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Spatial distribution of trace elements and potential contamination sources for surface sediments of the North-Western Black Sea, Romania

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It is essential to determine the concentrations of metals/metalloids in marine sediments and their contamination status to develop appropriate pollution control strategies and/or improve existing ones. Spatial distribution of aluminum (Al) and some trace elements, *i.e.*, arsenic (As), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn), accumulated in surface sediments of the north-western (NW) Black Sea (Romanian zone) was evaluated. Sediment samples were collected in 2019 from 32 stations located at water depths in the range of 12.7–149 m. The mean values ± standard deviations (*SD*) of element concentrations were as follows: 3.9 ± 1.6% for Al, 11.2 ± 10.2 mg/kg for As, 64.8 ± 27.0 mg/kg for Cr, 32.7 ± 15.0 mg/kg for Cu, 0.10 ± 0.09 mg/kg for Hg, 45.3 ± 23.8 mg/kg for Ni, 24.6 ± 9.6 mg/kg for Pb, and 68.0 ± 28.0 mg/kg for Zn. These values are not significantly different ($p > 0.05$) from those found in a previous study on surface sediments collected in 2018 from 22 stations located in the same area, but at lower water depths (13.5–67 m). Contamination factor (*CF*) was used to assess the contamination status of surface sediments. The mean values of *CF* (0.26–1.23) reveal low to moderate contamination with Pb and low contamination with the other elements. Principal component analysis (PCA) and correlation analysis indicated that As, Cu, Ni, Hg, Pb, and Zn were associated with clay, silt, and organic matter, suggesting that these elements mainly came from the Danube discharges and also from local anthropogenic sources, whereas Al, Cr, and partly Hg, Pb, and Zn originated from rock/soil weathering and erosion. The concentration levels of As, Cu, Hg, Ni, Pb, Zn, TOC, silt, and clay were higher in sediments collected from stations generally located at higher water depths (up to 118 m), suggesting that the TEs associated with the finer carriers were transported offshore by currents and waves, whereas the concentration levels of Al, Cr, Hg, and Zn were higher in sediments with lower levels of $CaCO_3$ content (10.1–24.3%), collected from shallower stations (water depths of 12.7–42.0 m).

KEYWORDS

trace element, Black Sea, sediments, contamination factor, PCA

1 Introduction

Trace elements (TEs) found in the coastal and marine ecosystems have become a serious concern towards ecological and human health risks due to their multiple sources, non-biodegradability, toxicity, bioaccumulation, and biomagnification along the aquatic food chain (Zhao et al., 2017; Wu et al., 2022; Zhou et al., 2022). They come from either natural sources (*e.g.*, river discharges, rainwater runoff, volcanic eruptions, wildfires, sand/dust storms, rock/soil weathering and erosion) or anthropogenic ones (including port activities, coastal tourism, discharges of domestic, municipal, agricultural, and industrial effluents into water bodies, burning of fossil fuels, waste incineration, construction, mining, and quarrying activities, crude oil refining and other industrial processes, offshore drilling for crude oil/gas and related transport) (Sánchez-García et al., 2010; Romano et al., 2022). Moreover, TEs can be produced *in situ* by marine organisms (Rubio et al., 2000).

TEs enter the sea mostly through the river discharges, either adsorbed onto inorganic and organic suspended particles or in dissolved form (Remeikaitė-Nikienė et al., 2018; Sun et al., 2020). Dissolved TEs rapidly come into the particulate phase, *e.g.*, via adsorption onto suspended particles, precipitation, flocculation (Karbassi et al., 2014; Karavoltsos et al., 2022). TEs associated with inorganic and organic suspended matter settle and accumulate in sediments, but they can be remobilized and released into the water under specific conditions, being more available to the biota, which could have significant detrimental effects on the ecosystem and human health (Omar et al., 2015; Oros, 2019). Accordingly, the surface sediments, which are both sinks and secondary sources of TEs, are important indicators of marine environment quality (Boran and Altınok, 2010; Perina et al., 2018).

Although fluvial inputs are relevant, direct discharges of wastewater/groundwater/rainwater/polluting products, coastal erosion, atmospheric deposition of particulate matter derived from natural and anthropogenic processes should not be neglected (Mülayim and Balkıs, 2015; Kay et al., 2022; Romano et al., 2022). Accumulation of TEs in marine sediments depends on various factors, *e.g.*, water depth, water physicochemical properties (pH, salinity, temperature, dissolved oxygen and organic matter content), sediment composition and texture, intensity/direction of winds, waves, and currents, fluvial, atmospheric, and other natural or anthropogenic inputs (Oros, 2019; Constantinescu et al., 2023). Multivariate analysis, especially PCA, is widely used to identify the main factors affecting the concentration of TEs in sediments and possible pollution sources/transport pathways (Martins et al., 2012; Kahal et al., 2018; Remeikaitė-Nikienė et al., 2018; El-Sorogy et al., 2020; Perumal et al., 2021; Vilhena et al., 2021; Wang et al., 2021; Kubra et al., 2022; Zhou et al., 2022).

The Romanian Black Sea waters are subject to multiple natural and anthropogenic pressures, determined by the Danube River discharges, rock/soil weathering and erosion, port and construction activities, coastal tourism, petrochemical industry, untreated/poorly treated wastewater discharges, offshore drilling for crude oil and gas, etc. (Catianis et al., 2016; Oros, 2019; Bucşe et al., 2020). Due to its very large drainage basin (801463 km^2), the Danube River, the second longest river in Europe, is a major pollution source in the NW Black Sea (Schmedtje et al., 2005; Sarı et al., 2018). Most of the studies on TE distribution in the Romanian Black Sea have focused especially on the coastal zone (Coatu et al., 2013; Catianis et al., 2016; Oros et al., 2016; Bucşe et al., 2020). Only a few researches, mainly conducted within different European projects (*e.g.*, MISIS, ANEMONE, BRIDGE), have investigated the distribution of TEs in deeper water areas.

The present study has aimed at: (i) assessing the spatial distribution of Al and some TEs, *i.e.*, As, Cr, Cu, Hg, Ni, Pb, and Zn, in the surface sediments from the coastal and marine environment (water depths of 12.7–149 m) of the NW Black Sea (Romanian area); (ii) evaluating their contamination status in the study area; (iii) establishing the effects of main environmental factors (water depth, sediment texture, organic matter and $CaCO_3$ content) on element accumulation and identifying possible contamination sources by applying statistical analysis. Accordingly, the paper brings new information on the current concentration levels of some elements in the surface sediments located at water depths of up to 150 m in the Romanian Black Sea. The Romanian monitoring program carried out according to the Marine Strategy Framework Directive (MSFD) requirements is mainly focused on the coastal waters, the contamination level in the deeper waters being less monitored and studied. The data brought by this paper cover the entire Romanian shelf and could be used in the revision of the Programme of Measures for Romania, but also in other national and/or regional management plans/strategies. Knowing the values of TE concentration in marine sediments, assessing their contamination status, identifying the factors that control the element distribution in sediments and possible contamination sources are essential to develop appropriate pollution control strategies and/or to strengthen existing strategies in support of the development of relevant blue economy sectors (*e.g.*, fisheries, aquaculture, coastal tourism) and, consequently, of increasing the well-being of coastal communities. Limiting/preventing the introduction of TEs into the marine ecosystem is a major challenge faced by scientists and managers.

2 Materials and methods

2.1 Study area

The research area, located along the Romanian coast of the Black Sea, consists of two sectors separated by Cape Midia (Figure 1).

The northern sector, which encompasses the maritime part of the Danube Delta Biosphere Reserve (DDBR), the largest biosphere reserve in the European Union (with an area of about 5800 km^2 and three main distributaries, *i.e.*, Chilia, Sulina, and Sf. Gheorghe), is strongly affected by the Danube discharges. The Danube is the most important supplier of pollutants to the Black Sea, its water and sediment discharges being of about 200 km^3/year (*cca.* 200000 Mt/year) and 25–35 Mt/year, respectively (Panin and Jipa, 2002;

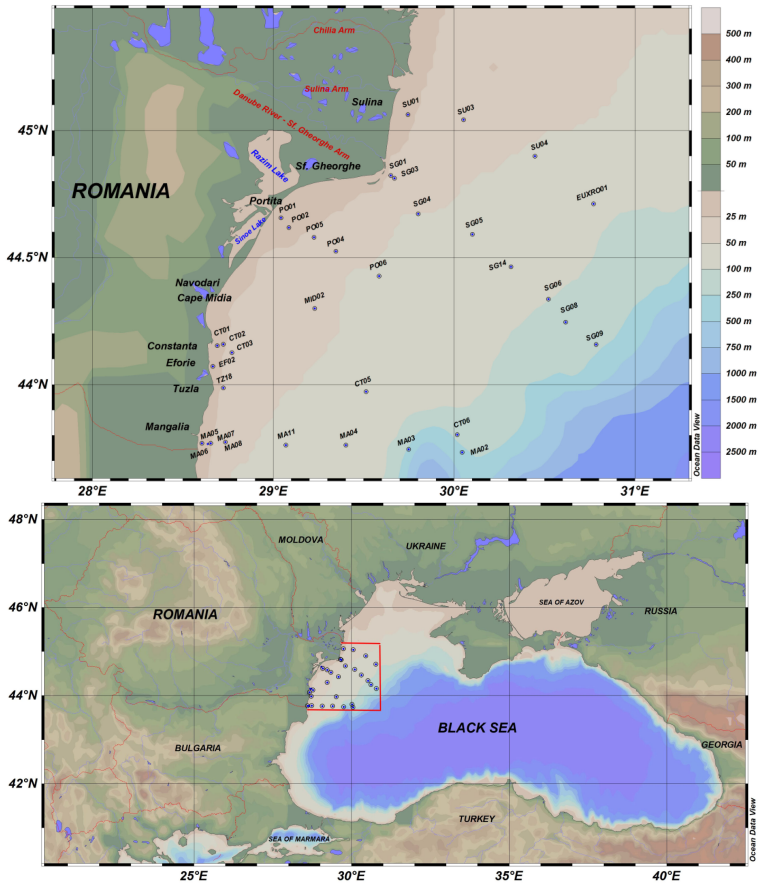

FIGURE 1
Map of the study area.

Bondar and Iordache, 2016). In addition to the Danube discharges, the sea-based activities, including maritime transport, oil and gas exploitation, are potential contamination sources in this sector.

The southern sector, extended from Cape Midia to the border with Bulgaria, is subject both to the influence of the Danube and to anthropogenic pressures resulted from port and construction activities, coastal tourism, petrochemical industry, agriculture, untreated/poorly treated wastewater discharges, etc. The port of Constanta, the largest port on the Black Sea, and the satellite ports of Mangalia and Midia are located in this area. The port of Constanta has specialized terminals that operate various products, including crude oil, diesel, gas, iron ore, bauxite, coal, coke, timber, chemicals, cement, construction materials (Bucşe et al., 2022). The oil terminal located in the port of Midia, which belongs to the city of Navodari, supplies crude oil for the nearby Petromidia Refinery, the largest Romanian oil refinery. In addition to the cities of Constanta, Mangalia, and Navodari, which are important tourist centers, the southern region of the study area also includes two other localities where tourism is quite developed, *i.e.*, the city of Eforie and commune of Tuzla. Wastewater treatment plants of Constanta, Eforie, and Mangalia are significant sources of organic matter and TEs, including Cd, Cr, Cu, Fe, Ni, Pb, and Zn (Lazăr et al., 2013). Moreover, offshore there are drilling platforms for oil and natural gas (Secrieru and Secrieru, 2002; Bucşe et al., 2020; Bucşe et al., 2022).

In the study area, the influence of the Danube freshwater extends to the south, towards Mangalia, due to the longshore current oriented from the Danube Delta to south, and also to the deep-sea zone (Panin and Jipa, 2002; Catianis et al., 2016; Constantinescu et al., 2023). Moreover, the Danube sandy sediments are remobilized from north to south, due to the longitudinal marine coastal current (Catianis et al., 2016). The jetties of the ports of Sulina, Midia, Constanta, and Mangalia are major obstacles for the transport of sediments, which are either deposited near the ports or redirected offshore (Ungureanu and Stanica, 2000). The sediment deficit from the seashore has caused a significant coastal erosion, especially in the southern sector (Ungureanu and Stanica, 2000; Anton et al., 2019).

2.2 Sediment sampling and characterization

Sediment samples were collected from 32 sampling stations (Figure 1), covering the Romanian shelf waters, in August–September 2019, on board the *RV Mare Nigrum*. The sampling

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stations were positioned as follows: 28 were along 5 transects, *i.e.*, Sulina–E (SU01, SU03, and SU04), Sf. Gheorghe–SE (SG01, SG03, SG04, SG06, SG08, SG09, and SG14), Portita–SE (PO01, PO02, and PO04–06), Constanta–SE (CT01–03, CT05, and CT06), and Mangalia–E (MA02–08, and MA11), one was between Sulina–E and Sf. Gheorghe–SE transects (EuxRO01), and other 3 were in the Midia, Eforie, and Tuzla areas (MID02, EF02, and TZ18). Water depths (h = 12.7–149 m) and coordinates of sampling stations are specified in Table 1.

Sediment samples were collected using a Van Veen grab sampler with an opening area of 0.12 m^2, and only their upper part (0–2 cm depth) was analyzed. The grain size of sediment samples was measured with a Mastersizer 2000E (ver. 5.20) laser diffraction granulometer (Malvern Instruments Ltd., Malvern, Worcestershire, UK) and Shepard's ternary diagram was used for their lithological classification.

Total organic carbon content (*TOC*) was determined using a titration method involving the oxidation of carbon with excess

TABLE 1 Water depths and coordinates of sampling stations.

No.	Station	Water depth, h (m)	Latitude (°)	Longitude (°)
1	SU01	16.6	45.0617	29.7450
2	SU03	34.6	45.0419	30.0517
3	SU04	52.3	44.8994	30.4467
4	EuxRO01	80.0	44.7111	30.7706
5	SG01	20.6	44.8233	29.6492
6	SG03	36.2	44.8119	29.6703
7	SG04	53.0	44.6722	29.8019
8	SG06	93.0	44.3361	30.5211
9	SG08	119	44.2447	30.6167
10	SG09	149	44.1569	30.7853
11	SG14	79.0	44.4628	30.3139
12	PO01	12.7	44.6559	29.0428
13	PO02	19.5	44.6178	29.0869
14	PO04	42.0	44.5243	29.3467
15	PO05	29.7	44.5795	29.225
16	PO06	53.0	44.4267	29.5853
17	MID02	43.5	44.2994	29.2297
18	CT01	17.0	44.1525	28.6911
19	CT02	27.7	44.1583	28.7236
20	CT03	33.2	44.1247	28.7714
21	CT05	65.0	43.9722	29.5133
22	CT06	92.0	43.8031	30.0178
23	EF02	16.3	44.0714	28.6664
24	TZ18	33.0	43.9869	28.7236
25	MA02	118	43.7333	30.045
26	MA03	71.0	43.7449	29.7482
27	MA04	66.3	43.7614	29.4019
28	MA05	16.1	43.7689	28.6061
29	MA06	26.0	43.7664	28.6383
30	MA07	33.0	43.7686	28.6542
31	MA08	44.0	43.7731	28.7364
32	MA11	56.0	43.7611	29.0694

potassium dichromate ($K_2Cr_2O_7$), in the presence of concentrated sulfuric acid (H_2SO_4), and the back titration of excess $K_2Cr_2O_7$ with Mohr's salt, using diphenylamine as an indicator (Gaudette et al., 1974). Calcium carbonate content ($CaCO_3$) was calculated based on a volumetric analysis method consisting in treating the sample with a hydrochloric acid (HCl) solution (0.5 N) and determining the excess acid by back titration with a sodium hydroxide (NaOH) solution (0.5 N), in the presence of phenolphthalein (Black, 1965).

The concentrations of aluminum (*Al*), arsenic (*As*), chromium (*Cr*), copper (*Cu*), nickel (*Ni*), lead (*Pb*), and zinc (*Zn*) were measured by X-ray fluorescence spectrometry using an ED-XRF SPECTRO XEPOS spectrometer (SPECTRO Analytical Instruments GmbH, Kleve, Germany). The concentration of mercury (*Hg*) was determined using a Milestone DMA-80 direct mercury analyzer (Milestone Srl, Sorisole, Bergamo, Italy). Samples were incinerated at 650°C to release Hg vapor that was trapped in a gold amalgamator and then desorbed for detection (at 260 nm) by atomic absorption spectroscopy (U.S. EPA, 2007).

The accuracy of element/compound analyses was evaluated using a certified reference material (CRM) from NCS Testing Technology Co., Ltd. (Beijing, China), *i.e.*, NCS DC 73022. The measured and certified values of element/compound concentration in NCS DC 73022, given as mean ± standard deviation (*SD*) in Table 2, indicate a high accuracy of analytical methods (the percent recovery values in the range of 95.7–104.8%). The precision of element/compound analyses was checked based on the relative standard deviation (*RSD*) of measured concentration values (triplicate measurements). The data summarized in Table 2 indicate a high precision of analytical methods (0.23% ≤ *RSD* ≤ 3.05%).

2.3 Contamination assessment

The contamination status of surface sediments was evaluated based on the contamination factor (*CF*), which was determined using Equation 1, where *E* is the element (Al, As, Cr, Cu, Hg, Ni, Pb, and Zn) concentration in the sample and E_b the background element concentration (Håkanson, 1980). Mean values of shale element concentrations reported by Turekian and Wedepohl (1961) (Al_b = 8% = 80000 mg/kg, As_b =13 mg/kg, Cr_b = 90 mg/kg, Cu_b = 45 mg/kg, Hg_b = 0.40 mg/kg, Ni_b = 68 mg/kg, Pb_b = 20 mg/kg, and Zn_b = 95 mg/kg) were used as background values, according to other studies on the element distribution in the Black Sea (Gedik and Boran, 2013; Alkan et al., 2021; Özşeker et al., 2022). The contamination status of sediments based on *CF* values is as follows: low contamination for *CF* < 1, moderate contamination for 1 ≤ *CF* < 3, considerable contamination for 3 ≤ *CF* < 6, and very high contamination for *CF* ≥ 6 (Håkanson, 1980).

$$CF = CF_E = \frac{E}{E_b}, \quad E = Al, As, Cr, Cu, Hg, Ni, Pb, Zn \tag{1}$$

2.4 Data processing

Statistical analysis was performed using XLSTAT ver. 2019.1 (Addinsoft, New York, NY, USA). The Pearson correlation coefficient (*r*) was used to evaluate the strength of the linear correlations between different parameters. One-way analysis of variance (ANOVA) was applied to determine whether the mean values of variables in different groups were significantly different ($p < 0.05$) or not. Characteristic parameters of sediments were processed using PCA, a multivariate technique that is widely used to reduce the dimensionality of large data sets (Vaalgamaa and Korhola, 2004; Belivermis et al., 2016; Bucşe et al., 2021; Kapranov et al., 2021; Calcan et al., 2022; Egri et al., 2022; Moloşag et al., 2023). Spatial distributions of *TOC*, $CaCO_3$, element concentrations, and contamination factors were visualized using the Ocean Data View (ODV) software, ver. 5.6.5 (Schlitzer, 2023).

TABLE 2 Mean ± *SD* of measured and certified values of element/compound concentration in certified reference material (NCS DC 73022), relative standard deviation (*RSD*) of measured concentration values (triplicate measurements), and percent recovery values.

Element/compound	Measured values		Certified values	Percent recovery values (%)
	Mean ± *SD* (mg/kg)	*RSD* (%)	Mean ± *SD* (mg/kg)	
Al_2O_3	134000 ± 1400	1.04	136100 ± 1200	98.5
As	291 ± 1	0.34	304 ± 20	95.7
Cr	69.8 ± 0.3	0.43	72 ± 3	96.9
Cu	497 ± 3	0.60	483 ± 20	102.9
Hg	0.113 ± 0.001	0.88	0.115 ± 0.023	98.3
Ni	30.4 ± 0.3	0.99	29 ± 1	104.8
Pb	131 ± 4	3.05	126 ± 5	104.0
Zn	874 ± 2	0.23	874 ± 19	100.0

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3 Results and discussion

3.1 Contents of sand, silt, clay, TOC, and $CaCO_3$ in surface sediments

Depending on the percentages of sand (*Sand*), silt (*Silt*), and clay (*Clay*), which are summarized in Table 3, the types of surface sediments collected from the sampling stations were mostly clayey silt and sandy silt.

Total organic carbon content (*TOC*) and calcium carbonate content ($CaCO_3$) in surface sediments are also summarized in Table 3, and spatial distributions of *TOC* and $CaCO_3$ are shown in Figure 2. The mean values ± *SD* of *TOC* (1.20 ± 0.73%) and $CaCO_3$ (33.0 ± 19.4%) were in a good agreement with those

TABLE 3 Contents of sand (*Sand*), silt (*Silt*), clay (*Clay*), total organic carbon (*TOC*), and calcium carbonate ($CaCO_3$) in surface sediments and sediment types in the study area.

No.	Station	*Sand* (%)	*Silt* (%)	*Clay* (%)	Sediment type	*TOC* (%)	$CaCO_3$ (%)
1	SU01	19.7	64.8	15.5	sandy silt	0.91	10.1
2	SU03	33.9	52.6	13.6	sand-silt-clay	0.60	47.1
3	SU04	14.2	73.5	12.4	sandy silt	1.46	57.3
4	EuxRO01	7.0	76.3	16.7	silt	2.60	47.2
5	SG01	8.5	69.4	22.2	clayey silt	0.87	10.5
6	SG03	8.0	71.3	20.7	clayey silt	1.48	11.7
7	SG04	16.4	62.4	21.2	clayey silt	2.04	35.9
8	SG06	8.6	73.6	17.8	clayey silt	2.17	45.6
9	SG08	11.7	67.2	21.1	clayey silt	2.15	47.4
10	SG09	15.1	68.1	16.7	clayey silt	1.37	52.0
11	SG14	9.2	77.2	13.7	silt	1.10	54.5
12	PO01	48.3	44.4	7.3	sand-silt-clay	0.11	24.3
13	PO02	14.7	70.3	15.0	clayey silt	0.78	13.6
14	PO04	15.7	68.9	15.3	sandy silt	2.54	12.2
15	PO05	10.5	69.3	20.3	clayey silt	1.47	11.1
16	PO06	9.0	70.8	20.2	clayey silt	2.11	11.8
17	MID02	12.7	66.2	21.1	clayey silt	1.27	50.7
18	CT01	80.3	16.6	3.1	sand	0.02	12.5
19	CT02	22.8	63.8	13.5	sandy silt	0.70	11.6
20	CT03	18.3	67.7	14.1	sandy silt	1.20	11.3
21	CT05	10.9	74.8	14.3	clayey silt	1.80	55.7
22	CT06	13.0	68.4	18.7	clayey silt	1.52	55.0
23	EF02	82.7	13.5	3.8	sand	0.08	14.5
24	TZ18	29.3	58.1	12.7	sandy silt	0.54	12.6
25	MA02	9.2	70.0	20.8	clayey silt	1.96	52.8
26	MA03	11.5	69.9	18.7	clayey silt	1.80	57.9
27	MA04	21.8	64.6	13.6	sandy silt	0.64	47.4
28	MA05	73.6	22.3	4.1	silty sand	0.43	19.1
29	MA06	62.0	30.2	7.8	silty sand	0.26	26.8
30	MA07	31.9	55.6	12.5	sandy silt	0.95	21.9
31	MA08	26.7	56.7	16.6	sandy silt	0.53	57.5
32	MA11	12.0	74.3	13.7	clayey silt	1.06	57.5

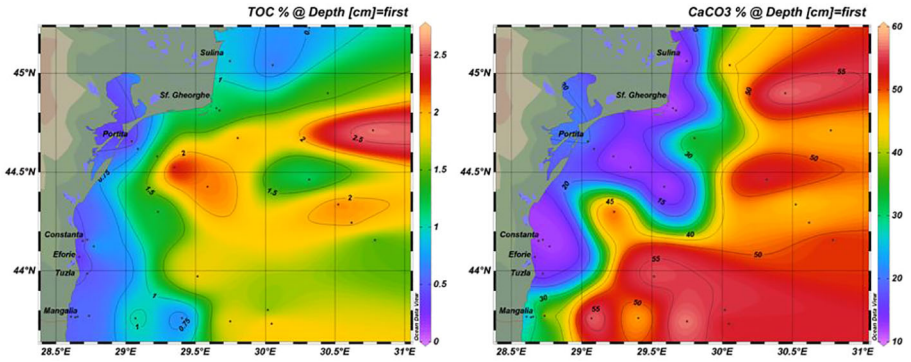

FIGURE 2
Spatial distributions of total organic carbon content (*TOC*) and calcium carbonate content ($CaCO_3$) in surface sediments in the study area.

obtained by Secrieru and Secrieru (2002) for surface sediments (0–2 cm depth) collected from Ukrainian, Romanian, and Bulgarian coasts of the Black Sea (1.53 ± 0.84% for *TOC* and 36.5 ± 24.4% for $CaCO_3$). According to the data presented in Table 1, Table 3, and Figure 2, higher levels of *Sand* (48.3–82.7%) as well as lower levels of *Clay* (3.1–7.8%) and *TOC* (0.02–0.43%) were found in sediments from the shallowest stations (water depths of 16–27 m) located south of the Danube mouth areas, *i.e.*, PO01, CT01, EF02, MA05, and MA06 (near Portita, Constanta, Eforie, and Mangalia). The sediments collected from the rest of the stations had the following percentages: *Sand* = 7.0–33.9%, *Silt* = 52.6–77.2%, *Clay* = 12.4–22.2%, and *TOC* = 0.53–2.60%. Higher values of *TOC* (> 2%) were determined in surface sediments from stations EuxRO01 (2.60%), PO04 (2.54%), PO06 (2.11%), SG04, SG06, and SG08 (2.04–2.17%), located at higher water depths (42–119 m). A particularly important component of marine sediments is $CaCO_3$. Its concentration varied between 10.1% and 57.9%, showing an increasing trend towards the sea (Figure 2). The slightly calcareous sediments ($CaCO_3$ in the range of 10–30%) and the calcareous ones ($CaCO_3$ in the range of 30–50%) were found at 16 stations and 6 stations, respectively. The lowest levels of $CaCO_3$ (10.1% and 10.5%) were identified in sediments from the stations near the mouths of Sulina (SU01) and Sf. Gheorghe (SG01) arms (water depths of 16.6 m and 20.6 m, respectively). Values of $CaCO_3$ above 50% were found in sediments from 10 stations located at water depths in the range of 43.5–149 m, *i.e.*, 3 stations in the eastern part of the study area (SU04, SG09, and SG14), 6 in the south (CT05, CT06, MA02, MA03, MA08, and MA11), and one in the west (MID02), the highest levels of $CaCO_3$ (57.5–57.9%) being determined along the Mangalia-E transect (stations MA03, MA08, and MA11).

3.2 Element concentrations in surface sediments and potential contamination sources

Concentrations of aluminum (*Al*), arsenic (*As*), chromium (*Cr*), copper (*Cu*), mercury (*Hg*), nickel (*Ni*), lead (*Pb*), and zinc (*Zn*) in surface sediments in the study area are specified in Supplementary Table 1, and their spatial distributions are shown in Figure 3. Higher levels of *As* (10.0–57.1 mg/kg), *Cu* (33.7–62.9 mg/kg), *Ni* (48.0–118.0 mg/kg), *Pb* (26.1–50.8 mg/kg), and *Zn* (68.8–135.0 mg/kg) were determined in sediments from stations PO04–06, SG01, SG03, SG06, EuxRO01, MID02, SU01, CT03, and MA02. Higher levels of *Hg* (0.08–0.45 mg/kg) were found in sediments from PO02, PO04–06, TZ18, SG01, SG03, SG04, SG06, EuxRO01, MID02, SU01, CT02, CT03, and MA07. Moreover, the maximum values of *Cu* (62.9 mg/kg), *Hg* (0.45 mg/kg), *Pb* (50.8 mg/kg), and *Zn* (135.0 mg/kg) were found in sediments from station PO4. Higher levels of *Al* (5.2–7.0%) and *Cr* (59.8–103.0 mg/kg) were determined in sediments from PO01, PO02, EuxRO01, SG01, CT02, CT03, TZ18, SU01, and PO04. Surface sediments collected from stations MA05–07, SG03, PO05, PO06, and MID02 had also high levels of *Cr* (60.8–114.0 mg/kg).

The study area is highly populated, especially in the summer season, and heavily anthropized, which could lead to widespread contamination with various TEs. On the one hand, the Danube River, containing various domestic, municipal, agricultural, and industrial effluents, is an important source of sediment contamination. On the other hand, there are various local anthropogenic contamination sources, including port activities (cargo and passenger transport, shipyard activities, cargo handling and storage), coastal tourism, constructions, petrochemical industry, wastewater discharges, offshore oil and gas extraction.

Fertilizers and pesticides from agricultural runoff can determine high concentrations of As, Cu, Ni, Pb, and Zn in surface sediments (Cox and Preda, 2005; Selvam et al., 2012; Remeikaitė-Nikienė et al., 2018; Vasiliu et al., 2020; Lin et al., 2021; Tang et al., 2022). As, Cr, Cu, Hg, Pb, and Zn derive from untreated/poorly treated wastewater discharges (Adamo et al., 2005; Cox and Preda, 2005; Selvam et al., 2012; Özkan, 2012; Vasiliu et al., 2020; Tang et al., 2022), whereas Ni, Pb, and Zn originate from waterborne transport (Cox and Preda, 2005; Selvam et al., 2012; Özkan, 2012; Tang et al., 2022). Anti-fouling paint used for ships is an important anthropogenic source of Cu and Zn (Cox and Preda, 2005; Lin et al., 2021). Offshore oil and gas drilling platforms (located near stations PO4 and PO5), crude oil refinery, and construction activities are potential sources of As, Cr, Cu, Hg, Ni, Pb, and Zn, which can enter the sea either through wastewater

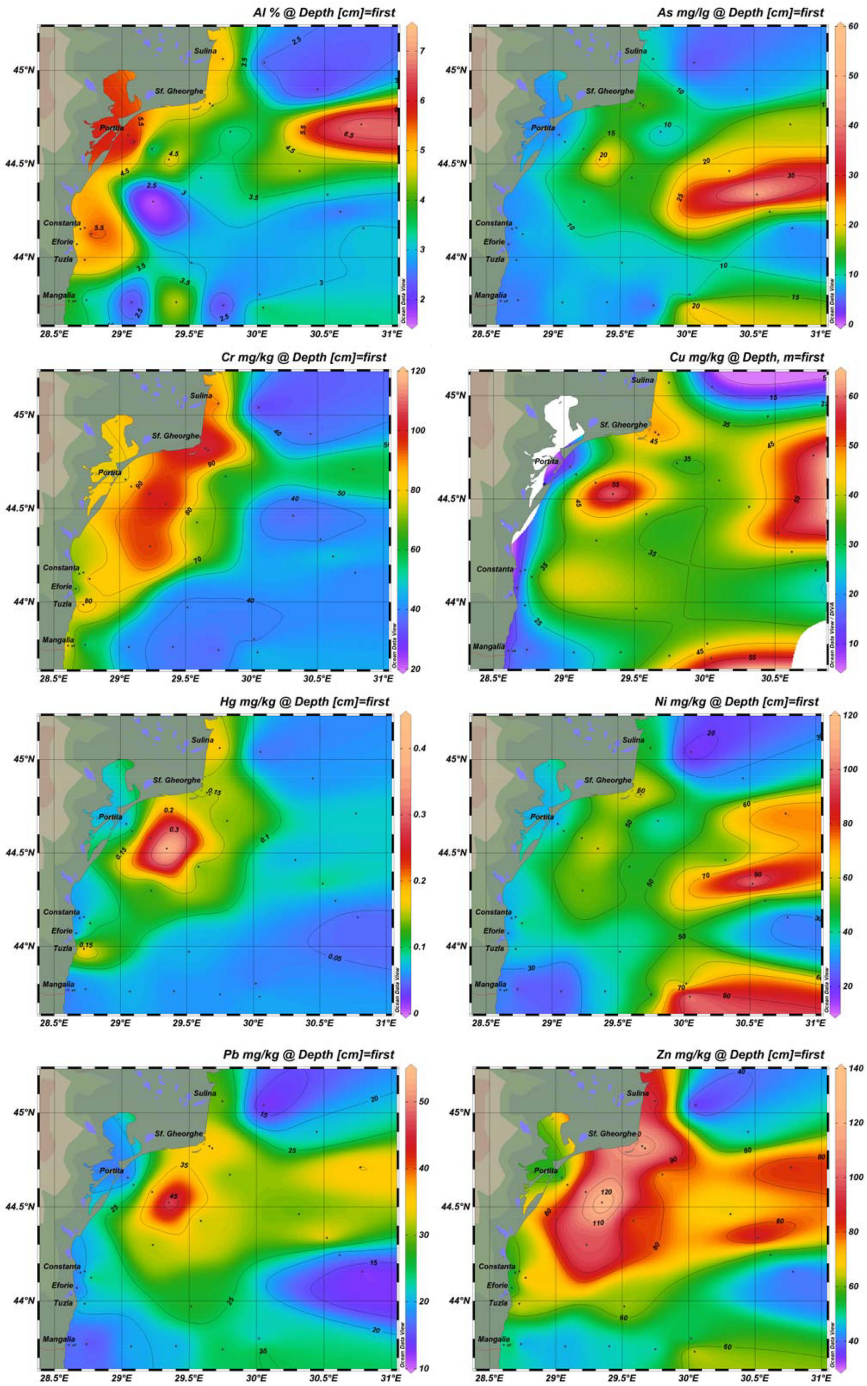

FIGURE 3
Spatial distributions of Al, As, Cr, Hg, Cu, Ni, Pb and Zn concentrations in surface sediments in the study area.

discharge or atmospheric dry/wet deposition (Adamo et al., 2005; Vasiliu et al., 2020; Lin et al., 2021). Moreover, rock/soil weathering and erosion are natural sources of TEs in surface sediments.

Potential sources of TEs and associations between selected parameters were identified by applying PCA and correlation analysis. A data matrix with 32 rows (number of samples) and 14 columns (number of variables, *i.e.*, *Al*, *As*, *Cr*, *Cu*, *Hg*, *Ni*, *Pb*, *Zn*, *h*, *TOC*, *Sand*, *Silt*, *Clay*, and $CaCO_3$) was used in PCA. The eigenvalues corresponding to PC1 (6.72), PC2 (3.74), and PC3 (1.21) were > 1. The first three principal components (PCs) explained 83.3% (48.0% + 26.7% + 8.6%) of the total variance. Only PC1 and PC2, explaining 74.7% of the total variance, were further used in PCA. The factor loadings and Pearson correlation coefficients (*r*) are summarized in Tables 4, 5. The results presented in Table 4 and PCA bi-plot (Figure 4) indicate that the most important variables are *As*, *Cu*, *Hg*, *Ni*, *Pb*, *Zn*, *TOC*, *Sand*, *Silt*, *Clay*, and to some extent *h* for PC1, and *Al*, *Cr*, *h*, $CaCO_3$, and to some extent *Hg*, *Pb*, and *Zn* for PC2.

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TABLE 4 Factor loadings.

No.	Variable		PC1	PC2
	Name	Symbol		
1	Al concentration	*Al*	-0.02	**-0.62**
2	As concentration	*As*	**0.70**	-0.01
3	Cr concentration	*Cr*	0.16	**-0.88**
4	Cu concentration	*Cu*	**0.95**	-0.02
5	Hg concentration	*Hg*	**0.59**	-0.57
6	Ni concentration	*Ni*	**0.79**	-0.06
7	Pb concentration	*Pb*	**0.87**	-0.39
8	Zn concentration	*Zn*	**0.78**	-0.59
9	Water depth	*h*	0.42	**0.76**
10	TOC percentage	*TOC*	**0.85**	0.27
11	Sand percentage	*Sand*	**-0.85**	-0.30
12	Silt percentage	*Silt*	**0.82**	0.30
13	Clay percentage	*Clay*	**0.81**	0.25
14	$CaCO_3$ percentage	$CaCO_3$	0.09	**0.93**

Significant levels of factor loadings are highlighted in bold.

According to the loadings for PC1 specified in Table 4 , As, Cu, Hg, Ni, Pb, and Zn (loadings of 0.59–0.95) were associated with clay, silt, and organic matter particles (loadings of 0.81–0.85). Correlation analysis also indicated that *As*, *Cu*, *Hg*, *Ni*, *Pb*, *Zn*, *Clay*, *Silt*, and *TOC* were directly correlated with each other ($0.28 \leq r \leq 0.93$) as well as each of them was inversely correlated with *Sand* ($-0.99 \leq r \leq -0.34$). Consequently, the sediment grain size and TOC content had a significant influence on the distribution of As, Cu, Hg, Ni, Pb, and Zn in surface sediments. Numerous studies in the related literature reported that clay, silt, and organic matter particles are important carriers of TEs in sediments (Rubio et al., 2000; Vaalgamaa and Korhola, 2004; Selvam et al., 2012; Özkan, 2012; Dou et al., 2013; Hu et al., 2013; Xu et al., 2016; Zhao et al., 2017; Perina et al., 2018; Remeikaitė-Nikienė et al., 2018; Sun et al., 2020;

TABLE 5 Correlation matrix.

Variable	*Al*	*As*	*Cr*	*Cu*	*Hg*	*Ni*	*Pb*	*Zn*	*h*	*TOC*	*Sand*	*Silt*	*Clay*	$CaCO_3$
Al	**1**													
As	0.05	**1**												
Cr	**0.45**	-0.01	**1**											
Cu	0.03	**0.67**	0.16	**1**										
Hg	0.17	0.28	**0.56**	**0.54**	**1**									
Ni	0.13	**0.85**	0.13	**0.80**	0.29	**1**								
Pb	0.15	**0.62**	**0.43**	**0.85**	**0.77**	**0.68**	**1**							
Zn	0.26	**0.55**	**0.65**	**0.75**	**0.79**	**0.63**	**0.93**	**1**						
h	**-0.35**	0.33	**-0.57**	**0.44**	-0.19	**0.35**	0.00	-0.15	**1**					
TOC	-0.20	**0.55**	-0.09	**0.84**	**0.39**	**0.60**	**0.67**	**0.48**	**0.60**	**1**				
Sand	0.15	**-0.40**	0.08	**-0.74**	-0.34	**-0.50**	**-0.59**	**-0.48**	**-0.51**	**-0.73**	**1**			
Silt	-0.10	**0.39**	-0.10	**0.71**	0.33	**0.47**	**0.58**	**0.45**	**0.49**	**0.70**	**-0.99**	**1**		
Clay	-0.27	**0.35**	0.03	**0.72**	0.33	**0.51**	**0.55**	**0.51**	**0.47**	**0.70**	**-0.88**	**0.80**	**1**	
$CaCO_3$	**-0.57**	0.07	**-0.80**	0.08	**-0.45**	0.02	-0.23	**-0.46**	**0.68**	0.30	**-0.36**	**0.38**	0.27	**1**

Values of Pearson correlation coefficient (r) highlighted in bold are different from 0 with a significance level $\alpha = 0.05$.

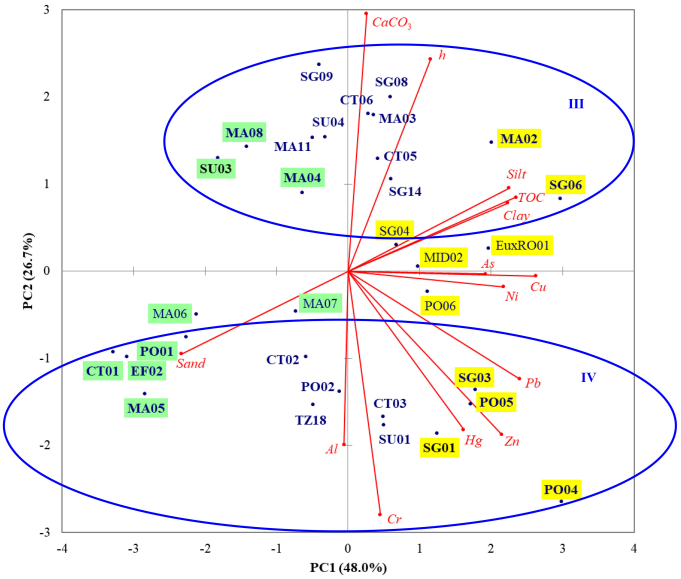

FIGURE 4
Projections of variables (*Al*, *As*, *Cr*, *Cu*, *Hg*, *Ni*, *Pb*, *Zn*, *h*, *TOC*, *Sand*, *Silt*, *Clay*, and $CaCO_3$) and samples (collected from 32 stations) on the factor-plane PC1–PC2; group I (9 stations highlighted in green): SU03, PO01, CT01, EF02, and MA04–08; group II (10 stations highlighted in yellow): EuxRO01, SG01, SG03, SG04, SG06, PO04–06, MID02, and MA02; group III (13 stations highlighted in bold): SU03, SU04, SG06, SG08, SG09, SG14, CT05, CT06, MA02–04, MA08, and MA11; group IV (13 stations highlighted in bold): SU01, SG01, SG03, PO01, PO02, PO04, PO05, CT01–03, EF02, TZ18, and MA05.

Wang et al., 2021; Zhou et al., 2022). On the one hand, the finer sediment fractions (clay and silt) have a higher specific surface area than the coarser fraction (sand), giving them more binding sites for the adsorption of TEs and organic matter (Rubio et al., 2000; Xu et al., 2016; Zhou et al., 2022). On the other hand, the organic matter coatings in these fine-grained sediments retain a variety of TEs (Rubio et al., 2000). The results of PCA and correlation analysis suggest that As, Cu, Hg, Ni, Pb, and Zn were associated with fine carriers (clay, silt, and organic matter particles) and these elements originated from common sources. Although the type of each source cannot be precisely identified, it can be assumed that As, Cu, Hg, Ni, Pb, and Zn came mainly from Danube discharges, containing domestic, municipal, agricultural, and industrial effluents, but also from local anthropogenic sources (*e.g.*, port and construction activities, coastal tourism, petrochemical industry, wastewater discharges, offshore oil and gas extraction).

The PCA bi-plot (Figure 4) indicates discrimination on the PC1 direction between the group I of stations highlighted in green (in the left quadrants) and group II of stations highlighted in yellow (in the right quadrants). For samples from group I of 9 stations, including SU03 (in the north-western part of the study area, near the mouth of the Sulina arm), PO01, CT01, and EF02 (in the west, near Portita, Constanta, and Eforie), and MA04–08 (in the south-west and south, along the Mangalia–E transect), the results of one-way ANOVA (Table 6) highlight that the mean values of *h*, *As*, *Cu*, *Hg*, *Ni*, *Pb*, *Zn*, *TOC*, *Silt*, and *Clay* are significantly lower ($p < 0.05$) than those for samples from group II of 10 stations, *i.e.*, EuxRO01 (in the eastern part of the study area, between Sulina–E and Sf. Gheorghe–SE transects), SG01, SG03, SG04, and SG06 (along the Sf. Gheorghe–SE transect), PO04–06 (along the Portita–SE transect), MID02 (in the west, near the port of Midia), and MA02 (in the south-east, along the Mangalia–E transect), whereas the mean value of *Sand* is significantly higher for samples from group I compared to that for samples from group II. Accordingly, the levels of *As*, *Cu*, *Hg*, *Ni*, *Pb*, *Zn*, *TOC*, *Silt*, and *Clay* were higher in sediments collected from group II of stations generally located at higher water depths(up to 118 m), suggesting that TEs associated with these finer carriers were transported offshore by currents and waves. The spatial distribution of sampling stations in groups I and II is shown in Supplementary Figure 1.

The loadings of *Al*, *Cr*, *Hg*, *Pb*, and *Zn* on PC2 (from -0.88 to -0.39) and their correlation coefficients ($0.15 \leq r \leq 0.93$) indicate that Al, Cr, and partly Hg, Pb, and Zn could have common sources. It can be assumed that these elements originated from rock/soil weathering and erosion. Accordingly, PC2 is related to natural sources of TEs. Al, a major constituent of aluminosilicate minerals, is a typical terrigenous element. Natural sources of Cr, Hg, Pb, and Zn in sediments were reported in several studies (Cox and Preda, 2005; Ip et al., 2007; Özkan, 2012; Dou et al., 2013; Hu et al., 2013; Omar et al., 2015; Xu et al., 2016; Belhadj et al., 2017; Zhao et al., 2017; El-Sorogy et al., 2020; Sun et al., 2020; Perumal et al., 2021; Tang et al., 2022). The correlation matrix (Table 5) highlights that *Al* and *Cr* are inversely correlated with *h* and $CaCO_3$ ($-0.80 \leq r \leq -0.35$). Moreover, inverse correlations were found between $CaCO_3$ and each of *Hg*, *Pb*, and *Zn* ($-0.46 \leq r \leq -0.23$). Weak positive correlations between *Al* and each of *Hg*, *Pb*, and *Zn* ($0.15 \leq r \leq 0.26$) indicate that Hg, Pb, and Zn derived from both anthropogenic and natural sources. Moreover, moderate positive correlations between *Cr* and each of *Hg*, *Pb*, and *Zn* ($0.43 \leq r \leq 0.65$) suggest that Cr, Hg, Pb, and Zn could have common anthropogenic sources, *e.g.*,

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TABLE 6 Mean values ± *SD* of characteristic variables of sediment samples from the groups of stations specified in Figure 4.

No.	Variable			Group I	Group II	Group III	Group IV
	Name	Symbol	Unit				
1	Al concentration	*Al*	%	3.97 ± 1.05 a	3.86 ± 1.74 a	2.93 ± 0.88 B	5.02 ± 1.33 A
2	As concentration	*As*	mg/kg	5.19 ± 1.47 b	20.0 ± 14.3 a	12.9 ± 14.8 A	9.77 ± 5.88 A
3	Cr concentration	*Cr*	mg/kg	58.3 ± 25.6 a	78.2 ± 26.5 a	38.5 ± 5.9 B	89.5 ± 18.7 A
4	Cu concentration	*Cu*	mg/kg	15.5 ± 6.3 b	48.1 ± 10.2 a	34.0 ± 13.0 A	30.7 ± 17.9 A
5	Hg concentration	*Hg*	mg/kg	0.05 ± 0.03 b	0.16 ± 0.11 a	0.06 ± 0.01 B	0.14 ± 0.12 A
6	Ni concentration	*Ni*	mg/kg	26.0 ± 8.1 b	69.1 ± 27.1 a	46.1 ± 33.4 A	43.6 ± 15.2 A
7	Pb concentration	*Pb*	mg/kg	15.0 ± 3.9 b	35.2 ± 6.6 a	21.4 ± 7.7 A	26.1 ± 11.9 A
8	Zn concentration	*Zn*	mg/kg	43.5 ± 11.5 b	98.1 ± 21.7 a	52.4 ± 18.3 B	79.9 ± 33.9 A
9	Water depth	*h*	m	29.6 ± 17.3 b	56.9 ± 30.7 a	79.9 ± 33.2 A	24.7 ± 9.4 B
10	TOC percentage	*TOC*	%	0.40 ± 0.31 b	1.85 ± 0.56 a	1.40 ± 0.58 A	0.86 ± 0.70 B
11	Sand percentage	*Sand*	%	51.2 ± 24.0 a	10.5 ± 3.3 b	15.2 ± 7.6 B	33.3 ± 28.1 A
12	Silt percentage	*Silt*	%	39.6 ± 19.2 b	69.8 ± 3.8 a	68.5 ± 7.2 A	53.9 ± 22.0 B
13	Clay percentage	*Clay*	%	9.16 ± 5.04 b	19.6 ± 2.2 a	16.3 ± 3.0 A	12.9 ± 6.5 A
14	$CaCO_3$ percentage	$CaCO_3$	%	30.1 ± 16.3 a	28.9 ± 18.9 a	52.9 ± 4.6 A	13.5 ± 4.0 B

Different lowercase letters indicate significant differences ($p < 0.05$) between mean values of variables in groups I and II; different uppercase letters indicate significant differences ($p < 0.05$) between mean values of variables in groups III and IV.

untreated/poorly treated wastewater discharges, offshore oil and gas extraction.

The PCA bi-plot (Figure 4) indicates discrimination on the PC2 direction between the two groups of stations highlighted in bold and using blue ellipses, *i.e.*, group III (in the upper quadrants) and group IV (in the lower quadrants). For samples from group III of 13 stations (located at water depths of 79.9 ± 33.2 m), including SU03 and SU04 (in the northern and north-eastern part of the study area, along the Sulina–E transect), SG06, SG08, SG09, and SG14 (in the east, along the Sf. Gheorghe–SE transect), CT05, CT06, MA02–04, MA08, and MA11 (in the south, along the Constanta–SE and Mangalia–E transects), the results of ANOVA (Table 6) reveal that the mean values of *Al*, *Cr*, *Hg*, and *Zn* are significantly lower ($p < 0.05$) than those for samples from group IV of 13 shallower stations (water depths of 24.7 ± 9.4 m), *i.e.*, SU01, SG01 and SG03 (in the north-western part of the study area, near the mouths of the Sulina and Sf. Gheorghe arms), PO01, PO02, PO04, and PO05 (in the west, along the Portita–SE transect), CT01–03, EF02, TZ18, and MA05 (in the west and south-west, near Constanta, Eforie, Tuzla, and Mangalia), whereas the mean values of *h* and $CaCO_3$ are significantly higher for samples from group III compared to those from group IV. The spatial distribution of sampling stations in groups III and IV is shown in Supplementary Figure 2.

The mean values ± *SD* and/or ranges of values of *As*, *Cr*, *Cu*, *Hg*, *Ni*, *Pb*, and *Zn* in surface sediments of the Black Sea, which were reported by different researchers, are summarized in Table 7. The mean values of TE concentrations in surface sediments collected in 2019 from 32 sampling stations (h = 12.7–149 m), which were obtained in this study, were not significantly different ($p > 0.05$) from those reported in our previous paper for surface sediments (0–2 cm depth) collected in 2018 from 22 stations located at lower water depths (h = 13.5–67 m) in the same area (Bucşe et al., 2020).

The state of the marine ecosystem in Romania (2006–2014) in terms of contaminant concentrations was evaluated by Coatu et al. (2013), Oros et al. (2016), and Oros (2019). Sediment samples were taken from 40 monitoring stations located along the entire Romanian coast of the Black Sea. Compared to the data reported for the period 2006–2011 (Coatu et al., 2013; Oros, 2019), the values of contaminant concentrations in the samples collected during 2012–2014 (Oros et al., 2016) were situated in general within the same variation ranges. The values of *Cr*, *Cu*, *Ni*, and *Pb*, characterized by high dispersions, depended on the element type, sediment composition and texture, *TOC*, water depth, anthropogenic and natural sources of contamination. The grain size and *TOC* of the sediments affected significantly their contaminant contents. The values of heavy metal contents for sediments with finer texture and higher levels of *TOC* were higher than those obtained for coarse sediments near the shore. The Danube discharges and anthropogenic inputs in the Constanta coastal zone were the main contamination sources in the study area. The values of *Cr*, *Cu*, *Ni*, and *Pb* found in our study were generally within the limits reported by Coatu et al. (2013), Oros et al. (2016), and Oros (2019).

Catianis et al. (2016) examined the effects of potential natural and anthropogenic sources of contamination (*e.g.*, Danube discharges, storm water runoff, waste discharges, accidental oil spills, oil refining, shipyard, and shipping activities) on

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TABLE 7 Concentrations of arsenic (*As*), chromium (*Cr*), copper (*Cu*), mercury (*Hg*), nickel (*Ni*), lead (*Pb*), and zinc (*Zn*) in surface sediments of the Black Sea during 1996–2019.

Area, year	*As* (mg/kg)	*Cr* (mg/kg)	*Cu* (mg/kg)	*Hg* (mg/kg)	*Ni* (mg/kg)	*Pb* (mg/kg)	*Zn* (mg/kg)	Reference
RO, 2019	11.2 ± 10.2 3.8–57.1	64.8 ± 27.0 27.0–114	32.7 ± 15.0 9.7–62.9	0.10 ± 0.09 0.02–0.45	45.3 ± 23.8 15.0–118	24.6 ± 9.6 11.4–50.8	68.0 ± 28.0 30.8–135	This study
RO, Midia, 2019	11.1	95.7	36.5	0.12	54.3	31.6	98.2	This study
RO, 2018	8.85 ± 4.23 3.42–17.2	73.3 ± 22.3 26.3–100.6	28.3 ± 15.3 6.87–52.5	0.11 ± 0.06 0.02–0.23	39.7 ± 13.3 19.3–59.3	24.4 ± 9.2 11.6–42.1	74.1 ± 29.5 28.0–118.5	Bucşe et al., 2020
RO, 2012–2014	–	63.6 ± 20.7	42.8 ± 26.2	–	49.8 ± 33.7	12.2 ± 11.5	–	Oros et al., 2016
RO, 2006–2011	–	44.6 ± 31.1 1.34–231	33.1 ± 27.5 0.53–147.8	–	36.5 ± 25.9 0.40–211.7	26.7 ± 26.2 0.10 –300.8	–	Coatu et al., 2013; Oros, 2019
RO, Midia, 2012	–	79.7 ± 21.5 32–113	43.5 ± 32.6 14.5–111	–	24.1 ± 5.82 15.4–32.0	37.9 ± 20.4 19.7–74.0	88.7 ± 37.6 48.2–156	Catianis et al., 2016
RO, Midia, 2011	13 ± 9.84 3–43	44 ± 17.15 21–85	40 ± 34.11 5–145	0.21 ± 0.26 0.02–1.09	28 ± 7.54 12–44	22 ± 19.68 2–92	87 ± 46.42 21–222	Catianis et al., 2016
UA, RO, BG, 1996	–	57.2 ± 41.9 1–120	30.7 ± 18.8 4.62–75.7	–	49.8 ± 34.8 1–117	19.4 ± 12.5 2.1–43.5	69.0 ± 57.0 1–174	Secrieru and Secrieru, 2002
BG	29.2 ± 52.2 0.01 –222.7	25.6 ± 25.5 3.0–109.5	80.0 ± 141 3.0–786.0	–	13.0 ± 8.6 1.0–28.0	16.0 ± 24.8 1.6–118.8	59.0 ± 47.0 14.8–265.5	Simeonov et al., 2000
TR, 2019	13.3 ± 0.8	–	76.7 ± 5.9	–	23.1 ± 1.0	42.3 ± 1.9	117.8 ± 4.5	Özşeker et al., 2022
TR (W coast), 2019	9.8 ± 0.4	–	59.4 ± 4.8	–	22.8 ± 1.9	41.2 ± 2.4	104.5 ± 4.7	Özşeker et al., 2022
TR (mid-coast), 2019	13.1 ± 0.9	–	65.3 ± 4.3	–	21.2 ± 1.8	39.3 ± 4.1	122.1 ± 10.5	Özşeker et al., 2022
TR (E coast), 2019	16.6 ± 1.5	–	102.5 ± 12.3	–	24.9 ± 1.4	46.1 ± 2.9	126.0 ± 6.9	Özşeker et al., 2022
TR (E coast), 2018	9.0 ± 1.8 6.0–12.1	48.4 ± 12.1 25.9–65.7	51.0 ± 11.8 26.0–74.1	–	30.0 ± 9.0 11.8–45.1	17.9 ± 8.5 11.4–46.6	122.4 ± 34.8 68.2–206.2	Alkan et al., 2021
TR (E coast), 2010	4.9–12.3	–	33.9–279.1	0.01–0.07	13.1–17.6	15.9–33.0	82.0–383.0	Gedik and Boran, 2013
TR (mid-coast), 2002–2003	–	53.1–99.3	32.9–64.9	–	7.9–49.3	12.1–224	110–262	Bakan and Özkoç, 2007

Element concentrations are expressed as mean values ± SD and/or ranges of values; W – west; E - east.

contamination status of surface sediment samples collected from the port of Midia during 2011 (24 samples) and 2012 (10 samples). They found that the surface sediments were not severely polluted with TEs. The values of *As*, *Cr*, *Cu*, *Hg*, *Pb*, and *Zn* in surface sediments collected from station MID02, which were obtained in our study, were within the ranges reported by Catianis et al. (2016).

Secrieru and Secrieru (2002) analyzed sediments collected in 1996 from 26 sampling stations covering almost the entire NW part

of the Black Sea (Ukrainian, Romanian, and Bulgarian areas). They assessed that oil drilling activities in Romania and Ukraine were important contamination sources in the study area. The levels of *Cr*, *Cu*, *Ni*, *Pb* and *Zn* reported in our study were generally within the ranges of those obtained by Secrieru and Secrieru (2002) for the top layer (0–2 cm depth) of the sediments (Table 7).

Simeonov et al. (2000) analyzed surface sediment samples from 4 different sampling sites of Bulgarian coast of the Black Sea, *i.e.*, Gulf of Bourgas, Gulf of Varna, and 2 lakes (Beloslavsko and Varnensko) serving as a natural buffer zone between the Gulf of Varna and industrial zone. Sediment samples were taken from 39 stations located at water depths in the range of 8–50 m. PCA suggested that Cu came mainly from natural sources, whereas As, Cr, Ni, Pb, and Zn originated from anthropogenic ones, *e.g.*, steelworks, oil refinery, glass production factory, cement and chemical plants. The mean values of *As* and *Cu* were higher than those obtained in our study, but that of *Ni* was lower. Generally, the levels of *Ni* in surface sediments along the Romanian coast of the Black Sea were higher than those reported for Bulgarian and Turkish areas (Table 7). The natural geochemical value for *Ni* in sediments from NW Black Sea was 5.9 mg/kg in the 1980s, but it is currently higher than 40 mg/kg (Berlinskyi and Safranov, 2016).

Özşeker et al. (2022) reported concentrations of some elements in surface sediments (0–5 cm depth) of the southern Black Sea (Turkish area). Sediment samples were collected in 2019 from 31 stations located at water depths in the range of 16–65 m. The mean values of *Cu*, *Pb*, and *Zn* were significantly higher than those found in our study, but that of *Ni* was lower. Their results revealed higher values of element concentrations for eastern Turkish coast compared to western and middle coasts (Table 7). Higher levels of *Cu* and *Pb* could be caused by landfills, international highway along the coast, and erosion of terrestrial material. Moreover, agrochemicals are important sources of Cu, Pb, and Zn.

Alkan et al. (2021) and Gedik and Boran (2013) determined element concentrations in surface sediments of the eastern Turkish coast of the Black Sea. Alkan et al. (2021) examined surface sediment samples (0–5 cm depth) collected in 2018 from 5 stations located in the drainage area of the Değirmendere Stream. Factor analysis suggested that As, Cr, Cu, and Ni came predominantly from stream discharges, whereas port activities were main sources of Pb and Zn. Gedik and Boran (2013) analyzed surface sediment samples (0–5 cm depth) taken in 2010 from 7 stations around the port of Rize. They assumed that As, Cu, Hg, Pb, and Zn originated from mining wastewater, Pb and Zn from motor vehicle emissions, Cu, Pb, and Zn from sewage discharge, industrial inputs, and surface runoff, and Ni from natural sources. The mean values of *Cu* and *Zn* reported by Gedik and Boran (2013) and Alkan et al. (2021) were significantly higher than those reported in our study, whereas the levels of *Pb* were similar.

Bakan and Özkoç (2007) evaluated the impact of anthropogenic activities on the accumulation of some elements in surface sediments of the middle Turkish coast. Surface sediment samples (0–5 cm depth) were collected in 2002–2003 from 5 stations around the city of Samsun. The main contamination sources in the study area were port activities and waste discharges. The mean values of *Cu*, *Pb*, and *Zn* were higher than those reported in our study, but that of *Ni* was lower.

3.3 Contamination factors

The values of contamination factors (CF_E, where E = Al, As, Cr, Cu, Hg, Ni, Pb, Zn) are summarized in Supplementary Table 2, and their spatial distributions are shown in Figure 5. The results presented in Supplementary Table 2 and Figure 5 indicate the following:

- a considerable contamination with As (CF_{As} = 4.39) and a moderate contamination with Cu (CF_{Cu} = 1.24), Ni (CF_{Ni} = 1.71), Pb (CF_{Pb} = 1.89), and Zn (CF_{Zn} = 1.05) for sediments collected from station SG06;

- a moderate contamination ($0 < CF_E < 3$ for all TEs and $1 \leq CF_E < 3$ for at least one TE) for sediments collected from 22 stations (SU01, SU04, EuxRO01, SG01, SG03, SG04, SG14, PO02, PO04–06, MID02, CT02, CT03, CT05, CT06, TZ18, MA02–05, and MA07);

- a low contamination ($0 < CF_E < 1$ for all TEs) for sediments collected from 9 stations (SU03, SG08, SG09, PO01, CT01, EF02, MA06, MA08, and MA11);

- the sediments from stations EuxRO01, SG06, and MA02, located at high water depths (80–118 m), had a moderate contamination with Cu, Ni, and Pb; the sediments from station SG06 (in the eastern part of the study area, along the Sf. Gheorghe–SE transect) had a considerable contamination with As and a moderate contamination with Zn, whereas those from stations EuxRO01 (in the east, between Sulina–E and Sf. Gheorghe–SE transects) and MA02 (in the south-east, along the Mangalia–E transect) had a moderate contamination with As; the TEs found in these sediments, which were associated with finer sediment fractions and organic matter, originated preponderantly from the Danube discharges, but also from local anthropogenic contamination sources;

- the sediments from station MID02, located in the area of influence of the Danube, had a moderate contamination with Cr, Pb, and Zn, mainly determined by the Danube discharges and anthropogenic inputs of pollutants from the port of Midia, oil refinery, and wastewater discharges;

- the sediments from stations SG01 and SG03 (located near the mouth of the Sf. Gheorghe arm) as well as PO04 and PO05 (located near the oil and gas drilling platforms) had a moderate contamination with Cr, Cu, Pb, and Zn; moreover, the sediments from stations SG03 and PO04 had a moderate contamination with As, whereas those from station PO04 also had a moderate contamination with Hg; the TEs found in these sediments mainly came from the Danube and wastewater discharges, but also from coastal tourism, oil and gas extraction, rock/soil weathering and erosion;

- the sediments from stations SU01 (near the port of Sulina), SU04 (along the transect Sulina–E), SG04 and SG14 (along the transect Sf. Gheorghe–SE), PO02 and PO06 (along the transect Portita–SE), CT02, CT03, CT05, and CT06 (along the transect Constanta–SE), TZ18 (near Tuzla), MA03, MA04, and MA07 (in

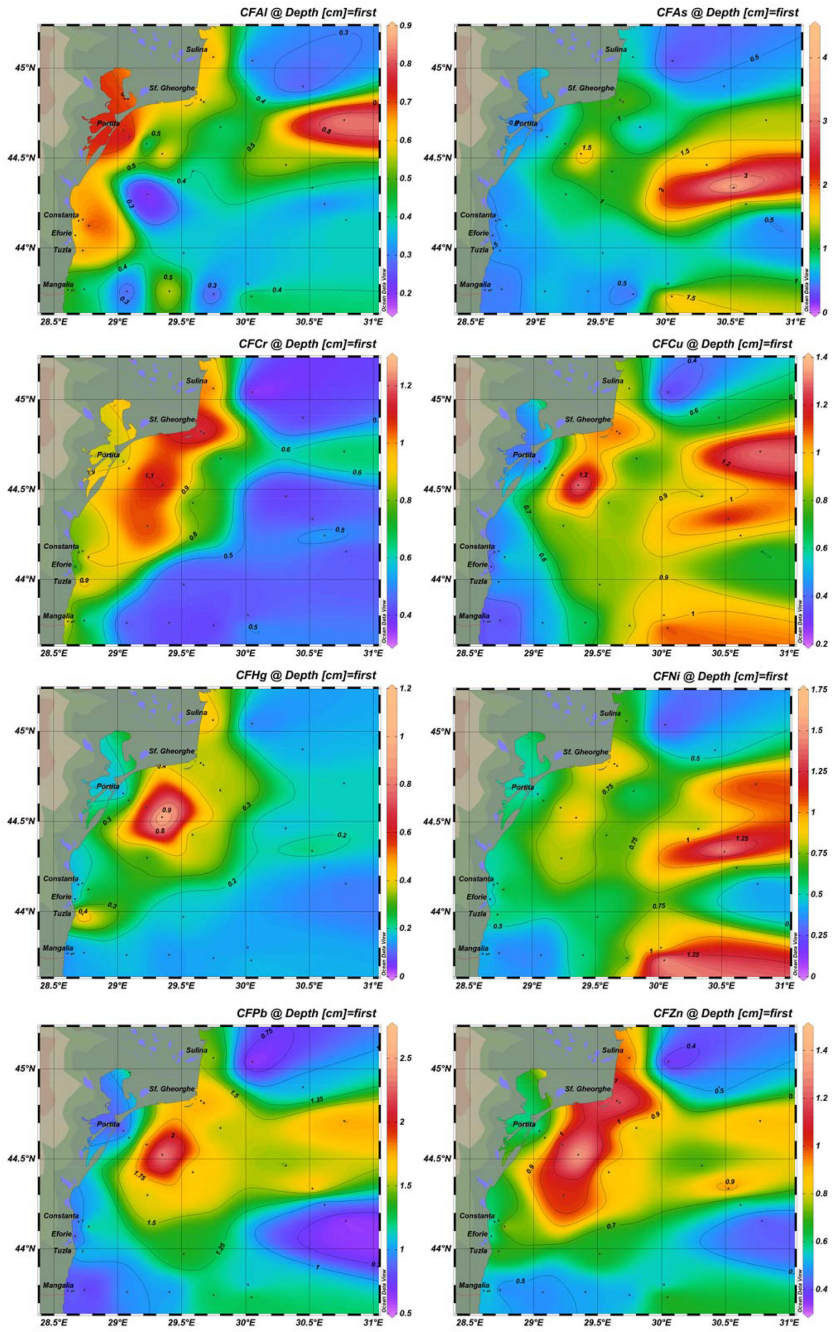

FIGURE 5
Spatial distributions of contamination factor (CF_E, E = Al, As, Cr, Cu, Hg, Ni, Pb, Zn) in surface sediments in the study area.

the south and south-west, along the transect Mangalia–E) had a moderate contamination with Pb; moreover, the sediments from station SU01 had a moderate contamination with Cr and Zn, those from PO02 and CT03 a moderate contamination with Cr, and those from SG14 and PO06 a moderate contamination with As; in addition to the contamination caused by the Danube discharges, the contamination at station TZ18 could also be determined by construction activities and household waste disposal (Mureşan et al., 2018), whereas that at stations PO02 (near the holiday village of Portita), SU01 (near the port of Sulina), and CT03 (near the port of Constanta) came from different anthropogenic inputs and also from rock/soil weathering and erosion; the contamination at stations SU04, SG04, SG14, PO06, CT02, CT05, CT06, MA03, MA04, and MA07 was determined by the Danube discharges and different local anthropogenic inputs;

- the sediments from station MA05 (near the port of Mangalia) had a moderate contamination with Cr, which can be the effect of rock/soil weathering and erosion (Ungureanu and Stanica, 2000);

- the sediments collected from stations SU03 (in the north, along the transect Sulina–E), SG08 and SG09 (in the east, along the

transect Sf. Gheorghe–SE, and characterized by higher water depths and $CaCO_3$ contents), PO01 (near the holiday village of Portita), CT01 (near the port of Constanta), EF02 (near Eforie tourist resort), MA06, MA08, and MA11 (in the south-west, along the transect Mangalia–E) had a low contamination ($0 < CF_E < 1$ for all TEs).

Based on the mean values of CF_E, *i.e.*, $CF_{Pb,m} = 1.23$, $CF_{As,m} = 0.86$, $CF_{Cu,m} = 0.73$, $CF_{Cr,m} = 0.72$, $CF_{Zn,m} = 0.72$, $CF_{Ni,m} = 0.67$, $CF_{Hg,m} = 0.26$, the sediments in the study area had a moderate contamination with Pb and a low contamination with the other TEs. However, it must be stated that the choice of background values in Equation 1 has an essential role in determining the contamination status of surface sediments.

4 Conclusions

This paper brings new information regarding the concentration levels of some elements (*i.e.*, Al, As, Cr, Cu, Hg, Ni, Pb, and Zn) in surface sediments collected in 2019 from 32 sampling stations located in the NW Black Sea (Romanian area), at water depths in the range of 12.7–149 m. The mean values of element concentrations were as follows: 3.9% for Al, 11.2 mg/kg for As, 64.8 mg/kg for Cr, 32.7 mg/kg for Cu, 0.10 mg/kg for Hg, 45.3 mg/kg for Ni, 24.6 mg/kg for Pb, and 68.0 mg/kg for Zn.

The results of statistical analysis highlighted that As, Cu, Ni, Hg, Pb, and Zn were associated with finer carriers, *i.e.*, clay, silt, and organic matter. Although it is difficult to identify exactly the type of each contamination source, it can be assumed that these elements mainly came from the Danube discharges and also from local anthropogenic sources, whereas Al, Cr, and partly Hg, Pb, and Zn originated from rock/soil weathering and erosion. On the one hand, the concentration levels of As, Cu, Hg, Ni, Pb, Zn, TOC, silt, and clay were higher in sediments collected from stations EuxRO01, SG01, SG03, SG04, SG06, PO04–06, MID02, and MA02, generally located at higher water depths (up to 118 m), suggesting that the TEs associated with the finer carriers were transported offshore by currents and waves. On the other hand, the concentration levels of Al, Cr, Hg, and Zn were higher in sediments collected from shallower stations (water depths of 12.7–42.0 m), *i.e.*, SU01, SG01, SG03, PO01, PO02, PO04, PO05, CT01–03, EF02, TZ18, and MA05, having lower levels of $CaCO_3$ content (10.1–24.3%).

The mean values of contamination factor indicated a moderate contamination with Pb ($CF_{Pb,m} = 1.23$) and a low contamination with the other elements ($0.26 \leq CF_{E,m} \leq 0.86$, E = Al, As, Cr, Cu, Hg, Ni, and Zn). Except for the sediments collected from 10 stations, *i.e.*, SU03 (in the northern part of the study area, along the transect Sulina–E), SG08 and SG09 (in the east, along the transect Sf. Gheorghe–SE, and characterized by higher water depths and $CaCO_3$ contents), PO01 (near the holiday village of Portita), CT01 (near the port of Constanta), EF02 (near Eforie tourist resort), MA05, MA06, MA08, and MA11 (in the south-west and south, along the transect Mangalia–E), which had a low contamination with Pb ($0.57 \leq CF_{Pb} \leq 0.99$), the sediments from the other 22 stations had a moderate contamination with Pb ($1.00 \leq CF_{Pb} \leq 2.54$). Moreover, except for the sediments collected from station PO4 (located near the oil and gas drilling platforms), which had a moderate contamination with Hg ($CF_{Hg} = 1.13$), the sediments from the other stations had a low contamination with Hg ($0.06 \leq CF_{Hg} \leq 0.65$).

Determining TE concentration levels in marine sediments, their contamination status, the factors controlling the element distribution, and possible contamination sources are essential for improving pollution control strategies either in coastal areas or in the Danube river watershed.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding authors.

Author contributions

AB: Conceptualization, Formal Analysis, Methodology, Software, Writing – original draft, Investigation. OCP: Conceptualization, Formal Analysis, Methodology, Software, Writing – original draft, Supervision, Validation, Writing – review & editing. DV: Conceptualization, Methodology, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing. FR: Investigation, Methodology, Writing – original draft. NL: Investigation, Methodology, Writing – original draft. BAI: Investigation, Methodology, Writing - review & editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2023.1310164/full#supplementary-material

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