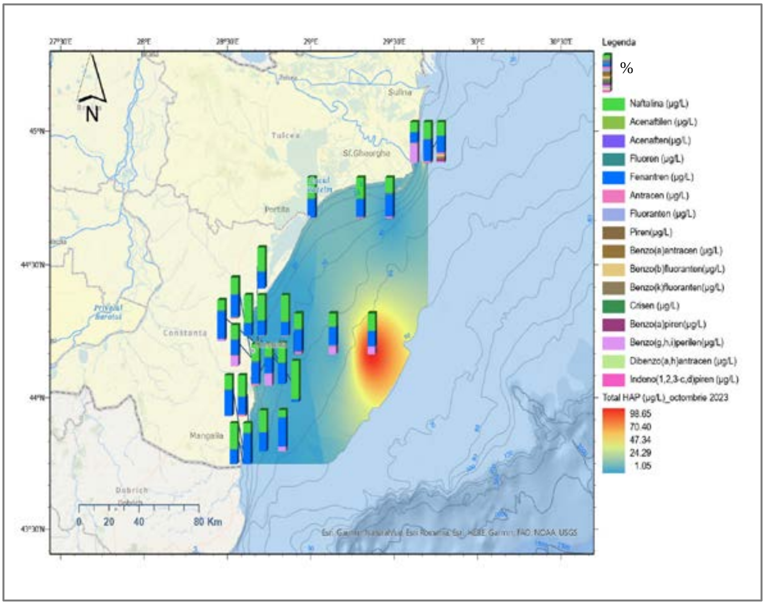


Fig. 9. Spatial distribution of polynuclear aromatic hydrocarbons (µg/L) and the percentage contribution of each compound to the total (%) in Romanian waters of the Black Sea, October 2023 (ArcGIS Desktop 10.7)

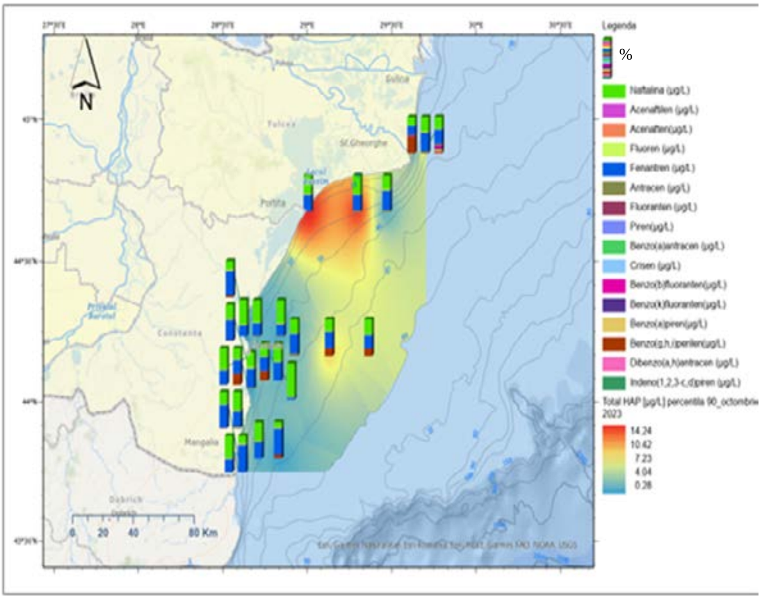


Fig. 10. Spatial distribution of polynuclear aromatic hydrocarbon concentrations (90th percentile) (µg/L) and the percentage contribution of each compound to the total (%) in Romanian waters of the Black Sea, October 2023 (ArcGIS Desktop 10.7)

Table 5. Descriptive statistics of polyaromatic hydrocarbons in Romanian waters of the Black Sea, October 2023

	N	Average	Median	Minimum	Maximum	Percentile 75th	Std. Dev.
Naphthalene (µg/L)	26	3,8420	0,8702	0,1019	41,484	3,1418	8,2730
Acenaftilen (µg/L)	26	0,0332	0,0093	0,0001	0,2727	0,0340	0,0583
Acenaften (µg/L)	26	0,0276	0,0082	0,0004	0,2083	0,0303	0,0443
Fluoren (µg/L)	26	0,2033	0,0519	0,0039	1,6596	0,1767	0,3580
Phenanthrene (µg/L)	26	4,0085	0,9454	0,0124	35,770	4,1912	7,4627
Anthracen (µg/L)	26	0,0961	0,0048	0,0001	1,1842	0,0368	0,2481
Fluoranten (µg/L)	26	0,0873	0,0006	0,0001	0,7846	0,0899	0,1875
Piren (µg/L)	26	0,0417	0,0047	0,0001	0,3209	0,0487	0,0766
Benzo[a]antracen (µg/L)	26	0,0001	0,0001	0,0001	0,0001	0,0001	0,0000
Crisen (µg/L)	26	0,0001	0,0001	0,0001	0,0017	0,0001	0,0003
Benzo[b]fluoranten (µg/L)	26	0,0643	0,0001	0,0001	1,6378	0,0001	0,3209
Benzo[k]fluoranten (µg/L)	26	0,0666	0,0001	0,0001	1,7229	0,0001	0,3378
Benzo[a]piren (µg/L)	26	0,0633	0,0001	0,0001	1,6448	0,0001	0,3225
Benzo(g,h,i)perilen (µg/L)	26	1,3326	0,0001	0,0001	18,412	0,1432	4,0757
Dibenzo(a,h)antracen µg/L)	26	0,0083	0,0001	0,0001	0,2042	0,0001	0,0400
Indeno(1,2,3-c,d)piren (µg/L)	26	0,0018	0,0001	0,0001	0,0252	0,0001	0,0055

The contaminant levels (HMs, POPs, PAHs) measured in seawater samples collected during 2023 fell within the historical range of variability observed over the last years, with no significant upward or downward trends. The new data collected in 2023 will be integrated into the existing dataset spanning 2018-2023, providing a more comprehensive foundation for the upcoming Marine Strategy Framework Directive (MSFD) ecological status assessment. In this respect, further statistical analyses will be conducted to evaluate long-term trends, identify potential sources of contaminants, and assess the overall ecological health of the marine environment for the last six years.

Nutrients

From the late 1970s to the early 1990s, especially in the 1980s (ICPDR, 2005), the Black Sea experienced a series of events that can be considered ecological disasters, such as the significant reduction, in only 10 years of the *Phyllophora field* in the northwestern region of the Black Sea (Mee, 1992, Gomoiu, 1992, Gomoiu, 1983). The increased river input of nutrients led to eutrophication, manifested by increased intensities of phytoplankton blooms and the appearance of cascading effects: reduced transparency, anoxia, mortalities, decomposition of dead organisms and oxygen consumption in the degradation process (Gomoiu, 1992). As a result, bottom waters became seasonally hypoxic or even anoxic, killing thousands of tons of benthic plants and animals (ICPDR – ICBS, 1999) and making the northwest of the Black Sea the largest highly eutrophicated marine area in the entire Mediterranean basin, from the Alboran Sea to the Sea of Azov (Zaitsev cited in Mee, 1999).

In the early 1990s, along with nutrient reduction measures that were adopted in the Danube basin, a decrease in nitrogen and phosphorus load was observed, resulting in the first signs of recovery (decrease in phytoplankton blooms, improvement of benthic oxygen regime and a significant increase in benthic macrofauna) (Gomoiu, 1992). Thus, in 2005, the northwestern Black Sea seemed to contain a severely modified but relatively functional ecosystem compared to the 1960s. Symptoms of dysfunction, such as the system's inability to recycle the high organic load it receives/produces, or the continued dominance of monospecific phytoplankton blooms, were still evident (BSC, 2007). According to the Transboundary Diagnostic Analysis (BSC, 2007), the coastal waters and continental shelf of the Black Sea were still predominantly eutrophic (rich in nutrients) and the central part was mesotrophic (medium nutrient level).

Thus, as a result of nutrient reduction in the Danube basin, eutrophication ceased to occur with the same effects and magnitudes, giving way to other events such as significant changes in the ecosystem from the "baseline" state, the 1960s (Oguz &Velikova, 2010).

Investigations into the fate and effect of nutrient concentrations in the marine environment is broad and multifaceted. Understanding nutrient concentrations in the marine environment is vital for assessing ecosystem health and developing effective management strategies. By tracking changes in nutrient levels over time and space, we can identify imbalances caused by natural fluctuations or human activities. This knowledge is crucial for distinguishing between natural and human-induced changes, allowing us to pinpoint sources of nutrient pollution and implement targeted management measures. Additionally, climate change can influence nutrient dynamics, further emphasizing the importance of monitoring and understanding these factors (Daskalov *et al.*, 2017).

Understanding how human activities like farming, fishing, and industrial processes affect the marine ecosystem is crucial for protecting it. Excessive nutrients and organic matter from these activities can lead to pollution and eutrophication, harming marine life and ecosystems. By connecting these activities to their impacts, we can better manage and protect our oceans.

During the studied period, two major sources of nutrients are distinguished at the Romanian Black Sea coast – the Danube and the neighboring area of the Constanta South treatment plant located within the Constanta Port (Constanta South station 10m). In Constanta South station 10m, phosphate and ammonium concentrations are much higher than in the Danube mouth area, registering extreme values, 30 and 300 times higher than averages, respectively (Table 6). However, it is considered an extremely limited effect given that on the 20m isobath (Constanta South station 20m) the values decrease significantly.

Table 6. Descriptive statistics of general physicochemical parameters and concentrations of dissolved nutrients in Romanian waters of the Black Sea, October 2023

Variable	N	Average	Minimum	Maximum	Percentile 25th	Percentile 75th	Std. Dev.
S [‰]	26	16,25	8,51	19,25	16,50	17,25	2,15
pH	26	8,45	8,26	8,95	8,37	8,45	0,15
O2 [cm3/L]	72	6,26	2,33	11,78	5,93	6,79	1,18
CBO5 [mgO2/L]	23	3,22	1,43	5,87	2,56	3,71	0,99
CCO-Mn [mgO2/L]	26	2,53	1,31	6,38	1,92	3,08	1,16
PO4[µM]	72	0,37	0,01*	12,53	0,06	0,27	1,47
TP[µM]	72	0,77	0,01*	12,97	0,34	0,69	1,58
Porg [µM]	72	0,41	0,01*	4,32	0,26	0,47	0,51
SiO4[µM]	72	7,81	1,40	47,40	3,95	6,95	8,57
NO2[µM]	72	0,13	0,03*	2,63	0,03	0,11	0,32
NO3[µM]	72	3,15	0,93	32,72	1,22	2,11	5,35
NH4[µM]	72	4,33	0,12*	114,20	1,17	4,43	13,31
DIN [µM] Sum of nitrate, nitrite, and ammonium	72	7,60	1,06	149,55	2,61	6,75	17,80

*undetected

The input of inorganic phosphorus (phosphates) predominates in the Sf. Gheorghe and Constanta South areas, while in the other areas the presence of organic phosphorus is observed, most likely resulting from the decomposition of phytoplankton

(Fig. 11). Once in seawater, dissolved organic phosphorus becomes an additional food source for microbial organisms (Nausch *et al.*, 2018).

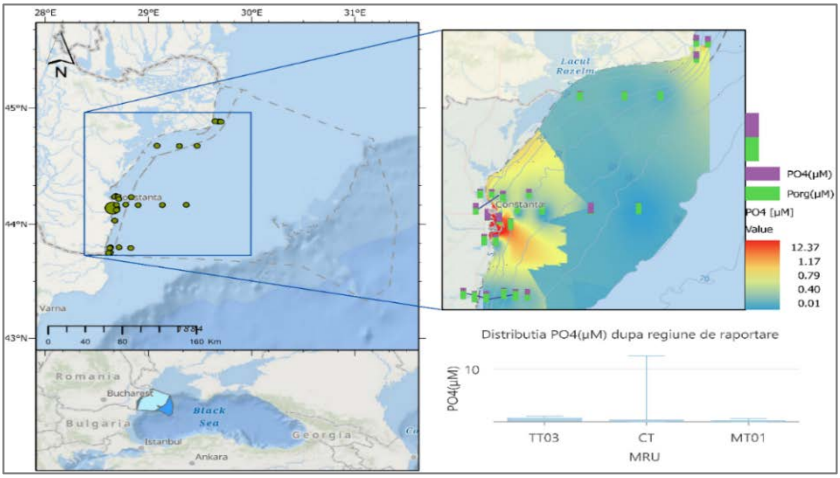


Fig. 11. Spatial distribution of dissolved phosphate concentrations in Black Sea surface waters, October 2023 (ArcGIS Desktop 10.7)

In surface waters, except for Constanta South, a significant decreasing gradient is observed from the northern to the southern area. However, in the northern area (between the Sf. Gheorghe profile and Constanta North) higher levels of inorganic phosphorus remain, even in a period of low flows of the Danube, which can lead to events of intense eutrophication and undesirable effects on the marine ecosystem (Fig. 12).

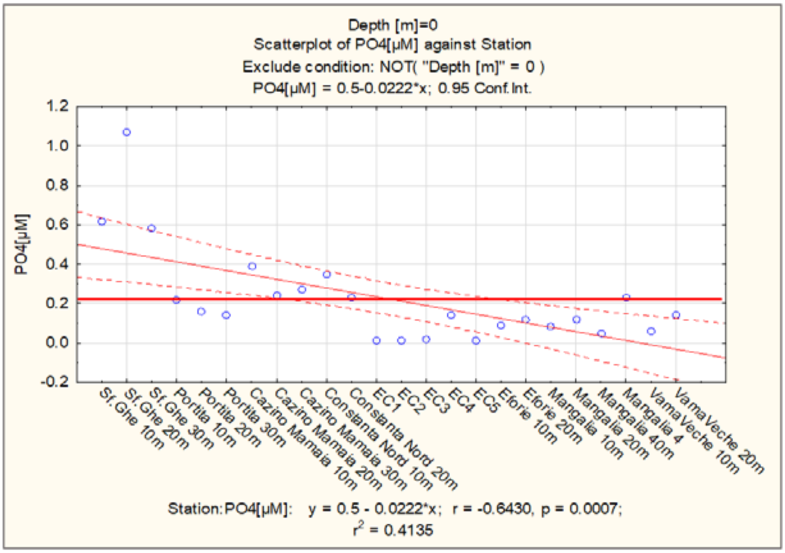


Fig. 12. Spatial distribution of dissolved phosphate concentrations in surface waters compared to the maximum allowable limit for marine waters (Statistica 14.0.1.25)

The concentrations of phosphates dissolved in the water column follow the increasing gradient with depth so that the maximum values are found at the water-sediment interface (Fig. 13). The accumulation of phosphorus in marine sediments can lead under hypoxia conditions, especially in summer during periods of stratification of the water column, to its release and intensification of eutrophication.

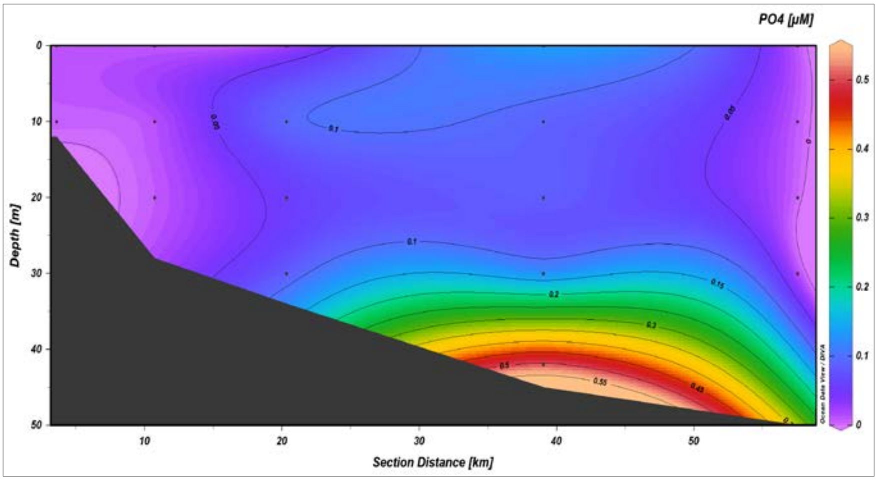


Fig. 13. Distribution of dissolved phosphate concentrations in the water column – East Constanta profile, October 2023 (ODV 5.1.7)

As with phosphorus, inorganic nitrogen input comes both from river sources, where nitrates predominate, and from coastal sources, where ammonium is predominant (Fig. 14), the preferred form of both phytoplankton and microbial organisms (Smith *et al.*, 2014).

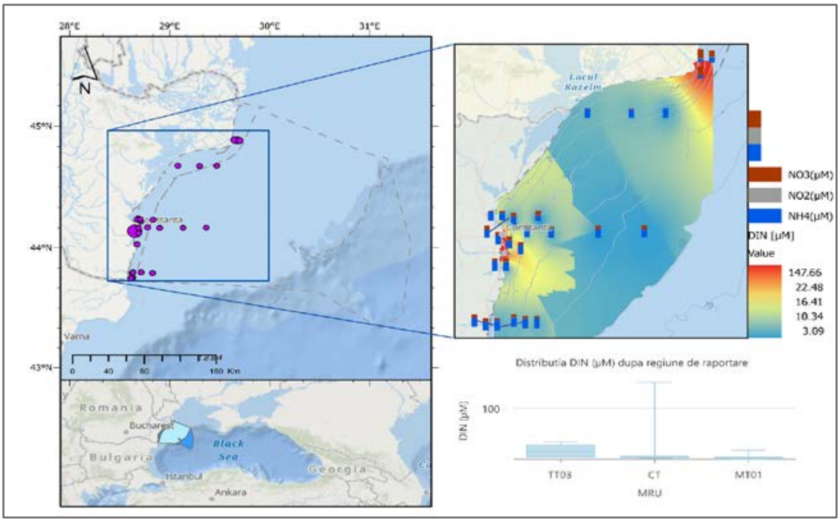


Fig. 14. Spatial distribution of dissolved inorganic nitrogen concentrations (sum of nitrates, nitrites and ammonium) in surface waters, October 2023 (ArcGIS Desktop 10.7)

In surface waters, except for Constanta South area, the significant decreasing gradient from the northern to the southern area is observed. However, in the area of direct influence of the Danube (Sf. Gheorghe profile) higher levels of inorganic nitrogen are maintained, even in a period of low flows of the Danube, which can lead to eutrophication-specific blooms impacting the pelagic habitat and the entire marine ecosystem (Fig. 15).

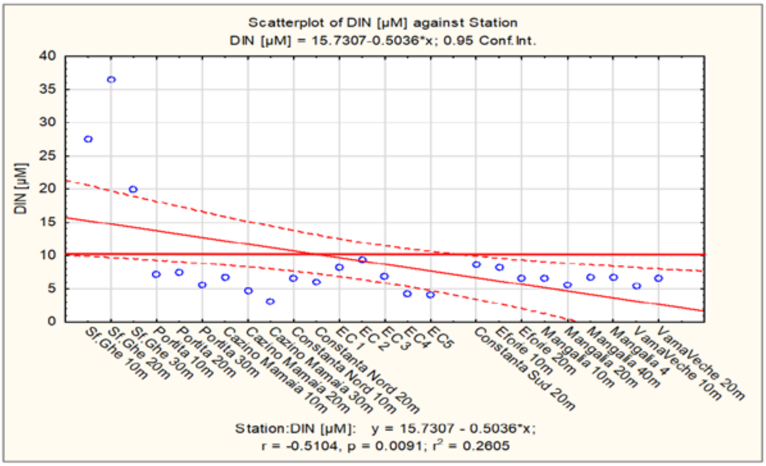


Fig. 15. Spatial distribution of concentrations of inorganic nitrogen (sum of nitrates, nitrites and ammonium) dissolved in surface waters within the maximum allowable limit for marine waters (Statistica 14.0.1.25)

In marine waters, concentrations of dissolved inorganic nitrogen in the water column follow the increasing gradient with depth such that maximum values are found at the water-sediment interface (stations EC4 and EC5). The effect of introducing inorganic nitrogen from coastal sources is observed up to the 30 m isobath (stations EC1-3) (Fig. 16).

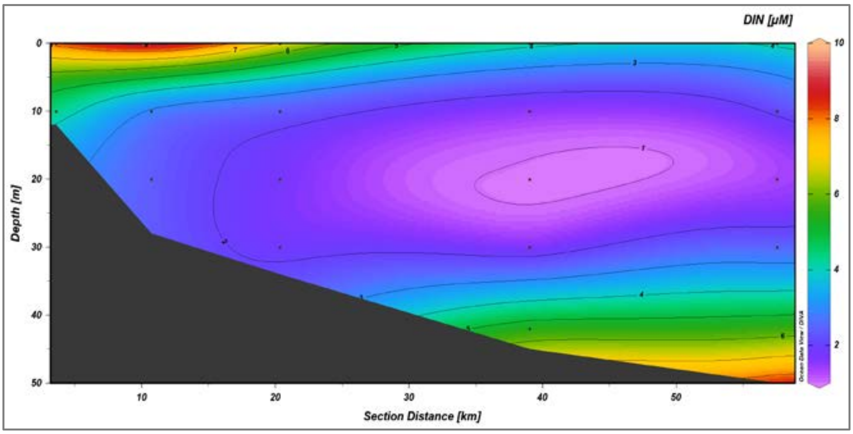


Fig. 16. Distribution of dissolved inorganic nitrogen concentrations (sum of nitrates, nitrites, and ammonium) in the water column – East profile Constanta, October 2023 (ODV 5.1.7)

CONCLUSIONS

Concentrations of heavy metals in transient, coastal, and marine national waters determined in 2023 were generally within natural variability limits. The differences in spatial distribution are correlated with the influence of localized sources, such as the Danube discharge area, discharges of treatment plants, port activities, naval traffic, etc. In 2023, there were few cases of exceedances of quality standards values for the marine environment.

Concentrations of persistent organic pollutants showed great variability in 2023, in marine surface waters along the Romanian coast. The dominant compounds were organochlorine pesticides, most compounds of this class having concentrations higher than quality standards for the marine environment, both in the northern area under fluvial influence and in the central and southern areas under anthropogenic pressures. Except for PCB 52, whose presence was observed in a few stations in the central coastal area, polychlorinated biphenyls had concentrations below the limit of detection.

The concentrations of polyaromatic hydrocarbons in the Romanian waters of the Black Sea in 2023 generally recorded values within the limits of normal variability. The differences in spatial distribution are correlated with the influence of sources such as the Danube discharge area, discharges from wastewater treatment plants, offshore activities, and naval traffic. It is noted that in 2023, except for benzo(g,h,i)perylene, in the Romanian waters of the Black Sea, there were no exceedances of the quality standard for the marine environment.

The introduction of nutrients into Romanian waters of the Black Sea represents a pressure on the marine ecosystem (directly on pelagic habitat) manifested by high concentrations of nutrients in sea waters. River nutrient input is a gateway from diffuse sources combining uses such as cultivation of living resources (especially agriculture) and urban and industrial uses. Although the pressure of Danube nutrients input slightly decreased recently, there remains a risk, especially with climate change potentially amplifying eutrophication and causing further damage to the marine ecosystem.

The higher-pressure intensity in urban and industrial coastal uses is sometimes manifested by extreme concentrations observed near sources. In 2017, 51.4% of wastewater discharged into the Black Sea was insufficiently treated, which contributed to maintaining the eutrophic status of Romanian Black Sea waters. Increasing the quality of water discharged into the sea (from wastewater treatment plants or industrial sources) will reduce the intensity of this pressure.

This is why robust implementation of ecosystem-based management is needed that also considers other pressures, such as coastal development, climate change, maritime transport, fisheries, etc. This requires continuous, integrated research, regular monitoring and assessments of pollutant levels and impacts. Such efforts need to be targeted and supported through continuous cooperation between scientists, policymakers and authorities, managers, and the general public.

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