Heavy Metalspatial Distribution and Pollution Assessment in the Surface Sediments of the North – Western Black Sea Shelf

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Abstract. 22 surface sediment samples were collected in August 2018 from the Romanian inner shelf (Nord-Western Black Sea). Concentrations of some metals (Al, Cr, Cu, Ni, Zn, As, Pb, and Hg), TOC content, and grain size of sediment samples were determined by specific techniques. The order of accumulation of heavy metals was Zn>Cr>Ni>Cu>Pb>As>Hg. Multivariate analysis indicated that As, Ni, Cu, Zn, Pb, and Hg concentrations had similar behavior and they were positively correlated with the clay content, whereas Al and Cr concentrations presented close patterns and they were negatively correlated with the water depth. Sediment pollution assessment indices (enrichment factor, contamination factor, and geo-accumulation index) suggested no/low pollution for most of the metals analyzed, excepting for Pb and Hg (moderate pollution). Values of pollution indices highlighted a higher sediment pollution with Pb and Hg along the Danube's plume direction, in the oil platform area (eastern edge of the Portita Bay), and partially in the Constanta and Mangalia area, suggesting the influence of port activities, tourism, urban wastewater discharges, oil and gas extraction.

Keywords: Black Sea, heavy metals, sediments, pollution indices, multivariate analysis

1.Introduction

Heavy metals are natural components of the Earth's crust, but in the last few decades they are released in the marine environment through sea port activities (*e.g.*, harbors, antifouling paints), oil and gas extraction, urbanization, industry, etc. On the other hand, the riverine discharges carry on high amounts of pollutants into the sea, either dissolved or adsorbed on the fine suspended particles [1].

North-Western (NW) Black Sea has faced to significant anthropogenic pressures since the 1970s, most of them linked to the Danube's discharges, which heavily impacted the Romanian shelf. The strong development of the industry, agriculture, and urbanization in the Danube's catchment area, along with the sea-based activities, during the last decades of the 20th century, led to a considerable increase in the heavy metals pollution level [2]. After 2000, once the Romania has started to implement the Water Framework Directive (2000/60/EC) and later Marine Strategy Framework Directive (2008/56/EC), the heavy metal introduction in the marine ecosystem has showed a decreasing trend. However, the heavy metal pollution still remains a major concern considering their accumulative behavior, which depends on various factors, including sediment type, total organic carbon (TOC) content, water depth [3–7].

Determination of metal concentrations in the surface sediments is essential to assess pollution level and establish the main factors influencing metal contamination. Some heavy metals, *e.g.*, Cu, Zn, Fe, Cr, are essential elements for life, whereas others (Pb, Hg, Ni, As, Cd) can be extremely harmful even at very low concentrations [7–13]. Especially for these toxic metals, it is important to identify their source (natural or anthropogenic), to assess the contamination level, and identify factors affecting their accumulation.

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Pollution indices, such as enrichment factor (*EF*), contamination factor (*CF*), and geo-accumulation index (*I_{geo}*), are widely used to evaluate the effect of anthropogenic activities on sediment quality [3,4,6,7,14–19]. Furthermore, multivariate exploratory techniques, especially Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA), can be successfully applied to determine the metal source and establish the impact of environmental factors on contamination level [3–7,14,18,20].

This study has aimed at: (i) describing the spatial distribution of some trace elements (As, Cr, Ni, Cu, Zn, Pb, and Hg) in the NW Black Sea sediments; (ii) assessing the sediment quality using some pollution indices (*EF*, *CF*, and *I_{geo}*); (iii) estimating the main environmental factors influencing the metal distribution and determining clusters of stations having dissimilar metal accumulation in the surface sediments by applying PCA and HCA.

2.Materials and methods
Study area
Sediment samples were collected from 22 sampling stations (water depths within 12–67 m), covering the Romanian inner shelf waters (NW Black Sea), during the research cruise aboard *R/V Mare Nigrum* conducted in August 2018. The stations considered in this study were near Sulina (SU01 and SU02), Sfantu Gheorghe (SG01, SG03–05), Portita (PO01, PO02, PO04, and PO05), Constanta (CT01–05), Eforie (EF02), Tuzla (TZ18), and Mangalia (MA04–08). Spatial distribution of selected stations is considered representative for the assessment of the metal pollution along the Romanian coast of the Black Sea. The map of the sampling stations considered in this study is shown in Figure 1, while their main characteristics in terms of coordinates and water depths are summarized in Table 1.
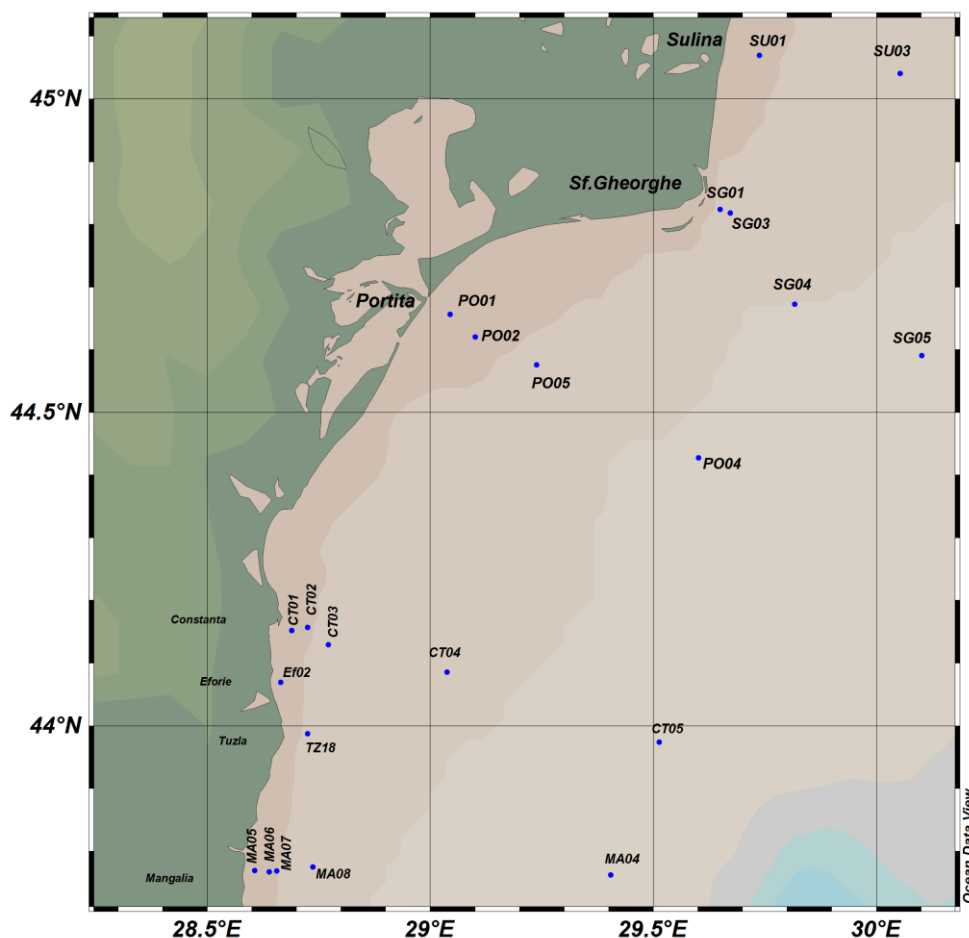

Figure 1. Map of sampling stations

Table 1. Main characteristics of sampling stations

No.	Station	Latitude (°)	Longitude (°)	Water depth h (m)
1	SU01	45.0700	29.7371	15
2	SU03	45.0412	30.0526	35
3	SG01	44.8240	29.6498	20
4	SG03	44.8186	29.6719	32.5
5	SG04	44.6730	29.8162	52
6	SG05	44.5911	30.1018	65
7	PO01	44.6566	29.0436	13.5
8	PO02	44.6203	29.1008	20
9	PO04	44.4281	29.6008	42.6
10	PO05	44.5761	29.2383	30.2
11	CT01	44.1525	28.6886	19
12	CT02	44.1569	28.7244	28
13	CT03	44.1300	28.7710	34.5
14	CT04	44.0860	29.0372	45.9
15	CT05	43.9743	29.5129	64.8
16	EF02	44.0697	28.6645	16
17	TZ18	43.9880	28.7245	33.8
18	MA04	43.7622	29.4036	67
19	MA05	43.7696	28.6061	16.8
20	MA06	43.7673	28.6390	27
21	MA07	43.7689	28.6550	35
22	MA08	43.7748	28.7360	44.8

Sediments sampling and analysis

Sediment samples were collected from the surface layer (0–2 cm depth) using a grab sampler with an opening mouth of 0.14 m². Each sample was subsampled for grain size and geochemical analyses, respectively. Sediment subsamples were stored in plastic bags and kept at 0–4 °C until subsequent analyses.

Grain sizes of sediments were determined with a Mastersizer 2000 laser diffraction granulometer (Mastersizer 2000E, ver. 5.20) and associated dispersion units (Malvern Instruments, U.K), measurement precision being of 1% and result reproducibility below 1%. Separate granulometric fractions are in accordance with Udden-Wentworth dimensional scale with sand/silt and silt/clay boundaries of 63 µm and 4 µm, respectively. The Shepard's ternary diagram was used for lithological classification of sediment samples [21].

Before geochemical analyses, the sediments were oven dried (24–48 h/105°C), ground, and homogenized with a mortar and pestle. TOC concentrations were determined using titration method [22].

Concentrations of Al, Cr, Cu, Ni, Zn, As, and Pb were measured by X-ray fluorescence spectrometry using an EDXRF Spectro Xepos spectrometer (Germany). Total Hg content was determined using an automatic mercury analyzer DMA 80 Milestone (Italy) by solid sample thermal decomposition, identification, and quantification of total Hg by atomic absorption spectrophotometry. To validate the analytical methodology, a certified reference material NCS DC 73022 was used. Measured and certified values of element/compound concentrations were compared (Table 2). For this material, all measured values were statistically similar to the certified values ($p<0.05$), demonstrating the reliability of the methodology and the estimated concentrations.

Table 2. Measured and certified values of
standard material ncs dc 73022

Element/compound	Measured value (mg/kg)	Certified value (mg/kg)
Cr	69.8	72±3
Al$_2$O$_3$	13.22	13.61±0.12
As	291	304±20
Ni	30.4	29±1
Cu	497	483±20
Pb	131	126±5
Zn	874	874±19
Hg	0.113	0.115±0.023

Pollution indices

The intensity of coastal sediment pollution was assessed based on several indices, *i.e.*, enrichment factor (*EF*), contamination factor (*CF*), and geo-accumulation index (*I$_{geo}$*). Since no background data of metals in uncontaminated marine sediments in the study area are available, the values of global Earth's shale concentration of metal *i*, $c_{i,b}$ (mg/kg dry matter), reported by Turekian and Wedepohl (1961) [23], were used as background values, *i.e.*, $c_{Al,b}$=80000 mg/kg, $c_{As,b}$=13 mg/kg, $c_{Pb,b}$=20 mg/kg, $c_{Cu,b}$=45 mg/kg, $c_{Hg,b}$=0.08 mg/kg, $c_{Ni,b}$=68 mg/kg, $c_{Cr,b}$=90 mg/kg, and $c_{Zn,b}$=95 mg/kg.

Pollution indices were determined based on Eqs. (1)–(3), where $c_{i,s}$ is the concentration of metal *i* in the sample and $c_{i,b}$ the background concentration of metal *i*. Pollution levels estimated depending on the values of pollution indices are specified in Table 3.

$$EF = EF_i = \frac{c_{i,s}}{c_{i,b}} \frac{c_{Al,b}}{c_{Al,s}} \tag{1}$$

$$CF = CF_i = \frac{c_{i,s}}{c_{i,b}} \tag{2}$$

$$I_{geo} = I_{geo,i} = \log_2\left(\frac{c_{i,s}}{1.5c_{i,b}}\right) \tag{3}$$

Table 3. Pollution levels depending on the values of pollution indices

No.	Index	Values	Pollution level	Reference
1	Enrichment factor (*EF*)	<1	No enrichment	[4-7,14,18,19]
		1–3	Minor enrichment	
		3–5	Moderate enrichment	
		5–10	Moderately severe enrichment	
		10–25	Severe enrichment	
		25–50	Very severe enrichment	
		>50	Extremely severe enrichment	
2	Contamination factor (*CF*)	<1	No/low contamination	[7,14,15,19]
		1–3	Moderate contamination	
		3–6	Considerable contamination	
		>6	Very high contamination	
3	Geo-accumulation index (*I$_{geo}$*)	<0	Uncontamined	[3,4,7,14,16,17,19]
		0–1	Uncontaminated to moderately	
		1–2	Moderately contaminated	
		2–3	Moderately to heavily contaminated	
		3–4	Heavily contaminated	
		4–5	Heavily to extremely contaminated	
		>5	Extremely contaminated	

Data processing

Spatial distributions of TOC content, metal concentrations, and pollution indices were visualized using the Ocean Data View (ODV) software, ver. 4.7.10 [24]. Univariate analysis (ANOVA one way) and multivariate exploratory techniques (PCA and HCA) were performed using Statistica, ver. 10 (StatSoft, Inc).

3.Results and discussions
Experimental data

Composition (expressed as percentages (P) of sand, silt, and clay) and type of surface (0–2 cm) sediments in the area considered in the study are specified in Table 4. Depending on their composition, the sediment types vary from silty sand to clayey silt.

Generally, the studied area is covered by clayey silt, except 6 stations. Silty sand sediments were found at the shallowest stations (water depths less than 20 m) located south of Danube's mouth areas, where the highest percentages of sand were determined, *i.e.*, 53.67% at PO01, 61.42% at CT01, and 66.02% at EF02. Sandy silt sediments were collected from the stations in the Mangalia area, either from the shallowest stations, MA05 (P_{sand}=32.77%) and MA06 (P_{sand}=36.75%), or from the deepest station, MA04 (P_{sand}=26.46%). The highest percentages of clay (36.90–48.50%) were observed in the Portita Bay (excepting the shallowest station, PO01) and in front of Sf. Gheorghe mouth (SG01), while the silt was dominant in front of Sulina mouth (65.40% at SU01 and 63.52% at SU03), at TZ18 (70.94%) and MA07 (71.67%) as well as along Sf. Gheorghe–SE and Constanta–SE transects, except the shallowest stations, SG01 and CT01 (66.91–67.99% and 63.58–69.04%, respectively).

Table 4. Composition and type of surface sediments

No.	Station	Sand content P_{sand} (%)	Silt content P_{silt} (%)	Clay content P_{clay} (%)	Sediment type
1	SU01	2.18	65.40	32.42	clayey silt
2	SU03	13.47	63.52	23.01	clayey silt
3	SG01	1.01	50.50	48.50	clayey silt
4	SG03	5.40	66.91	27.69	clayey silt
5	SG04	5.29	67.66	27.04	clayey silt
6	SG05	6.09	67.99	25.92	clayey silt
7	PO01	53.67	40.27	6.07	silty sand
8	PO02	0.40	54.81	44.79	clayey silt
9	PO04	1.52	61.58	36.90	clayey silt
10	PO05	1.70	50.96	47.34	clayey silt
11	CT01	61.42	29.54	9.04	silty sand
12	CT02	4.65	64.98	30.38	clayey silt
13	CT03	3.28	69.04	27.68	clayey silt
14	CT04	5.04	63.58	31.38	clayey silt
15	CT05	5.23	64.75	30.02	clayey silt
16	EF02	66.02	29.49	4.50	silty sand
17	TZ18	5.82	70.94	23.24	clayey silt
18	MA04	26.46	47.57	25.98	sandy silt
19	MA05	32.77	54.48	12.75	sandy silt
20	MA06	36.75	51.82	11.43	sandy silt
21	MA07	4.37	71.67	23.97	clayey silt
22	MA08	17.87	54.96	27.17	clayey silt

The values of TOC and metal concentrations in the surface sediments for each station are specified in Table 5. Descriptive statistics in terms of minimum (min) and maximum (max) values, mean, median, standard deviation (SD), and coefficient of variation (CV) for TOC and each metal concentration are also summarized in Table 5.

Data presented in Table 5 and Fig. 2 highlight TOC concentrations in the surface sediments of the investigated area between 0.092% and 1.779%, with a minimum in front of the Constanta harbor (CT01) and a maximum in the deepest station from the Portita Bay (PO04). Lower TOC concentrations (<0.5%) were observed at stations PO01 and MA05, while quite high concentrations

(>1.5%) were found at stations SG04, SG05, PO04, and CT05, where the Danube's plume influence is stronger, as well as at stations MA06 and MA07.

Table 5. Total organic carbon and metal concentrations in the surface sediments

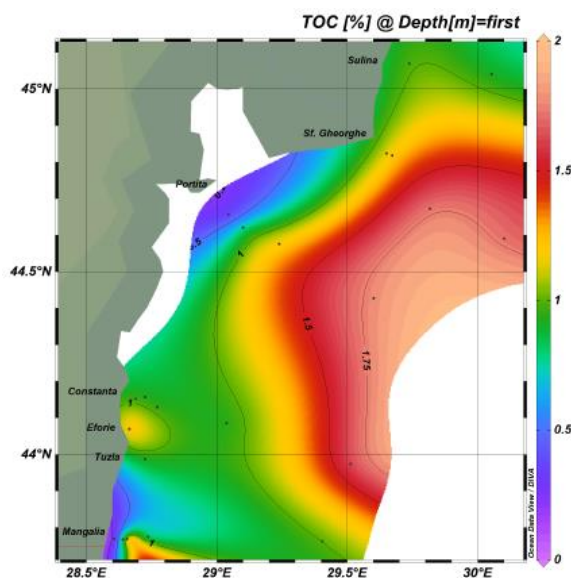| No.	Station	TOC (%)	$c_{Al,s}$ (mg/kg)	$c_{As,s}$ (mg/kg)	$c_{Cr,s}$ (mg/kg)	$c_{Ni,s}$ (mg/kg)	$c_{Cu,s}$ (mg/kg)	$c_{Zn,s}$ (mg/kg)	$c_{Pb,s}$ (mg/kg)	$c_{Hg,s}$ (mg/kg)
1	SU01	0.993	63140	14.43	91.75	56.20	52.08	110.5	33.18	0.170
2	SU03	0.905	23590	5.665	43.28	26.09	20.13	56.35	17.24	0.060
3	SG01	1.098	64930	15.71	100.55	58.35	46.67	115.0	35.04	0.215
4	SG03	1.237	60640	17.16	94.90	59.30	51.80	115.5	36.30	0.140
5	SG04	1.732	31900	11.40	58.74	38.24	32.13	74.70	29.17	0.115
6	SG05	1.717	34170	7.680	49.05	42.36	35.19	71.65	25.90	0.150
7	PO01	0.308	50550	4.965	75.30	31.87	13.72	51.55	14.46	0.040
8	PO02	0.941	56040	10.06	92.60	52.00	38.23	100.5	31.78	0.195
9	PO04	1.779	57010	11.70	93.55	58.65	52.47	118.5	42.07	0.230
10	PO05	1.152	56980	10.31	90.80	52.70	41.17	103.0	33.13	0.195
11	CT01	0.092	47750	4.530	72.75	24.83	9.290	41.51	13.56	0.030
12	CT02	0.618	53890	10.03	88.65	41.00	22.98	72.20	22.69	0.085
13	CT03	1.147	59540	11.36	96.95	52.95	38.69	108.5	33.10	0.155
14	CT04	1.291	35960	9.160	56.95	36.35	28.81	77.05	26.71	0.120
15	CT05	1.650	22510	5.570	27.74	36.74	33.42	55.80	24.54	0.090
16	EF02	1.202	46550	4.205	66.15	24.52	6.950	40.57	13.15	0.020
17	TZ18	0.909	54120	6.455	88.95	36.39	19.03	63.75	20.76	0.070
18	MA04	0.999	19910	3.420	26.26	19.28	13.11	27.96	11.58	0.040
19	MA05	0.142	42020	3.790	76.30	22.65	7.450	42.32	12.71	0.070
20	MA06	1.597	40540	4.230	84.95	23.84	6.865	36.84	13.15	0.030
21	MA07	1.589	54850	15.31	78.50	47.77	32.24	94.15	27.87	0.140
22	MA08	0.609	29790	7.590	57.80	30.50	20.16	52.60	17.69	0.120
	Min	0.092	19910	3.420	26.26	19.28	6.865	27.96	11.58	0.020
	Max	1.779	64930	17.16	100.6	59.30	52.47	118.5	42.07	0.230
	Mean	1.078	45745	8.850	73.29	39.66	28.30	74.11	24.35	0.113
	Median	1.123	49150	8.420	77.40	37.49	30.47	71.93	25.22	0.118
	SD	0.500	13980	4.232	22.26	13.29	15.30	29.49	9.195	0.064
	CV	0.464	0.306	0.478	0.304	0.335	0.541	0.398	0.378	0.569

Figure 2. TOC spatial distribution in the surface sediments of the Romanian inner shelf

Data summarized in Table 3 emphasize that metal concentrations in the surface sediments present a relatively large spatial variability in the studied area, percent CVs ranging from 30.4% (for Cr) to
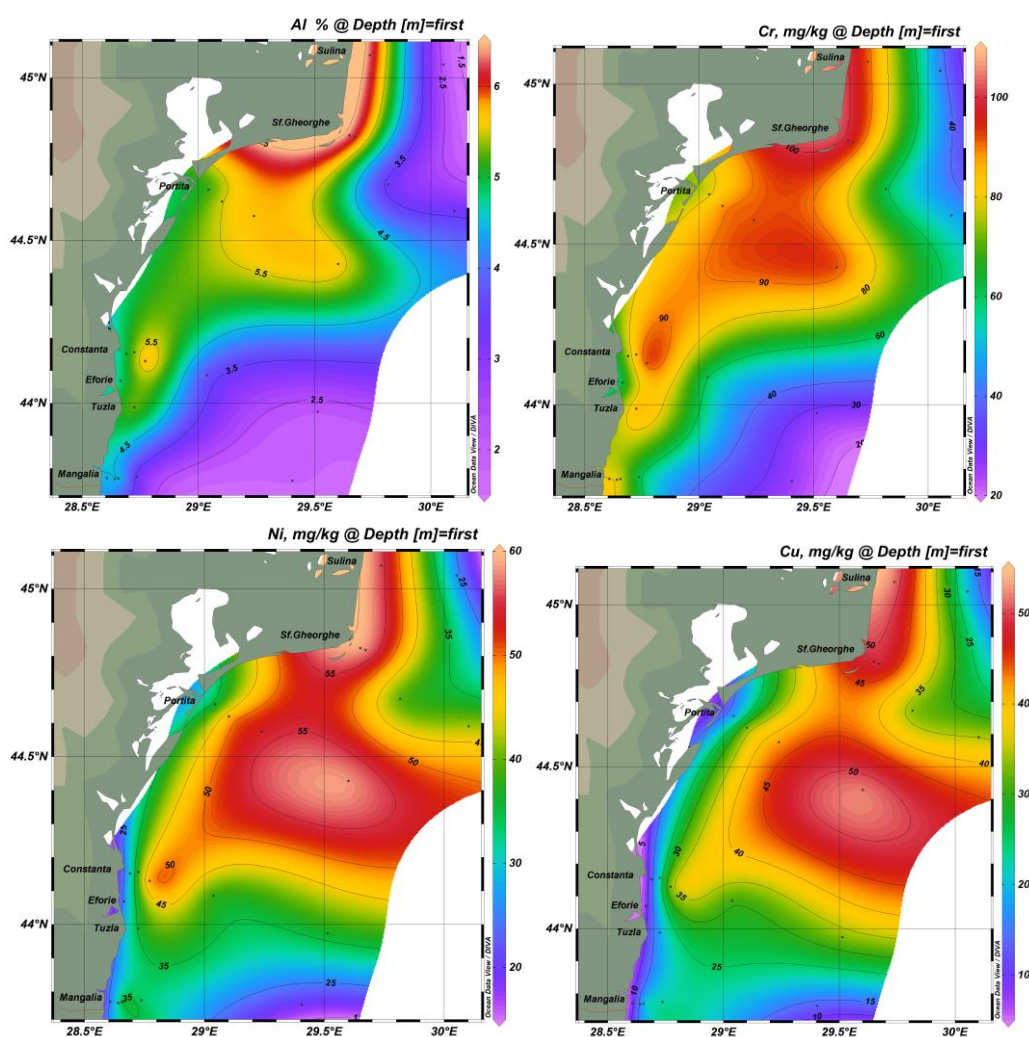
56.9% (for Hg). Spatial distributions of metals in the surface sediments, which are shown in Fig. 3, highlight the following issues:

(i) the highest values of Al concentration, *i.e*., 60640–64930 mg/kg, were detected in the Danube's mouth area (SU01, SG01, and SG03), due to the strong influence of the Danube's input, whereas minimum values (19910 and 22510 mg/kg) were found in the deepest stations from the southern part of the studied area (MA04 and CT05);

(ii) the highest values of Cr concentration (>90 mg/kg) were noticed not only in the Danube's mouth area (SU01, SG01, and SG03), but also in the Portita Bay (PO02, PO04, and PO05) and Constanta area (CT03); similar to Al, the lowest values of Cr concentration (26.26 and 27.74 mg/kg) were measured at the deepest stations from the southern part of the studied area (MA04 and CT05);

(iii) Ni, Cu, and Zn had similar concentration patterns, with higher values (58.35–59.30 mg/kg, 46.67–52.47 mg/kg, and 110.5–118.5 mg/kg) in the Danube's mouth area (SU01, SG01, and SG03) and at the deepest station of the Portita Bay (PO04); minimum values of Ni and Zn concentration (19.28 mg/kg and 27.96 mg/kg) were measured at station MA04, while the lowest levels of Cu concentration (6.865–7.450 mg/kg) were detected at shallower stations EF02, MA05, and MA06;

(iv) the highest levels of As concentration (15.71 mg/kg and 17.16 mg/kg) were at stations SG01 and SG03, while maximum values of Pb and Hg concentration (42.07 mg/kg and 0.23 mg/kg) were at station PO04; minimum values of As and Pb concentration (3.42 mg/kg and 11.58 mg/kg) were at station MA04, while the lowest level of Hg concentration (0.02 mg/kg) was at station EF02.
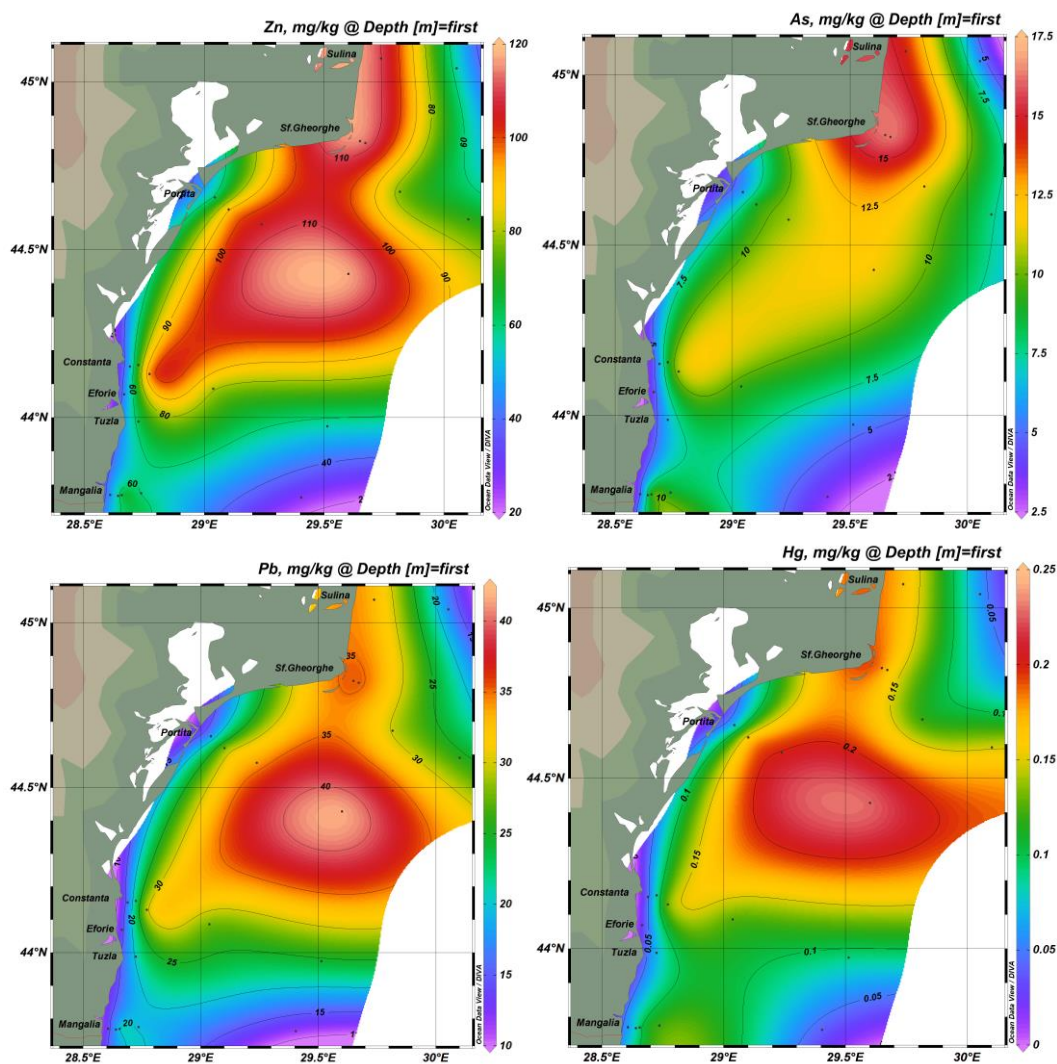
Figure 3. Spatial distribution of Al, Cr, Ni, Cu, Zn, As, Pb, and Hg in the surface sediments of the Romanian inner shelf

Previous works carried out in the period 1997–2007 showed also a large spatial variability of the heavy metals in the surface sediments of the Romanian shelf [25]. Generally, the metal concentrations determined within 1997–2007 were quite higher than the values measured in this study, *e.g.*, $c_{Cr,s}$=34.17–144.26 mg/kg, $c_{Ni,s}$=63.69–87.84 mg/kg, $c_{Cu,s}$=3.40–185.49 mg/kg, $c_{Pb,s}$=5.25–119.75 mg/kg, $c_{Hg,s}$=0.022–0.61 mg/kg.

Statistical processing of experimental data

PCA, which was performed on 8 metal (Al, Cr, Ni, Cu, Zn, As, Pb, and Hg) concentrations, TOC content, water depth, percentages of sand, silt, and clay, highlighted two principal components (PCs) with eigenvalues greater than 1, which account for 84.51% of total variance (TV). The results shown in Figure 4 and Table 6 emphasize the following aspects: (i) PC1, explaining 61.96% of TV, is characterized by high negative loads for As, Ni, Cu, Zn, Pb, Hg, and clay contents as well as a high positive load for sand percentage; (ii) PC2, accounting for 22.56% of TV, presents a high positive load for water depth (*h*) as well as high negative loads for Al and Cr concentrations. Pearson correlation coefficient matrix (Table 7) confirms: (i) high positive correlations among As, Ni, Cu, Zn, Pb, Hg, and clay contents, high negative correlation between clay and sand percentages (P_{clay} and P_{sand}), as well as high negative correlations between P_{sand} and concentration of each metal in this group; (ii) high

positive correlation between Al and Cr contents ($c_{Al,s}$ and $c_{Cr,s}$) as well as high negative correlations between h and $c_{Al,s}$ and h and $c_{Cr,s}$.

Accordingly, As, Ni, Cu, Zn, Pb, and Hg concentrations have similar behavior and they are positively correlated with clay content, whereas Al and Cr contents present close patterns and they are negatively correlated with water depth. More studies in the related literature pointed out that clay particles are important carriers of heavy metals as well as that the water depth can have a significant effect on spatial distributions of metals in the surface sediments [4–7].

Data depicted in Figs. 5 and 6 reveal three main clusters, *i.e.*: (i) cluster I, consisting of stations PO01, CT01, EF02, MA05, and MA06, characterized by the lowest values of h (13.5–27 m), P_{clay} (4.50–12.75%), $c_{As,s}$ (3.79–4.97 mg/kg), $c_{Cu,s}$ (6.87–13.72 mg/kg), $c_{Pb,s}$ (12.71–14.46 mg/kg), and $c_{Hg,s}$ (0.004–0.070 mg/kg), as well as the highest levels of P_{sand} (32.77–66.02%); (ii) cluster II, including stations SU03, SG04, SG05, CT04, CT05, MA04, and MA08, distinguished by high values of h (35–67 m) and lowest levels of $c_{Al,s}$ (19910–35960 mg/kg) and $c_{As,s}$ (26.26-58.74 mg/kg); (iii) cluster III, containing stations SU01, SG01, SG03, PO02, PO04, PO05, CT02, CT03, TZ18, MA07, differentiated by the lowest values of P_{sand} (0.40–5.82%) and the highest levels of $c_{Al,s}$ (53890–64930 mg/kg).
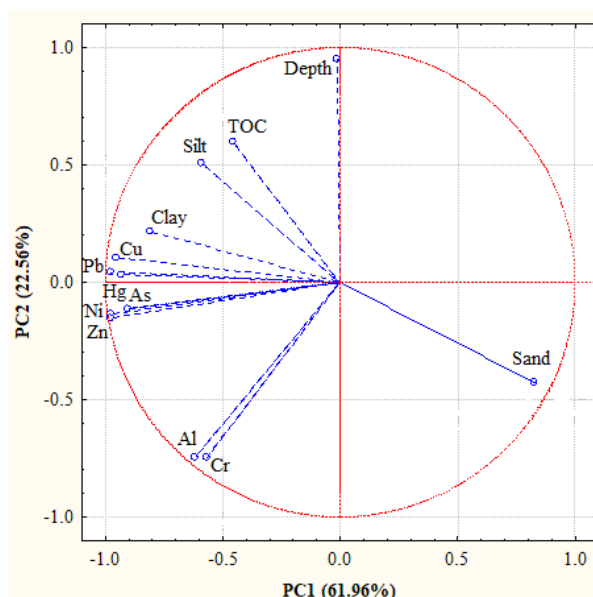

Figure 4. Projections of variables on PC1-PC2 plane

Table 6
Factor coordinates of variables

No.	Variable		PC1	PC2
	Name	Simbol in Fig. 4 and Table 7		
1	Water depth	Depth	-0.01	0.95
2	TOC concentration	TOC	-0.45	0.59
3	Al concentration	Al	-0.62	-0.75
4	As concentration	As	-0.90	-0.11
5	Cr concentration	Cr	-0.57	-0.75
6	Ni concentration	Ni	-0.98	-0.14
7	Cu concentration	Cu	-0.96	0.10
8	Zn concentration	Zn	-0.98	-0.15
9	Pb concentration	Pb	-0.98	0.04
10	Hg concentration	Hg	-0.93	0.03
11	Sand percentage	Sand	0.83	-0.43
12	Silt percentage	Silt	-0.59	0.51
13	Clay percentage	Clay	-0.81	0.22

Table 7. Pearson correlation coefficient matrix

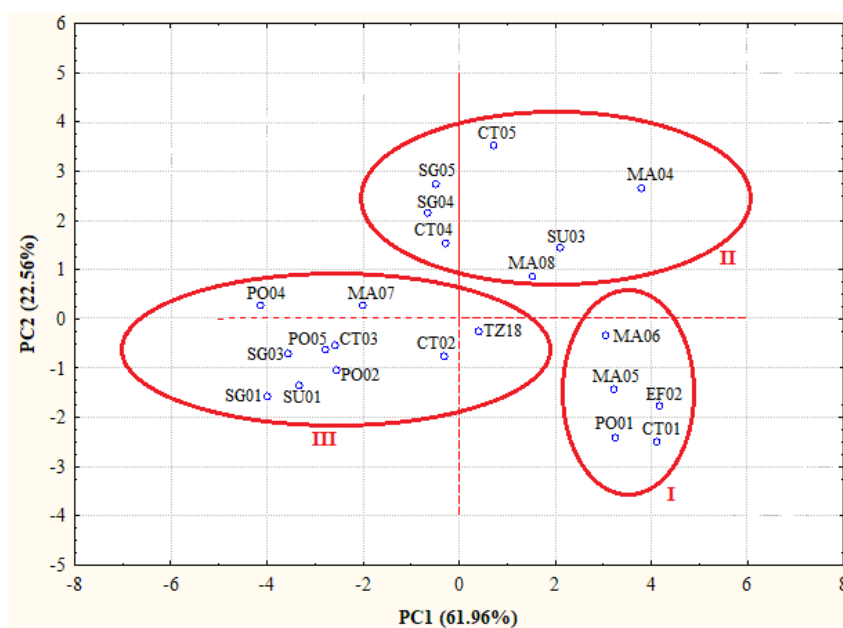| Variable	Depth	TOC	Al	As	Cr	Ni	Cu	Zn	Pb	Hg	Sand	Silt	Clay
Depth	1.00	0.56	-0.67	-0.10	-0.70	-0.10	0.12	-0.13	0.07	0.05	-0.38	0.43	0.21
TOC	0.56	1.00	-0.10	0.36	-0.12	0.38	0.48	0.36	0.51	0.39	-0.49	0.49	0.33
Al	-0.67	-0.10	1.00	0.64	0.95	0.72	0.49	0.71	0.57	0.51	-0.18	0.03	0.28
As	-0.10	0.36	0.64	1.00	0.56	0.90	0.86	0.91	0.86	0.77	-0.67	0.51	0.63
Cr	-0.70	-0.12	0.95	0.56	1.00	0.63	0.40	0.64	0.51	0.47	-0.19	0.06	0.26
Ni	-0.10	0.38	0.72	0.90	0.63	1.00	0.95	0.98	0.96	0.90	-0.71	0.47	0.73
Cu	0.12	0.48	0.49	0.86	0.40	0.95	1.00	0.94	0.97	0.90	-0.78	0.54	0.78
Zn	-0.13	0.36	0.71	0.91	0.64	0.98	0.94	1.00	0.97	0.91	-0.72	0.48	0.73
Pb	0.07	0.51	0.57	0.86	0.51	0.96	0.97	0.97	1.00	0.92	-0.77	0.53	0.77
Hg	0.05	0.39	0.51	0.77	0.47	0.90	0.90	0.91	0.92	1.00	-0.76	0.44	0.86
Sand	-0.38	-0.49	-0.18	-0.67	-0.19	-0.71	-0.78	-0.72	-0.77	-0.76	1.00	-0.85	-0.84
Silt	0.43	0.49	0.03	0.51	0.06	0.47	0.54	0.48	0.53	0.44	-0.85	1.00	0.43
Clay	0.21	0.33	0.28	0.63	0.26	0.73	0.78	0.73	0.77	0.86	-0.84	0.43	1.00

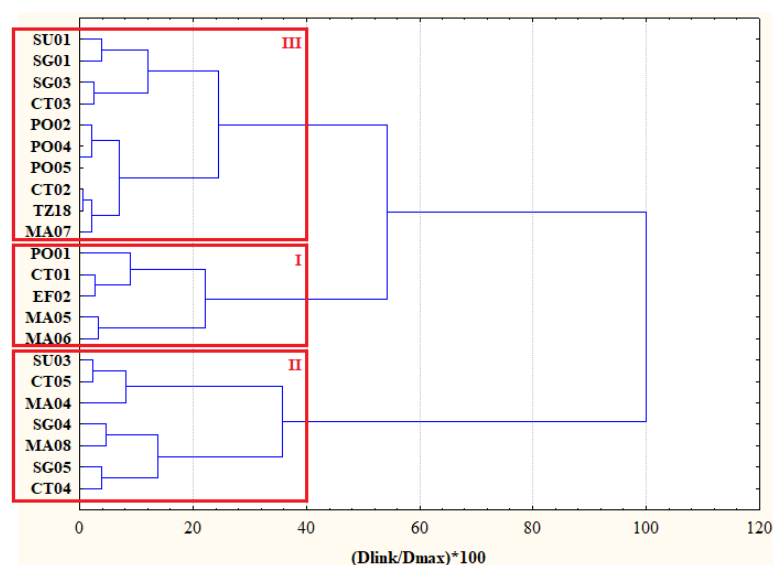**Figure 5.** Projections of cases (stations) on PC1-PC2 plane

Figure 6. Tree diagram for 22 cases
(complete linkage and Euclidean distances)

Data shown in Figure 5 indicate good discriminations between clusters I and III on the PC1 direction and between clusters I and II on the PC2 direction.

PC1 coordinates of stations belonging to clusters I (3.05–4.19) and III (-4.13–0.42) highlight a discrimination between stations in cluster III, characterized by lowest percentages of sand (0.40–5.82%) and higher levels of clay (27.68–48.50%) and heavy metals, *i.e.*, As (6.46–17.16 mg/kg), Ni (36.39–59.30 mg/kg), Cu (19.03–52.47 mg/kg), Zn (72.20–118.5 mg/kg), Pb (22.69–42.07 mg/kg), and Hg (0.085–0.230 mg/kg), and those in cluster I with highest percentages of sand (32.77–66.02%) and lower levels of clay (4.50–12.75%), As (3.79–4.97 mg/kg), Ni (22.65–31.87 mg/kg), Cu (6.87–13.72 mg/kg), Zn (36.84–51.55 mg/kg), Pb (12.71–14.46 mg/kg), and Hg (0.004–0.070 mg/kg).

PC2 coordinates of stations in clusters I (from -2.51 to -0.34) and II (0.85–3.52) show a distinction between stations in cluster I, differentiated by the lowest values of water depth (13.5–27 m) and higher levels of Al (40540–50550 mg/kg) and Cr (66.15–84.95 mg/kg), and those in cluster II with higher values of water depth (35–67 m) and lower levels of Al (19910–35960 mg/kg) and Cr (26.26–58.74 mg/kg).

Pollution indices

Descriptive statistics (minimum, maximum, mean, median, standard deviation, and coefficient of variation) related to pollution indices corresponding to each metal, *i.e.*, EF, CF, and I_{geo}, which were estimated using Eqs. (1)–(3), are summarized in Table 8.

.

Table 8. Descriptive statistics for pollution indices

Pollution index	Metal Descriptives	As	Cr	Ni	Cu	Zn	Pb	Hg
Enrichment factor (*EF*)	Min	0.56	1.10	0.61	0.27	0.73	1.13	0.43
	Max	2.20	1.86	1.92	2.64	2.09	4.36	4.39
	Mean	1.21	1.43	1.06	1.15	1.40	2.24	2.52
	Median	1.22	1.41	1.07	1.21	1.49	2.25	2.58
	SD	0.45	0.18	0.31	0.60	0.43	0.85	1.24
	CV	0.37	0.13	0.30	0.52	0.31	0.38	0.49
Contamination factor (*CF*)	Min	0.26	0.29	0.28	0.15	0.29	0.58	0.25
	Max	1.32	1.12	0.87	1.17	1.25	2.10	2.88
	Mean	0.68	0.81	0.58	0.63	0.78	1.22	1.41
	Median	0.65	0.86	0.55	0.68	0.76	1.26	1.47
	SD	0.33	0.25	0.20	0.34	0.31	0.46	0.80
	CV	0.48	0.30	0.34	0.54	0.40	0.38	0.57
Geo-accumulation index (*I_geo*)	Min	-2.51	-2.36	-2.40	-3.30	-2.35	-1.37	-2.58
	Max	-0.18	-0.43	-0.78	-0.36	-0.27	0.49	0.94
	Mean	-1.31	-0.97	-1.45	-1.52	-1.06	-0.41	-0.38
	Median	-1.22	-0.80	-1.44	-1.15	-0.99	-0.25	-0.03
	SD	0.73	0.55	0.51	0.98	0.62	0.59	1.03
	CV	0.56	0.57	0.36	0.64	0.59	1.44	2.68

Spatial distributions of EF_i (Figure 7) show values between 0.27 and 4.39 (no, minor, and moderate pollution), with a minimum for Cu at the station EF02 and a maximum for Hg at the station SG05. ANOVA one way test followed by Tuckey (HSD) multiple comparison test revealed significant higher values only for Pb and Hg.

Values of EF_i greater than 3, suggesting moderate enrichment, were found only for Pb (maximum of 4.36) and Hg (maximum of 4.39). Higher values of EF_{Pb} and EF_{Hg} found at stations SG04 (3.66 and 3.61), SG05 (3.03 and 4.39), CT04 (2.97 and 3.34), and CT05 (4.36 and 4.00), which are situated on the Danube's plume direction, can be related to the riverine discharges. Moreover, higher levels of EF_{Hg} (3.42–4.03) were detected at stations located in the Portita Bay (except PO01), most probable linked to the oil and gas extraction activities in this area, at station SG01 (3.31), due to the direct
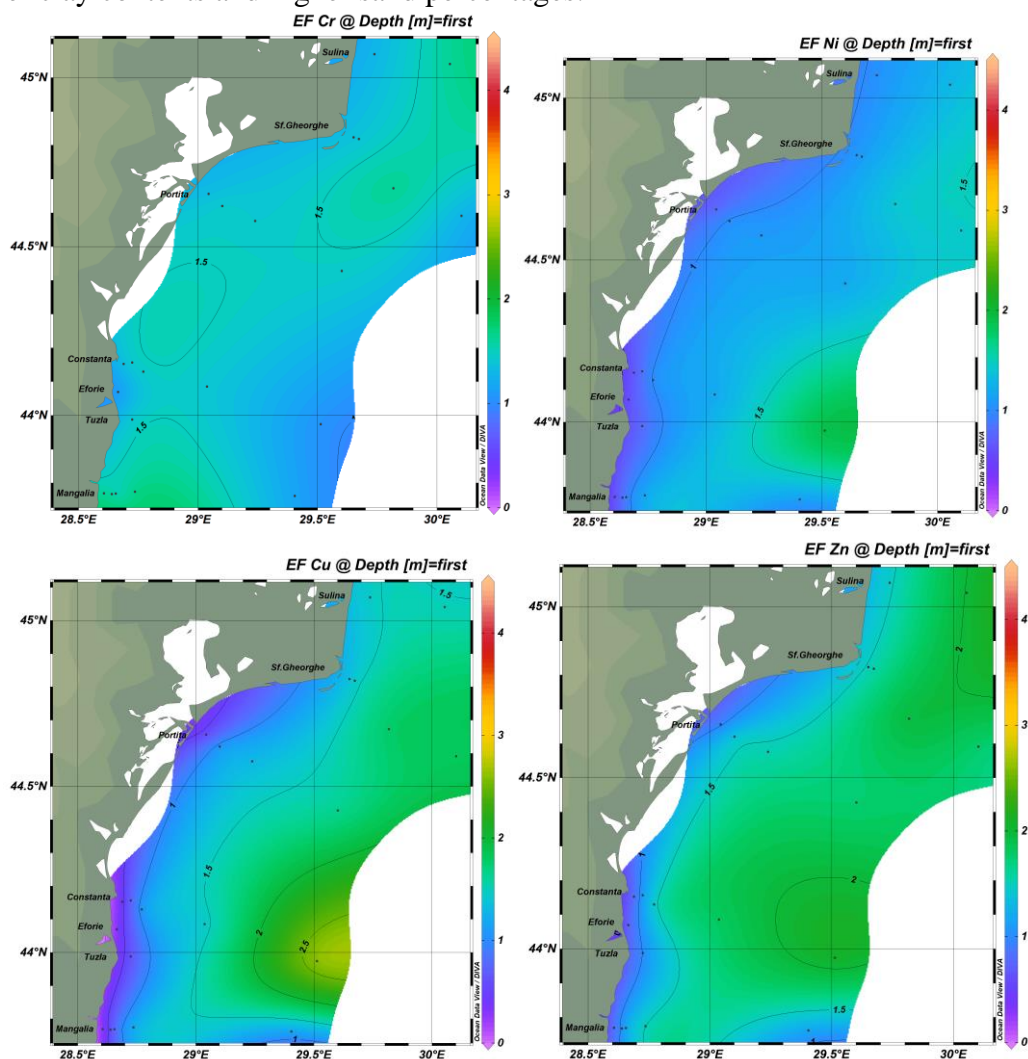
influence of the Sf. Gheorghe branch, and also at station MA08 (4.03), possibly related to the local regime of currents carrying on the wastewater and industrial discharges.

Lower levels of EF_{Pb} (1.13–1.30) and EF_{Hg} (0.43–0.79) were observed at shallow stations PO01, CT01, EF02, and MA06, characterized by lower clay contents (4.50–11.43%) and higher sand percentages (36.75–66.02%). Moreover, the lowest values of EF_i for Pb (1.13) and Hg (0.43) were found at the station EF02, from which sediments with the lowest clay content (4.50%) and the highest sand content (66.02%) were collected. These findings suggest the influence of the sediment type on the pollution level.

All values of EF_{Cr} (1.10–1.86) were in the range of 1–3 (minor enrichment), with higher ones in the shallower waters in front of Mangalia, *i.e.*, stations MA05 (1.61), MA06 (1.86), and MA08 (1.72), and on the Danube's plume direction, including stations SU03 (1.63) and SG04 (1.64).

68% of values of EF_{Ni} (0.61–1.92) and EF_{Cu} (0.27–2.64) are between 1 and 3, higher ones being on the Danube's plume direction, at stations SG04 (1.41 and 1.79), SG05 (1.46 and 1.83), and CT05 (1.92 and 2.64). 73% of values of EF_{As} (0.56–2.20) and EF_{Zn} (0.73–2.09) are in the range of 1–3, maximum levels being determined on the Danube's plume direction, at stations CT05 for Zn and SG04 for As, respectively.

Similar to Pb and Hg, the lowest values of EF_i for Ni (0.62), Cu (0.27), Zn (0.73), and As (0.56) were found at the station EF02, where the sediments had the lowest clay content and the highest sand content. Morever, lower levels of EF_i, *i.e.*, 0.56–0.64 for As, 0.61–0.74 for Ni, 0.27–0.48 for Cu, 0.73–0.86 for Zn, were also found at the stations PO01, CT01, EF02, MA05, and MA06, characterized by lower clay contents and higher sand percentages.
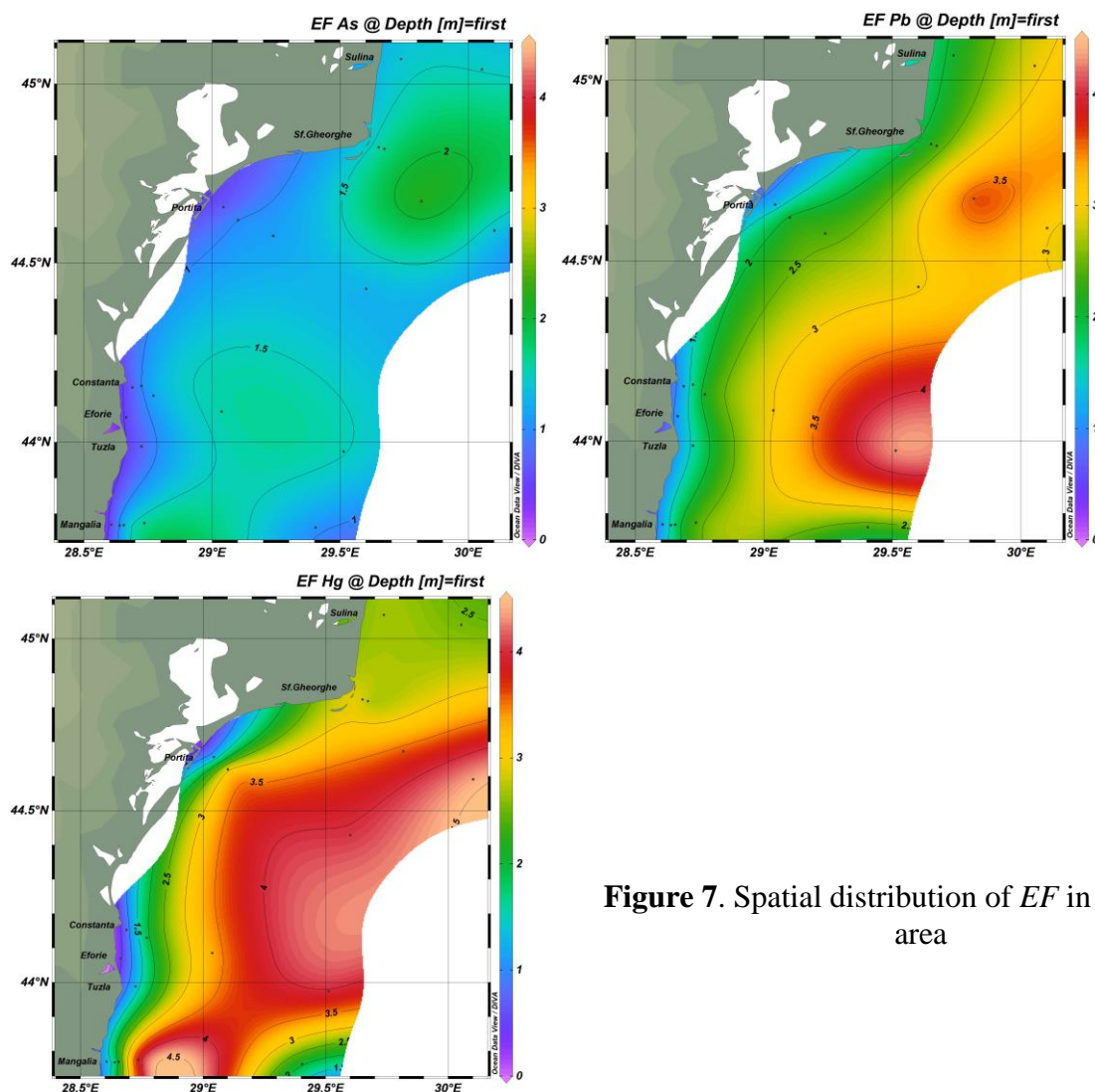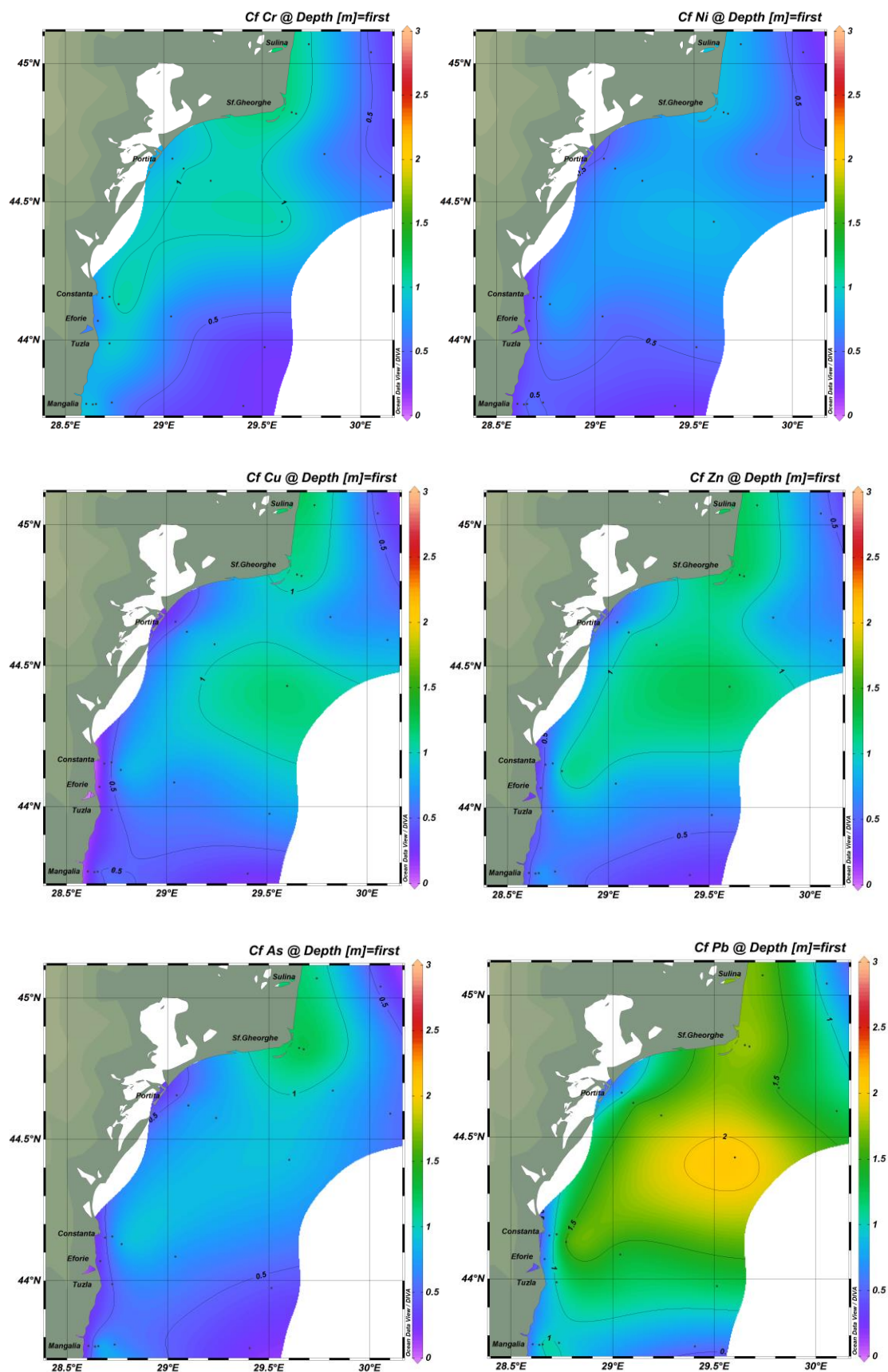
Figure 7. Spatial distribution of *EF* in the studied area

Spatial distributions of CF_i (0.15–2.88), which are shown in Figure 8, emphasize low ($CF_i<1$) and moderate ($1<CF_i<3$) metal contamination for all 22 stations. Similar to EF_i, ANOVA one way test followed by Tuckey (HSD) multiple comparison test revealed significant higher values of CF_i only for Hg and Pb as compared to the rest of analyzed elements. Referring to the values of CF_{Pb} (0.58–2.10) and CF_{Hg} (0.25–2.88), there is a moderate contamination at 13 stations (SU01, SG01, SG03–05, PO02, PO04, PO05, CT02–05, and MA07) for both metals as well as at stations TZ18 for Pb and MA08 for Hg. Relatively higher values of CF_{Pb} and CF_{Hg} detected at stations CT02, CT03, TZ18, MA07, and MA08 are most probable linked to the coastal anthropogenic pressures resulting from the port activities, tourism, and urban wastewater discharges.

Values of CF_{Ni} (0.28–0.87) indicate only low contamination. Values of CF_{Cr} (0.29–1.12) and CF_{Zn} (0.29–1.25) are more than 1 in the Danube's mouth area (SU01, SG01, and SG03), in the Portita Bay (PO2, PO4, and PO5), and in the Constanta area (CT03). Values of CF_{Cu} (0.15–1.17) and CF_{As} (0.26–1.32) are higher than 1 in front of the Danube's mouths (SU01, SG01, and SG03) as well as at the eastern limit of the Portita Bay (PO04) for Cu and at station MA07 for As.

The lowest values of CF_i were found generally at the easternmost station from the Mangalia area, MA04 (CF_{Cr}=0.29, CF_{Ni}=0.28, CF_{Zn}=0.29, CF_{As}=0.26, and CF_{Pb}=0.58), where the Danube's influence is significantly weaker. The values of CF_i for Cu and Hg were minimum at stations characterized by higher levels of P_{sand} (CF_{Cu}=0.15 at stations EF02 and MA06 and CF_{Hg}=0.25 at station EF02).
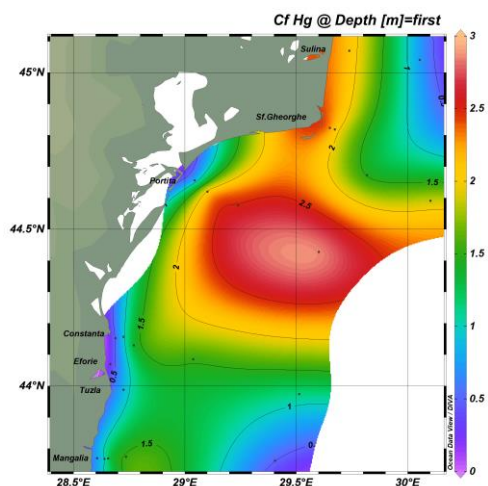
Figure 8. Spatial distribution of *CF* in the studied area

Characteristic values of $I_{geo,i}$ for *i*=As, Cr, Ni, Cu, Zn are below 0, indicating unpolluted sediments with respect to these elements. Levels of both $I_{geo,Pb}$ (-1.37–0.49) and $I_{geo,Hg}$ (-2.58–0.94) are in the range of 0–1 at 3 stations in the Danube's mouth area (SU01, SG01, and SG03), 3 stations in the Portita Bay (PO2, PO4, and PO5), and 1 station in the Constanta area (CT03), whereas values of $I_{geo,Hg}$ are higher than 0 at the stations SG05 (0.3) and MA07 (0.2), indicating uncontaminated to moderately contaminated sediments. Spatial distributions of $I_{geo,Pb}$ and $I_{geo,Hg}$ in the studied area are shown in Figure 9.
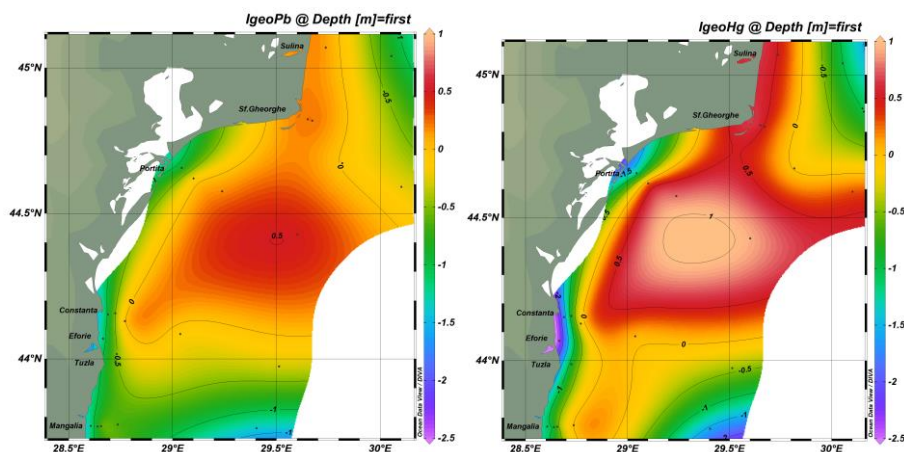

Figure 9. Spatial distribution of I_{geo} for Pb and Hg in the studied area

4. Conclusions

Spatial distributions of some trace elements (As, Cr, Ni, Cu, Zn, Pb, and Hg) and Al in the surface sediments collected from NW Black Sea were determined. Mean values of heavy metal concentrations (0.11–74.11 mg/kg) decreased in the order: Zn>Cr>Ni>Cu>Pb>As>Hg. The elements considered in this study showed relatively large spatial variability with higher concentrations in front of the Danube's mouths and at eastern edge of the Portita Bay.

Multivariate analysis revealed that As, Ni, Cu, Zn, Pb, and Hg concentrations had similar behavior and they were positively correlated with the clay content, whereas Al and Cr contents presented close patterns and they were negatively correlated with the water depth. Three clusters of stations having dissimilar metal accumulation in the surface sediments were obtained.

Different indices used to evaluate the degree of pollution of the Romanian inner shelf sediments suggest that most metal concentrations in the sediments were, generally, at natural levels. Dominant heavy metal pollution in the Romanian inner shelf sediments came from Pb and Hg. The values of *EF*, *CF*, and I_{geo} indices suggest a higher sediment pollution with Pb and Hg along the Danube's plume

direction, the oil platform area (eastern edge of the Portita Bay), and partially in the Constanta and Mangalia areas, indicating the influence of oil and gas extraction, port activities (ships berthing, shipyards, handling activities of bulky goods and sewage outfall), tourism, and urban wastewater discharges.

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