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Spatial distribution and ecological risk evaluation of toxic metals in the southern Black Sea coastal sediments

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ABSTRACT

Spatial distribution and ecological risk levels of toxic metals (Cu, Pb, Zn, Ni, Co, As, Sr, V, and La) in sediments from the southern Black Sea coastal (Türkiye) were evaluated. The sediment samples were taken in April and May 2019 from thirty-one stations, from depths ranged between 16 and 65 m. The average metal concentrations (in dry weight) varied from 59.4 ± 4.8 to 102.5 ± 12.3 for Cu, 39.3 ± 4,1 to 46.1 ± 2.9 for Pb, 104.5 ± 4.7 to 126 ± 6.9 for Zn, 21.2 ± 1.8 to 24.9 ± 1.4 for Ni, 9.8 ± 0.4 to 16.6 ± 1.5 for As, 16.7 ± 0.5 to 18.2 ± 0.9 for Co, 68.2 ± 11.4 to 123.3 ± 13.5 for Sr, 82.7 ± 13.1 to 97.3 ± 4.3 for V, and 16.2 ± 1.8 to 23.6 ± 1.8 μg g^{-1} for La. Geoaccumulation index (I_{GEO}), Sediment enrichment factor (SEF), and pollution load index (PLI) indicated that Cu and Pb are above the pollution limits. Thus, continuous pollution monitoring programs should be established. Moreover, measures should be implemented more effectively to prevent pollution.

1. Introduction

The Black Sea is a unique ecosystem representing the world's largest landlocked sea with a surface area of 4.2 × 10^5 km^2 and a volume of 5.3 × 10^5 km^3 with a maximum depth of 2200 m (Özsoy and Ünlüata, 1997). The total coastal length of the Black Sea, including the Sea of Azov, is 4869 km. 3456 km of this is the coasts of Ukraine (1756 km, 36.1 %) and Türkiye (1700 km, 34.9 %) (Üniversitesi et al., 2019). It is among the most vulnerable bodies of water on the earth due to its rare hydrochemical, hydrographic, geographical, and geological features and its exposure to significant human-induced effects (Tuncer et al., 1998). One of the most notable characteristics of the Black Sea's oceanography is that freshwater input surpasses water loss through evaporation. It is connected to the Aegean Sea via the Bosporus, the Sea of Marmara, and the Dardanelles (Ozseker et al., 2013; Sezgin et al., 2017). Both natural and anthropogenic influences have a significant impact on the Black Sea (Mutlu, 2021; Ozseker, 2021; Ozseker et al., 2016; Terzi et al., 2020). The largest rivers of the Europe (Danube, Dnieper, and the Dniester) discharge into the north-west (Sezgin et al., 2017). The Danube, which is one of Europe's largest rivers, has a major impact on the Black Sea environment. (Mee, 1992; Muftuoglu, 2013). These rivers drain the industrial centers and agricultural areas of Central and Eastern Europe and transport a substantial amount of anthropogenic and natural pollutants (Sarı et al., 2018). Türkiye has numerous large and minor rivers that empty into the Black Sea as well.

The pollution levels in river and marine environments have increased due to global urbanization, population, and industry particularly in the last 150 years (Sarı et al., 2018). Urbanization in the Black Sea continues to increase rapidly along the entire coastal area. Unfortunately, the settlements' domestic wastes are released directly into the sea or streams without being treated. As a result, the transportation of anthropogenic contaminants from rivers has had a negative impact on the Black Sea sediments and water in recent centuries (Mülayim and Balkis, 2015; Sarı et al., 2018; Terzi et al., 2022; Yiğiterhan and Murray, 2008). Due to its geographical position, intense river inputs, and limited water change, the Black Sea had become one of the most polluted sea in terms of toxic metals (Bat et al., 2019).

Sediments are particles consisted of several substances at the bottom of water bodies. Depending on the environmental influence of rivers, biogeochemical processes, and hydrodynamic structure, coastal marine sediments have become a significant accumulation area for toxic metals. Thus sediments are considered as a sink for the toxic metals in marine environment. In addition, sediments can reflect the level of aquatic pollution and are an indicator of aquatic environmental pollution with

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this feature (Ali Azadi et al., 2018; Galkus et al., 2012; Selvaraj et al., 2004). Many biogeochemical reactions occur when sediments deposited by toxic metals. During these reactions, transfer of toxic metals from pore water to deep seawater takes place. As a result, the geochemistry of bottom sediments influences the chemistry of the water column. Thus, heavy metals accumulated in polluted sediments create a toxic effect not only for benthic organisms, but also for the living organisms in the water column (Ozseker, 2021). Because of their accumulative behavior, toxic metals in aquatic ecosystems are considered serious pollutants (Monikh et al., 2015; Saiful et al., 2015; Bibak et al., 2018). They are often regarded as the most significant anthropogenic pollutants in marine and coastal habitat (Sreenivasulu et al., 2018). Pollution sources in surrounding estuaries and rivers are linked to toxic metal pollution in coastal ecosystems. The majority of anthropogenic metals found in coastal areas are of terrestrial origin. Industrialization, urbanization, mining, and other human-induced activities make the greatest contribution (Ip et al., 2007; Ozseker, 2021). The metals, such as copper (Cu), lead (Pb), zinc (Zn), mercury (Hg), arsenic (As), nickel (Ni), and cobalt (Co) in aquatic ecosystems are regarded as toxic pollutants (Forstner and Wittmann, 1983; Özşeker, 2019). Therefore, sediments play a key role in determining toxic metal pollution in aquatic ecosystems since they are sinks for these elements (El Nemr and El-Said, 2017; Abrahim and Parker, 2008; Yeşim Özkan et al., 2012; Parween et al., 2021). Sediment analyses are widely used in defining the toxicity of metals, environmental quality assessment, and digenetic studies (Longhini et al., 2022; Shaw, 1990; Soliman Alshami and A, 2018; Zhang et al., 2021). Physical, chemical, and biological processes can return contaminants from sediments to the water column following precipitation. Several chemical and physicochemical parameters influence the mobility of toxic metals in the sediment layer (Ali et al., 2021; Ziyath et al., 2011). These factors are the mechanisms controlling. For this reason, it is important to consider these factors in evaluating the toxicity of metals for the environment and to associate them with the physicochemical parameters of the environment (Ali et al., 2021; Ozseker, 2021). There has been several studies determining the toxic metal contamination in the bottom sediments of the Black Sea (Alkan et al., 2018; Alkan et al., 2021; Ozkan and Buyukisik, 2012; Ozseker et al., 2013; Ozseker and Eruz, 2016), however the mentioned studies are very limited in the sample size and area. Thus, the aim of this study is to investigate the spatial distribution of natural and anthropogenic toxic metal pollution in the southern Black Sea's coastal sediments. In addition, pollution load index (PLI), sediment enrichment factor (SEF), sediment quality guideline (SQG), and geo-accumulation index (I_{GEO}), were used to reveal the pollution, natural and anthropogenic separation, and ecological effect of metals in Black Sea coast of Türkiye.

2. Materials and methods

2.1. Study area and sampling

The Turkish coast of the Black Sea, which has an approximate coastal length of 1100 km, was chosen as the research area. It is located between the coordinates 41.216868 N - 30.445846 E and 41.457114 N - 41.355802 E on the southern coast of Türkiye. The sediment samples were taken in April and May 2019 from thirty-one stations, with depths varying between 16 and 65 m. Station numbers between 1 and 10 represent the coasts of the southwestern Black Sea Region (WB), those between 11 and 20 represent the coasts of the middle Black Sea region (MB), and those between 21 and 31 represent the coasts of the southeastern Black Sea region (EB) (Fig. 1). While determining the stations, industrial and domestic discharge points, river discharge areas, and intense residential areas were considered.

The sediment samples from each station were collected in triplicate using an Ekman Grab (Zárate et al., 2021). The sediment layer from the top 5 cm was processed for further analysis. Each sample was homogenized and stored in polyethylene containers. Immediately after sampling, sediment physicochemical parameters; pH, oxygen, salinity, and temperature were measured in situ. pH was measured using a Hach Lange HQ40D multimeter from the sediment water mix (1:2 w/v). Temperature, salinity, and dissolved oxygen were measured using a Conductivity, Temperature, and Depth sensor (CTD) probe. A modified Walkley–Black titration method with a <0.05 % detection limit was used to determine total organic carbon (TOC) (Gelman et al., 2012). To prevent any metal contamination from the equipment, plastic tools were used to handle the sediments. The samples were stored in a cooler and transported to the laboratory, then, kept at −18 °C to prevent contamination prior to the analysis. Metals tend to accumulate in the fine-grained fractions of sediments, hence, categorizing sediments by grain size is an important factor affecting the metals accumulation capacity of sediments (Chileshe et al., 2020; Sharma et al., 2020; Zhang et al., 2014). A vibratory sieve shaker (AS200, Retsch, Duesseldorf, Germany) was used to categorize the particles; clay (≤0.063 mm), sand (0.063–2 mm), and gravel (2 mm) (Fantong et al., 2014). Since toxic metals tend to accumulate in the smaller fractions of the sediments (Maslennikova et al., 2012; Nazneen and Patel, 2016), clay fractions with <63 μm was used for the metal analyses (Morillo et al., 2004). A total of ten toxic metals (Copper (Cu), Lead (Pb), Zinc (Zn), Nickel (Ni), Cobalt (Co), Arsenic (As), Strontium (Sr), Vanadium (V), Lanthanum (La) and Aluminum (Al)) were measured using an inductively coupled plasma mass spectrometer (ICP-MS) at the ACME laboratory (Vancouver, BC, Canada). The analysis' precision ranged between 95.79 and 130.49 %. STD-DS 7 was used as the reference material for determining the accuracy of metal analysis in sediment samples. The detection limits for the toxic metals were as follows: 0.1 μg g^{-1} for Cu, 1 μg g^{-1} for Zn, 0.1 μg g^{-1} for Ni, 0.1 μg g^{-1} for Co, 0.6 μg g^{-1} for As, 1 μg g^{-1} for Sr, 2 μg g^{-1}

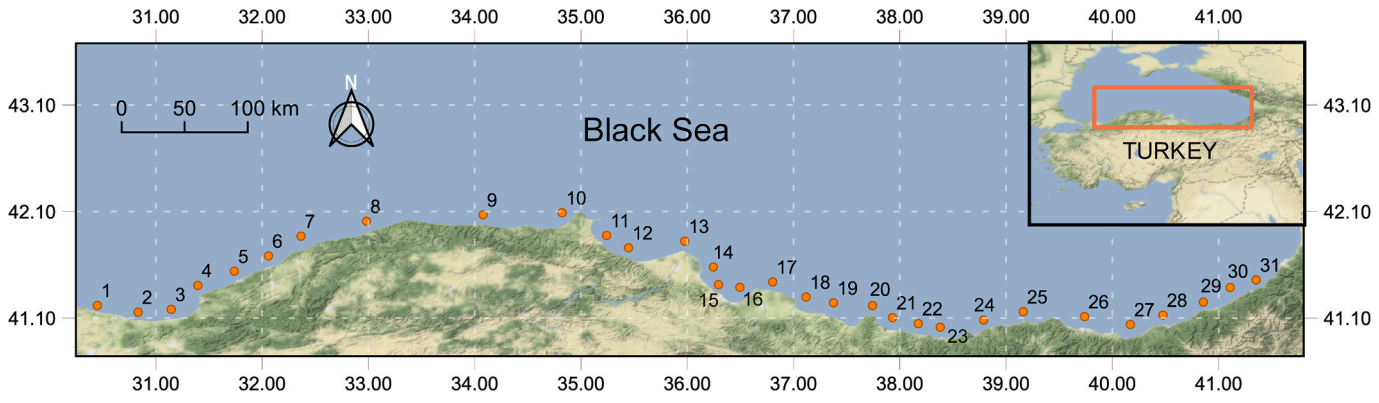


Fig. 1. Map of the study area.

for V, 1 μg g^{-1} for La, 0.01 % for Al in sediments.

2.2. Sediment pollution indexes

The pollution load index (PLI) proposed by Tomlinson et al. (1980) was used for determining toxic metal contamination level from a holistic view of the sampling area (Kowalska et al., 2018). The PLI was estimated according to Eqs. (1) and (2).

$$CF = C_{\text{Metal concentration}} / C_{\text{Background concentration of the same metal}} \quad (1)$$

$$PLI = (Cf\ 1 \times Cf2 \times Cf3 \times \cdots \times Cn)^{1/n} \quad (2)$$

After geochemical normalization, the Sediment Enrichment Factor (SEF) is used to assess the degree of contamination caused by each element individually (Kowalska et al., 2018). Metal concentrations in the upper continental crust (UCC) were used as background reference values (Rudnick et al., 1985). Although there is no definite agreement about the selection of the element to be used in normalization, elements that are geochemically inactive and easily found in fine-grained materials such as aluminum, iron, zircon, and titanium are generally used (Migaszewski et al., 2014). Because of its resemblance to the metal concentration in silicate crustal rocks, Al was chosen for geochemical normalization (Faměra et al., 2018). SEF was estimated using the following Eq. (3);

$$SEF = (C_M/C_{Al})_{\text{Sample}} / (C_M/C_{Al})_{\text{Earths crust}} \quad (3)$$

where $(C_M/C_{Al})_{Sample}$ is the ratio of the measured metal concentration and Al (C_{Al}) in the sediment sample, and $(C_M/C_{Al})_{Earth's\ crust}$ is the ratio of the measured metal (C_M) and the reference ratio of Al in the Earth's crust (Sinem Atgin et al., 2000).

The geoaccumulation index (I_{GEO}) was used to estimate the contribution level of anthropogenic effects to the toxic metal abundance by using following Eq. (4) (Liu et al., 2019):

$$I_{GEO} = log_2{}^{[Cn/(1.5Bn)]} \quad (4)$$

where C_n is the measured concentration of the toxic metal n in the sediment, Bn is the geochemical background concentration for element n which is either directly measured in un-impacted sediment of the area or taken from the literature (Turekian et al., 1961). Classification and definition values of the pollution indexes are given in Table 1.

2.3. Statistical methods

The normal distribution of the data was tested using the Shapiro-Wilk test. The data did not satisfy the normal distribution; thus, nonparametric tests were used to analyze the data. The difference in metal concentrations between the regions was checked using the Kruskal-Wallis test. In case significant differences were noticed, Dunn's test was used as a post hoc test to determine the differing regions. The relationship between toxic metals, physicochemical properties were assessed using the Spearman correlation. Principal component analysis was conducted to reduce the dimension of the data to identify multivariate effects of metals. The clustering stations were determined using the k-means clustering method. Redundancy analysis (RDA) was used to determine the effects of measured environmental factors on the heavy metal distribution. The environmental parameters with <10 variance inflation factor (VIF) were selected for the RDA. The analyses were done by R programming language (R 4.1.2) (R Core Team, 2021) using vegan (Oksanen et al., 2020), factominer (Lê et al., 2008), and rstatix (Kassambara, 2021). Data were visualized using ggplot2 (Wickham, 2016).

3. Results and discussion

3.1. Evaluation of physicochemical properties and sediment characterization

The physicochemical properties and sediment characteristics in the presented study are similar to the general coastal oceanographic features of the Black Sea. However, when analyzed within itself, there are differences between regions. The physicochemical properties and sediment grain size are given in detail in Table 2. The sand fractions were found to be dominant (>63.5 %) in the sediment layer. It is known that metals transition from solid sediment surfaces to pore water and hence from pore water to water column with the effect of physicochemical parameters. In this context, sediment porosity is an important factor in benthic studies (Zhang et al., 2014). In the present study, the porosity varies between 41.5 % and 60.5 %. TOC concentration, another important factor affecting metal mobility, was between 0.31 % and 1.84 %. When the physicochemical parameters related to the mobility of metals were examined, a difference was observed between the stations depending on the depth. Also, values of pH, temperature, salinity, and oxygen in the stations ranged between 6.12 to 8.20, 7.29 to 12.84 °C, 18.21 to 18.81 ‰, and 6.89 to 8.60 mg/L, respectively.

3.2. Evaluation of toxic metal concentrations in sediments

Spatial concentrations of toxic metals (Cu, Pb, Zn, Ni, Co, As, Sr, V, and La) in the coastal sediment samples are given in Fig. 2. Toxic metal concentrations in surface sediments of WB (stations between 1 and 10) varied from 35.1 to 78.1 μg g^{-1} for Cu, from 33.1 to 54.4 μg g^{-1} for Pb, from 84 to 134 μg g^{-1} for Zn, from 16.4 to 35.1 μg g^{-1} for Ni, from 15.2 to 36.7 μg g^{-1} for Co, from 8 to 12.3 μg g^{-1} for As, from 55 to 124 μg g^{-1} for Sr, from 71 to 98 μg g^{-1} for V, and from 15 to 24 μg g^{-1} for La.

Toxic metal concentrations in MB (stations between 11 and 20) varied from 46.3 to 89.2 μg g^{-1} for Cu, from 19.9 to 53.5 μg g^{-1} for Pb, from 99 to 207 μg g^{-1} for Zn, from 17 to 34.1 μg g^{-1} for Ni, from 15.1 to 31.1 μg g^{-1} for Co, from 9.4 to 17.2 μg g^{-1} for As, from 50 to 148 μg g^{-1} for Sr, from 77 to 120 μg g^{-1} for V, and from 8 to 24 μg g^{-1} for La.

Toxic metal concentrations in EB (stations between 21 and 31) varied from 58.3 to 170.5 μg g^{-1} for Cu, from 27.4 to 62.3 μg g^{-1} for Pb, from 90 to 160 μg g^{-1} for Zn, from 15.1 to 31.1 μg g^{-1} for Ni, from 16.4 to 19.8 μg g^{-1} for Co, from 10.5 to 28.7 μg g^{-1} for As, from 52 to 226 μg g^{-1} for Sr, from 80 to 131 μg g^{-1} for V, and from 14 to 35 μg g^{-1} for La (Fig. 2).

Table 1
Classification and definition values of pollution indices.

PLI			SEF			I_{GEO}		
Class	Range	Remark	Class	Range	Remark	Class	Range	Remark
1	<0–0	Non pollution	1	1–3	Minor enrichment	0	≤1	Uncontaminated
2	0–1	Low pollution	2	3–5	Moderate enrichment	1	0–1	Uncontaminated-Moderately
3	1–2	Moderate pollution	3	5–10	Moderate-severe enrichment	2	1–2	Moderately
4	2–4	High pollution	4	10–25	Severe enrichment	3	2–3	Moderately-Heavily
5	4–8	Very high pollution	5	25–50	Very severe enrichment	4	3–4	Heavily
6	8–16	Extremely pollution	6	>50	Extremely Severe enrichment	5	4–5	Heavily-Extremely
						6	≥5	Extremely

Table 2
Physicochemical properties of the coastal sediments in the present study.

Area	Station	Depth (m)	Gravel (%)	Sand (%)	Clay (%)	Porosity (%)	TOC[a] (%)	Salinity (‰)	pH	Oxygen (%)	Oxygen (mg/L)	Temperature (°C)
Western Black Sea Region (WB)	1	16	2,4	54,6	43	57	0,52	18,77	7,96	80,8	8,6	12,84
	2	20	2,8	50,1	47,1	58,6	0,54	18,21	7,95	79,8	8,4	12,26
	3	22	2,8	49,4	47,8	59,7	0,57	18,46	7,56	79,8	8,4	12,26
	4	41	1,2	74,3	24,5	44,2	0,52	18,72	7,97	70,9	7,38	7,97
	5	35	6,7	68,3	25	46,3	0,58	18,68	7,61	72,6	7,58	8,07
	6	20	1,6	40,7	57,7	58,6	0,56	18,62	7,63	70,9	7,49	9,76
	7	52	5,3	70,6	24,1	46,2	0,55	18,77	7,74	65,7	7,31	7,38
	8	60	4,7	54,9	40,4	56,2	0,31	18,79	8,2	63,6	7,2	7,30
	9	65	1,9	73,5	24,6	43,5	0,31	18,81	8,18	63,6	7,18	7,29
	10	45	15,6	60,1	24,3	48,5	0,5	18,72	7,95	72,6	7,37	7,37
	11	30	10,4	56,4	33,2	56,2	0,48	18,62	7,97	77,7	8,02	8,07
	12	28	4,3	70,1	25,6	46,2	0,51	18,56	7,9	75,7	7,96	8,61
	13	50	5,6	45,1	49,3	57,3	0,52	18,75	7,96	63,4	7,1	7,38
	14	27	1,8	66,1	32,1	46,4	0,52	18,59	7,9	78,5	8,04	8,28
Middle Black Sea Region (MB)	15	17	7,3	70,6	22,1	46,2	0,54	18,62	7,82	81,3	8,57	12,31
	16	30	6,2	75,1	18,7	44,5	0,63	18,62	7,41	76,4	7,9	8,01
	17	28	2,5	59,7	37,8	55,1	0,56	18,59	7,65	75,6	7,52	8,28
	18	34	2,6	63,7	33,7	47,3	0,6	18,68	7,5	74,2	7,5	7,83
	19	51	1,9	74,1	24	42,8	0,84	18,77	7,49	68,6	7,08	7,31
	20	42	3,7	68,3	28	46,5	0,71	18,72	7,87	70,1	7,11	7,45
	21	45	11,5	55,7	32,8	56	1,84	18,77	6,8	69,1	7,1	7,55
	22	50	8,6	70,5	20,9	46,1	1,61	18,76	6,82	66,7	6,89	7,36
	23	34	2,4	80,1	17,5	41,5	0,71	18,68	7,24	76,8	7,71	7,83
	24	30	6,5	72,4	21,1	44,2	0,65	18,59	7,36	75,9	7,52	8,28
Eastern Black Sea Region (EB)	25	18	3,1	47,2	49,7	60,5	0,6	18,62	7,85	82,4	8,41	8,35
	26	25	1,9	70,3	27,8	46	0,61	18,56	7,74	80,23	8,11	12,77
	27	30	4,6	54,8	40,6	56,8	1,91	18,62	6,12	75,61	7,52	9,16
	28	18	2,9	60,3	36,8	48,2	0,9	18,65	7,65	82,11	8,23	12,21
	29	22	7,8	66,5	25,7	48,2	0,78	18,21	7,67	81,64	7,98	9,39
	30	26	5,4	70,7	23,9	45,5	0,78	18,51	7,67	79,81	7,72	9,16
	31	18	9,1	69,4	21,5	44,3	0,91	18,60	7,1	81,66	8,54	12,40

[a] Dry weight for TOC.

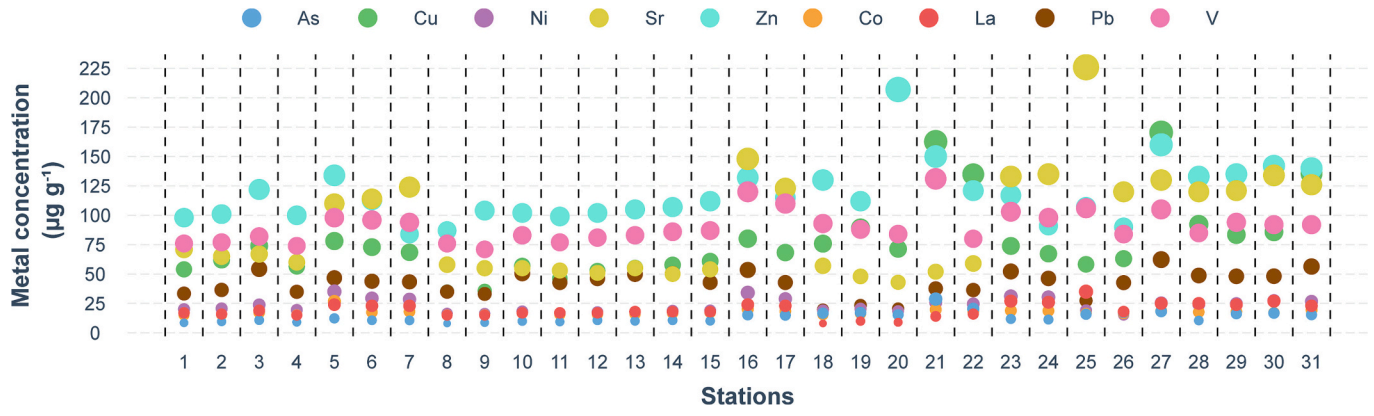


Fig. 2. Change in metal concentrations according to stations.

Total and regional average toxic metal concentrations are given in Table 3. The highest average concentrations of toxic metals were detected in the Eastern Black Sea region (EB) (stations between 21 and 31). The lowest average toxic metal concentrations were found in the Western Black Sea Region (WB) for Cu, Zn, As, and V. Besides, for Pb, Ni, Co, Sr, and La, the lowest average values were found in Middle Black Sea Region (MB) (Table 3).

The toxic metal concentrations measured on the Black Sea coastal sediments were compared to suitable reference values, according to worldwide average shale value (WASV), continental crust values (CCV), toxicity reference values (TRV), and sediment quality guideline (SQGs) (Table 3). According to this comparison, the Cu, Pb, Zn, and As concentrations were higher than the reported reference values (WASV, CCV, and TRV), while the Co, Sr, V, and La concentrations were found to be lower. Ni, on the other hand, was low according to WASV and CCV values, but high according to TRV value. Moreover, known numerical SQGs (according to probable effect concentration) of the concentrations of toxic metals were compared (MacDonald et al., 2000). In the comparison made according to the sediment quality guideline (SQGs), the values of Cu, Ni, and As were found to be lower than the effect range median (ERM) and probable effect level (PEL) values and higher than effect range low (ERL) and threshold effect level (TEL) values. While the mean concentration of Zn was low compared to SQG, Pb was found to be low except for the TEL value (Table 3).

3.3. Statistical evaluation

Toxic metal concentrations among the regions were significantly different except for Ni and Pb (Kruskal-Wallis test, $p < 0.05$). As, Cu, La, and Sr concentrations were found to be significantly higher in EB (16.61

Table 3
Metal content (μg g^{-1}) of present study and its comparison with reference values.

Metal	Surface coastal sediment				Reference values						
	Average conc. (present study)										
	WB	MB	EB	Overall	WASV[a]	CCV[b]	TRV[C]	SQGs[d]			
								ERM	ERL	PEL	TEL
Cu	59.4 ± 4.8	65.3 ± 4.3	102.5 ± 12.3	76.7 ± 5.9	45.0	55.0	16.0	270	34	108.2	18.7
Pb	41.2 ± 2.4	39.3 ± 4.1	46.1 ± 2.9	42.3 ± 1.9	20.0	12.5	31.0	218	46.7	112.2	30.2
Zn	104.5 ± 4.7	122.1 ± 10.5	126 ± 6.9	117.8 ± 4.5	95.0	70.0	110.0	410	150	271	124
Ni	22.8 ± 1.9	21.2 ± 1.8	24.9 ± 1.4	23.1 ± 1.0	68.0	75.0	16.0	51.6	20.9	42.8	15.9
As	9.8 ± 0.4	13.1 ± 0.9	16.6 ± 1.5	13.3 ± 0.8	13.0	1.8	6.0	70	8.2	41.6	7.2
Co	17.3 ± 1.1	16.7 ± 0.5	18.2 ± 0.9	17.4 ± 0.4	19.0	25.0	n.i	n.i	n.i	n.i	n.i
Sr	77.9 ± 8.5	68.2 ± 11.4	123.3 ± 13.5	90.9 ± 7.8	300.0	375.0	n.i	n.i	n.i	n.i	n.i
V	82.7 ± 3.1	90.9 ± 4.3	97.3 ± 4.3	90.5 ± 2.3	130.0	135.0	n.i	n.i	n.i	n.i	n.i
La	18.4 ± 1.2	16.2 ± 1.8	23.6 ± 1.8	19.6 ± 1.1	92.0	30.0	n.i	n.i	n.i	n.i	n.i

n.i. not included, WASV[a] worldwide average shale value (Turekian et al., 1961), CCV[b] continental crust values (Rudnick et al., 1985), TRV[c] toxicity reference values (MacDonald et al., 2000) SOGs[d] Numeric Sediment Quality Guideline, ERL Effect Range Low, ERM Effect Range Median, TEL Threshold Effect Level PEL Probable Effect Level (EPA, 2008).

± 1.52 μg g^{-1}, 102.52 ± 2.32 μg g^{-1}, 23.64 ± 1.77 μg g^{-1}, and 123.27 ± 13.55 μg g^{-1} respectively) compared to the other regions (Fig. 3). On the other hand, As concentration in WB (9.82 ± 0.41 μg g^{-1}) and Sr concentration in MB (68.2 ± 11.44 μg g^{-1}) were significantly lower (Fig. 3).

Principal component analysis (PCA) was used to determine the main drivers of the spatial distribution of the toxic metals. The first two components with eigenvalues > 1 were used to construct the PCA biplot. The cumulative contribution of the first two principal components was 70.1 % (46.3 % and 23.8 % for PC1 and PC2, respectively). The variance on the PC 1 (x-axis) was mainly driven by Cu, Ni, Co, Sr, V, and La. Besides, the variance on the PC 2 (y-axis) was highly contributed by Zn, As, and La (Fig. 4A). The stations were segregated into three clusters determined by the k-means clustering method (Fig. 4B). Cluster 2 was mainly affected by Zn, As, Cu, and V concentrations, on the other hand, cluster 3 was found to be affected by Co, Ni, Sr, and La. The redundancy analysis plot was constructed using the environmental variables with <10 variance inflation factor (VIF) which were pH, salinity, temperature, clay, and TOC. In this context, pH and TOC were the most effective physicochemical parameters on toxic metal composition. A significant difference between the regions was determined in terms of metal compositions (PERMANOVA, F = 5.81, $p < 0.05$). A pairwise PERMANOVA revealed that the toxic metal composition in EB was significantly different from WB and MB ($p < 0.01$) which is also visually segregated in RDA analysis (Fig. 4B).

The detailed correlation coefficients are given in Fig. 5. According to

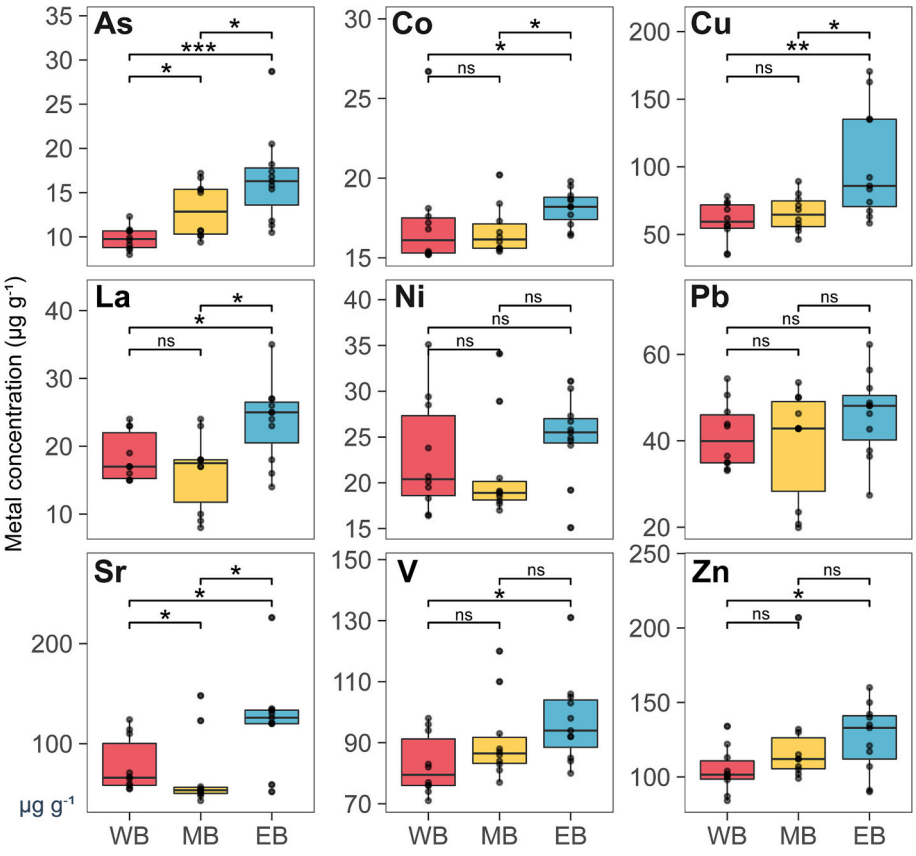


Fig. 3. The concentrations of each toxic metal by region and the pairwise comparisons with Dunn's test (ns: not significant, *: $p < 0.05$, **: $p < 0.01$, ***: $p < 0.001$).

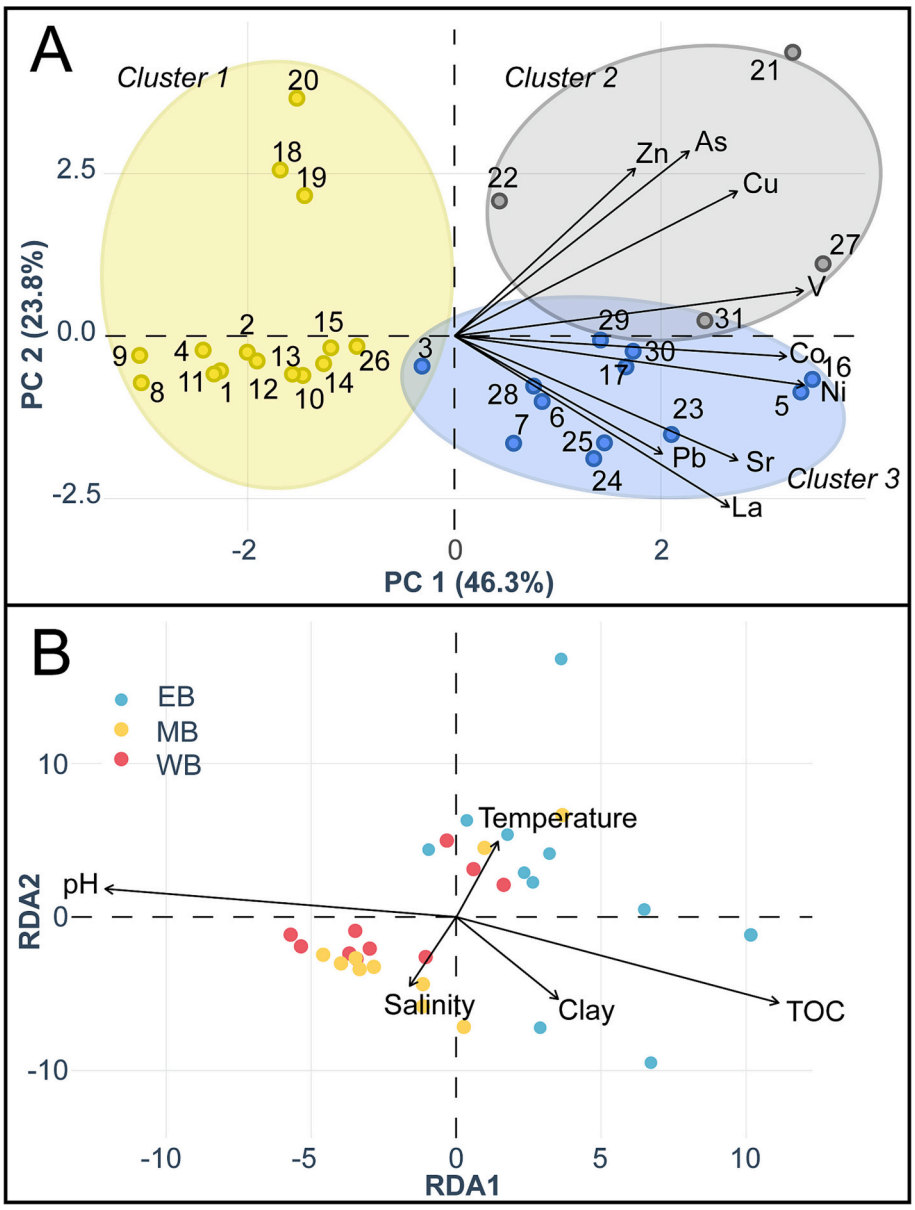


Fig. 4. Principal component analysis (PCA) biplot for metal concentration in the Black Sea sediments (A). The ellipses in A show the clusters based on k-means clustering. Redundancy analysis results (B).

the Spearman's rank correlation test: Zn and Cu exhibited a strong positive correlation, Cu also showed a significant positive correlation with As, Ni, and Co. Significant correlations between Sr and La, and V, Co, and Ni were noticed. As and Cu exhibited a strong positive correlation with TOC. pH and salinity were negatively correlated with toxic metal concentrations.

3.4. Evaluation of sediment pollution indexes

Many indices are used in the literature to assess the extent of heavy metal contamination in sediment (Huang et al., 2020; Jiang et al., 2017; Matys Grygar and Popelka, 2016). In this study, sediment enrichment factor (SEF), pollution load index (PLI), and geoaccumulation index (I_{GEO}), which are widely used in the literature, were used to evaluate the extent of metal pollution (Huang et al., 2020; Lan et al., 2022; Ozseker, 2021). The values of SEF and I_{GEO} are given in Fig. 6A. The SEF of toxic metals in the Black Sea Coastal Sediments were Pb > Cu > Zn > As > Co > V > Ni > Sr > La. The highest SEF and I_{GEO} values were determined in Eastern Black Sea Region (Fig. 6A). The SEF value of Cu and Pb were found to be in the range of 5–10 (moderately severe enrichment); As and Zn were found to be in the range of 3–5 (indicating moderate enrichment); Co, Ni, V, Sr, and La were found to be in the range of 1–3 (indicating minor enrichment) for all the region.

The geoaccumulation index (I_{GEO}) which is a commonly accepted indicator, was used to evaluate the anthropogenic effect levels (Zahran et al., 2015). The sediment samples were considered moderately contaminated by I_{GEO} since Cu and Pb were between the range of $0 < I_{GEO} < 1$. Besides, the other toxic metals were considered uncontaminated because $I_{GEO} < 0$ was determined for the coast of the Black Sea Region (Fig. 6A).The terrestrial mineralogical structure plays a determinative role in the toxic metal concentrations in the bottom sediments. The Eastern Black Sea region of Türkiye is very rich in mineral deposits, especially Cu and Pb (Aydın, 2004; Inci et al., 2011). Considering that it is the region with the highest rainfall in Türkiye, terrestrial material, rich in Cu and Pb elements at a high rate due to erosion, is discharged to the Southeastern Black Sea Coast. Hence, the accumulation of the mentioned toxic metals in the study area is inevitable due to natural processes. There is also intensive agricultural activities in the southern

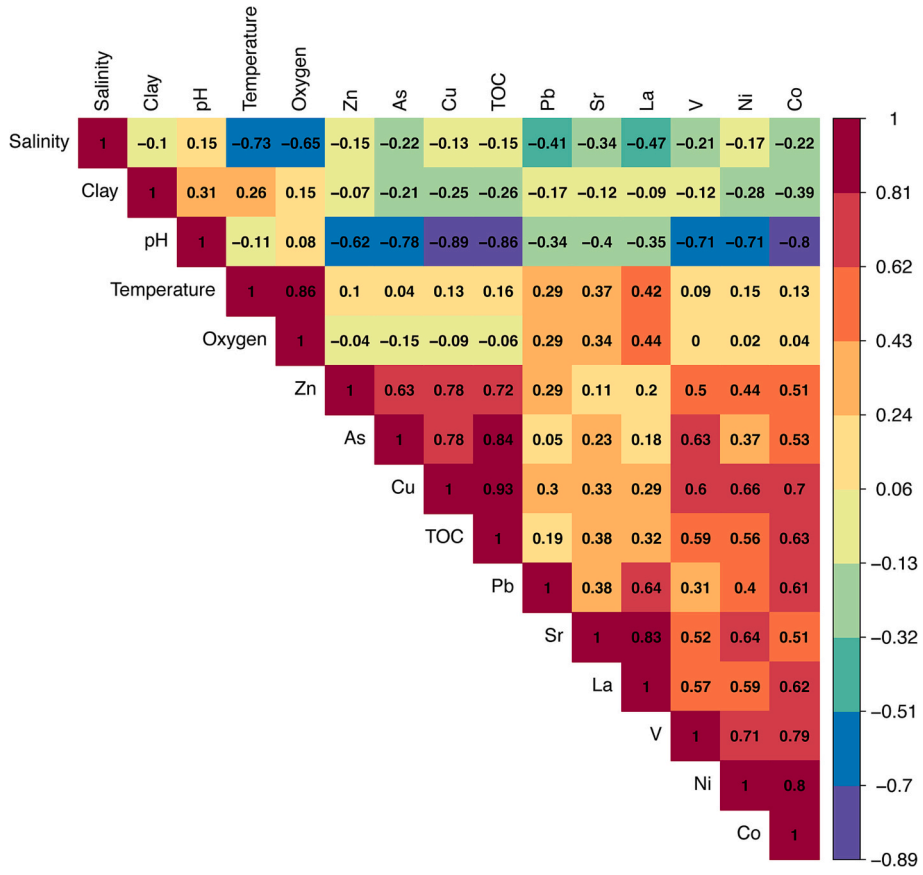


Fig. 5. The correlation between physicochemical properties and metal concentrations in the coastal sediment samples.

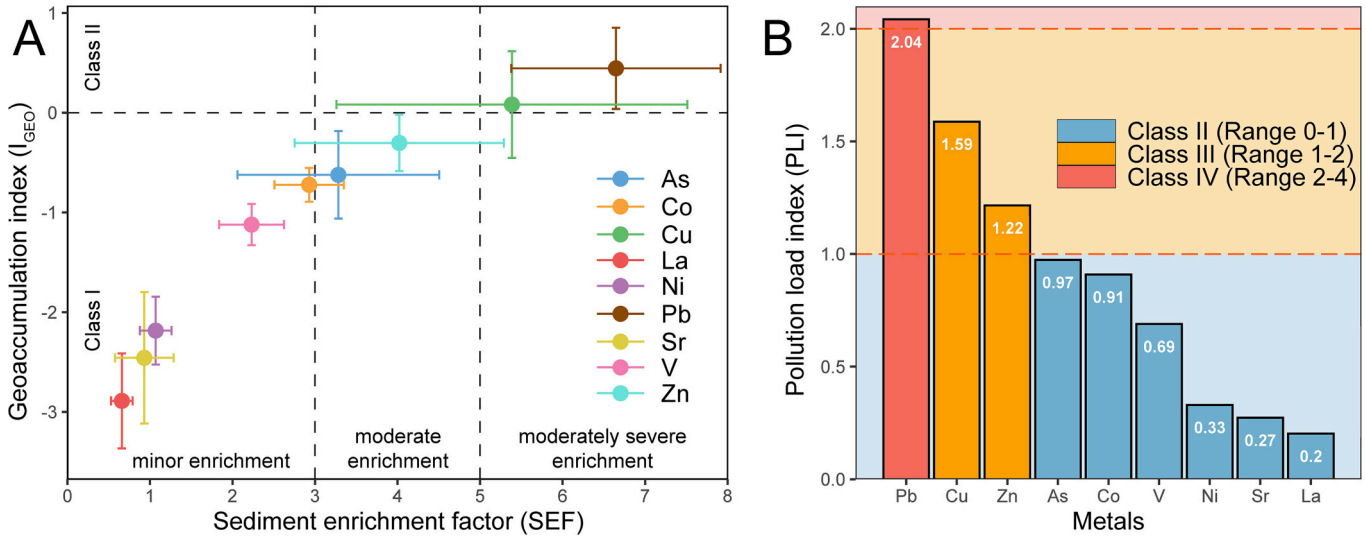


Fig. 6. Overall comparison of I_{GEO}, SEF (A), and PLI (B) values.

coastal area of the Black Sea in which the use of agrochemicals containing Cu and Pb is a common practice. These pollutants can be transported to marine environment with precipitation and surface waters. Another possible transportation way of Cu and Pb is the intensive landfill practices and the international highway along the coast.

Similar results were found in the evaluation made according to the PLI method. In this classification, the pollution level of metals was evaluated in three sub-categories. The Pb was considered moderately polluted because of class 4 (range 2–3). The Cu and Zn were considered unpolluted to moderately because of class 3 (range 1–2). The other metals were considered unpolluted because of class 2 (range 0–1) (Fig. 6B).

There are many studies about metal pollution on both the northern and southern shores of the Black Sea. However, many of these studies represent local study areas (Table 4). In addition, there are compilation studies in which these local studies are brought together (Altaş and Büyükgüngör, 2007; Raykov et al., 2020). In this study, the current status of toxic metals in the coastal sediments of approximately 1100 km

Table 4
Heavy metal levels (μg g^{-1} dry wt) in sediment from coast of the Black Sea.

Area	Cu	Pb	Zn	Ni	Cr	Co	Cd	References
SWBS	40–72	20–38	83–184	57–93	73–117	13–21	0.18–0.53	(Ozkan and Buyukisik, 2012)
SEBS	58–72	18–44	84–124	50–141	54–147	20–29	0.24–0.45	(Ozkan and Buyukisik, 2012)
SBS	15–87	12–66	24–138	11–202	13–224	<20	n.i	(Yücesoy Eryılmaz et al., 1992)
SWBS	20–47	19–51	50–111	34–88	51–135	9–19	n.i	(Ergin, 2005)
SEBS	507	39	484	n.i	n.i	n.i	0.02	(Topcuoğlu et al., 2003)
SBS	66	26	146	n.i	135	23	0.38	(Yiğiterhan and Murray, 2008)
SEBS	62–301	67–137	89–288	20–99	23.2–94.7	n.i	n.i	(Ozseker, 2021)
Overall	2.9–407	2.5–79.8	n.i	n.i	n.i	n.i	0.04–1.93	(Sur et al., 2012)
SEBS	34–279	15.9–33	82–383	13.1–17.6	n.i	n.i	0.1–1.4	(Gedik and Boran, 2013)
MBS	3.03	0.28	8.14	n.i	n.i	n.i	0.006	(Bat et al., 2019)
SEBS	22–2334	14–158	50–1828	n.i	n.i	n.i	0.2–2.1	(Alkan et al., 2015)
SEBS	n.i	n.i	n.i	53–148	n.i	n.i	n.i	(Alkan et al., 2021)
NWBS	20–34	21–29	31–52	n.i	n.i	n.i	n.i	(Peycheva et al., 2017)
NWBS	0.5–148	0.1–300.7	n.i	0.4–211.7	1.34–231	n.i	0.01–9.63	(Coatu et al., 2013)
NWBS	n.i	13.1–24.2	32.5–48.8	n.i	n.i	90.1–119	14.3–18.7	(Mititelu et al., 2018)
SWBS	2.1–237	17–129	57–899	39–809	1.6–290	3–22.9	0.5–14.3	(Sarı et al., 2018)
NWBS	n.i	22	n.i	28	44.17	n.i	n.i	(Catianis et al., 2016)
NBS	20.6	n.i	52.5	24	n.i	n.i	3.5	(Yevgenevich Dyatlov, 2015)

n.i. not included; SWBS: South West Black Sea; SEBS: South East Black Sea; SBS: South Black Sea; MBS; Middle Black Sea; NWBS: North West Black Sea; NBS; North Black Sea.

on the southern coasts of the Black Sea was evaluated in detail. When the results obtained from the study (Table 3) are compared with the studies previously reported (Table 4) in the Black Sea, it is seen that toxic metals such as Ni, Cr, Co, and As are in high concentrations on the southwest Black Sea coasts, and metals such as Cu, Zn and Pb are in high concentrations on the southeast Black Sea coasts, similar to previous studies. Most of the studies have focused on toxic metals such as Cu, Pb, Ni, Zn, Co, As, Cd and Cr. In this presented study, toxic metals such as La, Sr, and V were examined in detail, and it was determined that the results were below acceptable values. In addition, it is seen that the metal values tend to increase in the Southeastern Black Sea Coasts. Pollution indices methods such as SEF, PLI, and I_{GEO}, which we have applied to reveal the pollution dimension of metals, also confirm this result.

Most cities on the Black Sea coast of Türkiye suffer from local environmental problems due to the unconscious discharge of untreated domestic and industrial waste (Bat et al., 2018). There are many sources of metal pollution in coastal sediments (Ekoa Bessa et al., 2021). Especially on the southern Black Sea coasts, the most important metal sources are domestic and industrial discharges and terrestrial transport due to erosion (Ocakoğlu et al., 2018; Stan et al., 2019). Although, large rivers such as Kızılırmak, Yeşilırmak, and Sakarya directly discharge from the central and western Black Sea coasts, there are many large and small river discharging from the eastern Black Sea coasts. Considering the general current system of the Black Sea, it is known that the sediment transport is from west to east and many pollutants in the western Black Sea region are transported eastwards (Staneva et al., 2001).

4. Conclusion

In this study, which was carried out on the southern coasts of the Black Sea, the current situation of the pollution on the Turkish coasts of the Black Sea was evaluated by interpreting toxic metals according to different indices. For this purpose, 31 sampling points covering domestic and industrial discharge points, freshwater discharge areas, and settlements were evaluated. It was determined that the toxic metals Cu and Pb were above the pollution levels for the Black Sea coasts. While As and Zn elements were detected at the pollution limit level, other elements were determined below the pollution levels. In addition, the Turkish coast of the Black Sea was divided into 3 regions; the west, middle and east. According to this comparison result, it was seen that the highest metal values were in the eastern Black Sea coasts of Türkiye. In the long run, routine pollution monitoring studies should be established in the Black Sea to evaluate and control the toxic metal pollution levels. Moreover, laws should be implemented more effectively to prevent pollution.

CRediT authorship contribution statement

Koray Özşeker: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing, Data curation. **Coşkun Erüz:** Conceptualization, Methodology, Writing – review & editing, Resources. **Yahya Terzi:** Formal analysis, Data curation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

Abrahim, G.M.S., Parker, R.J., 2008. Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. Environ. Monit. Assess. 136, 227–238.
Ali Azadi, N., Mansouri, B., Spada, L., Sinkakarimi, M.H., Hamesadeghi, Y., Mansouri, A., 2018. Contamination of lead (Pb) in the coastal sediments of north and south of Iran: a review study. Chem. Ecol. 34, 884–900.
Ali, M.M., Hossain, D., Al-Imran, Khan, M.S., Begum, M., Osman, M.H., 2021. Environmental pollution with heavy metals: a public health concern. In: Heavy Met. - Their Environ. Impacts Mitig.
Alkan, N., Alkan, A., Akbaş, U., Fisher, A., 2015. Metal pollution assessment in sediments of the southeastern Black Sea coast of Türkiye. Soil Sediment Contam. 24, 290–305.
Alkan, N., Alkan, A., Erüz, C., 2018. Determination of metals in water and sediment samples of the Sürmene River, Türkiye. In: Exergy for a Better Environment And Improved Sustainability, 2. Springer, pp. 175–181.
Alkan, A., Alkan, N., Aktaş, M., 2021. Comparison of Ni enrichment and background concentrations in the Southeastern Black Sea sediments. Environ. Forensic 22, 364–371.
Altaş, L., Büyükgüngör, H., 2007. Heavy metal pollution in the Black Sea shore and offshore of Türkiye. Environ. Geol. 52, 469–476.
Aydın, F., 2004. Mineral Chemistry, Petroleum And Petrojenez of Volcano of Değirmendere Valley. Karadeniz Technical University.
Bat, L., Öztekin, A., Şahin, F., Arıcı, E., Özsandıkçı, U., 2018. An overview of the Black Sea pollution in Türkiye. Mediterr. Fish. Aquac. Res. 1, 66–86.

Bat, Levent, Şahin, Fatih, Öztekin, A., 2019. In: Assessment of Heavy Metals Pollution in Water And Sediments and Polychaetes in Sinop Shores of The Black Sea, 22, pp. 806–816.
Bibak, M., Sattari, M., Agharokh, A., Tahmasebi, S., Imanpour Namin, J., 2018. Assessing some heavy metals pollutions in sediments of the northern Persian Gulf (Bushehr province). Environ. Health Eng. Manag. 5, 175–179.
Catianis, I., Ungureanu, C., Magagnini, L., Ulazzi, E., Campisi, T., Stanica, A., 2016. Environmental impact of the Midia Port - Black Sea (Romania), on the coastal sediment quality. Open Geosci. 8, 174–194.
Chileshe, M.N., Syampungani, S., Festin, E.S., Tigabu, M., Daneshvar, A., Odén, P.C., 2020. Physico-chemical characteristics and heavy metal concentrations of copper mine wastes in Zambia: implications for pollution risk and restoration. J. For. Res. 31, 1283–1293.
Coatu, V., Ţigănuş, D., Oros, A., Lazăr, L., 2013. Analysis of hazardous substance contamination of the marine ecosystem in the Romanian black Sea coast, part of the Marine Strategy Framework Directive (2008/56/EEC) implementation. Rech. Mar. 43, 144–186.
Ekoa Bessa, A.Z., Ngueutchoua, G., Kwewouo Janpou, A., El-Amier, Y.A., Njike Njome Mbella Nguetnga, O.-A., Kankeu Kayou, U.R., Bisse, S.B., Ngo Mapuna, E.C., Armstrong-Altrin, J.S., 2021. Heavy metal contamination and its ecological risks in the beach sediments along the Atlantic Ocean (Limbe coastal fringes, Cameroon). Earth Syst. Environ. 5, 433–444.
El Nemr, A., El-Said, G.F., 2017. Assessment and Ecological Risk of Heavy Metals in Sediment and Molluscs From the Mediterranean Coast; Assessment and Ecological Risk of Heavy Metals in Sediment and Molluscs From the Mediterranean Coast.
EPA, 2008. EPA's Report on the Environment. US Environmental Protection Agency (US EPA). Tech. rep.
Ergin, M., 2005. Metal pollution at sea, 1-jeologic and anthropologic heavy metal pollution in the Black Sea, Aegean Sea and Mediterranean Sea sediments. Mar. Pollut. 21, 161–176.
Faměra, M., Matys Grygar, T., Elznicová, J., Grison, H., 2018. Geochemical normalization of magnetic susceptibility for investigation of floodplain sediments. Environ. Earth Sci. 77.
Fantong, E.B., Takeuchi, A., Kamishima, T., Doke, R., 2014. Assessment of the relationship between ESR signal intensity and grain size distribution in shear zones within the Atotsugawa fault system, central Japan. Int. J. Geosci. 05, 1282–1299.
Forstner, U., Wittmann, G.T., 1983. Metal Pollution in the Aquatic Environment.
Galkus, A., Joksas, K., Stakeniene, R., Lagunaviciene, L., 2012. Heavy metal contamination of harbor bottom sediments. Pol. J. Environ. Stud. 21.
Gedik, K., Boran, M., 2013. Assessment of metal accumulation and ecological risk around Rize Harbor, Türkiye (Southeast Black Sea) affected by copper ore loading operations by using different sediment indexes. Bull. Environ. Contam. Toxicol. 90, 176–181.
Gelman, F., Binstock, R., Halicz, L., 2012. Application of the Walkley-Black titration for the organic carbon quantification in organic rich sedimentary rocks. Fuel 96, 608–610.
Huang, Z., Liu, C., Zhao, X., Dong, J., Zheng, B., 2020. Risk assessment of heavy metals in the surface sediment at the drinking water source of the Xiangjiang River in South China. Environ. Sci. Eur. 32.
Inci, M., Şarli, B., Çelik, A., Demirtaş, A., Baydilli, N., Akpek, M., Kaya, M.G., 2011. Sphalerite associated with pyrrhotite-chalcopyrite ore occurring in the Kotana Fe-skarn deposit (Giresun, NE Türkiye): exsolution or replacement. Turk. J. Earth Sci. 20, 307–320.
Ip, C.C.M., Li, X.D., Zhang, G., Wai, O.W.H., Li, Y.S., 2007. Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. Environ. Pollut. 147, 311–323.
Jiang, Y., Chao, S., Liu, J., Yang, Y., Chen, Y., Zhang, A., Cao, H., 2017. Source apportionment and health risk assessment of heavy metals in soil for a township in Jiangsu Province, China. Chemosphere 168, 1658–1668.
Kassambara, A., 2021. rstatix: Pipe-friendly Framework for Basic Statistical Tests.
Kowalska, J.B., Mazurek, R., Gąsiorek, M., Zaleski, T., 2018. Pollution indices as useful tools for the comprehensive evaluation of the degree of soil contamination–a review. Environ. Geochem. Health 40, 2395–2420.
Lan, D.Y., Zhang, H., Wu, T.W., Lü, F., Shao, L.M., He, P.J., 2022. Repercussions of clinical waste co-incineration in municipal solid waste incinerator during COVID-19 pandemic. J. Hazard. Mater. 423, 127144.
Lê, S., Josse, J., Husson, F., 2008. {FactoMineR}: a package for multivariate analysis. J. Stat. Softw. 25, 1–18.
Liu, B., Wang, J., Xu, M., Zhao, L., Wang, Z., 2019. Spatial distribution, source apportionment and ecological risk assessment of heavy metals in the sediments of Haizhou Bay national ocean park,China. Mar. Pollut. Bull. 149, 110651.
Longhini, C.M., Rodrigues, S.K., Costa, E.S., da Silva, C.A., Cagnin, R.C., Gripp, M., Lehrback, B.D.C., Mill, G.N., de Oliveira, E.M.C., Hermogenes, C.de C.M., Rodrigues, D.G.F., David, A.M., Gramlich, K.C., Bisi Júnior, R.da C., Gomes, A.A.P., da Silva Filho, J.P., Almeida, J.F., de Souza, K.F., Luz Junior, W.A.R., Poleze, L.M.B., Barros, R.R., Rigo, D., Ghisolfi, R.D., Neto, R.R., Sá, F., 2022. Environmental quality assessment in a marine coastal area impacted by mining tailing using a geochemical multi-index and physical approach. Sci. Total Environ. 803, 149883.
MacDonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch. Environ. Contam. Toxicol. 39, 20–31.
Maslennikova, S., Larina, N., Larin, S., 2012. The effect of sediment grain size on heavy metal content. Lakes Reserv. Ponds 6, 43–54.
Matys Grygar, T., Popelka, J., 2016. Revisiting geochemical methods of distinguishing natural concentrations and pollution by risk elements in fluvial sediments. J. Geochem. Explor. 170, 39–57.
Mee, L.D., 1992. The Black Sea in crisis: a need for concerted international action. Ambio 21, 278–286.
Migaszewski, Z.M., Gałuszka, A., Migaszewski, A., 2014. The study of rare earth elements in farmer's well waters of the Podwiśniówka acid mine drainage area (south-central Poland). Environ. Monit. Assess. 186, 1609–1622.
Mititelu, M., Moroşan, E., Neacşu, S.M., Ioniţă, E.I., 2018. Research regarding the pollution degree from Romanian black sea coast. Farmacia 66, 1059–1063.
Monikh, F.A., Maryamabadi, A., Savari, A., Ghanemi, K., 2015. Heavy Metals' Concentration in Sediment, Shrimp and Two Fish Species From the Northwest Persian Gulf.
Morillo, J., Usero, J., Gracia, I., 2004. Heavy metal distribution in marine sediments from the southwest coast of Spain. Chemosphere 55, 431–442.
Muftuoglu, A.E., 2013. Transportation of pollutants of the Danube river into the (wefile:///C:/Users/asus/Desktop/2004-Selva-MPBfile:///C:/Users/asus/Desktop/TamakiEstuary-AssessmentofheavymetalEF.Pdf-kalpakkamcoastalsediments.pdfstern) black sea. Asian J. Chem. 25, 5013–5018.
Mülayim, A., Balkis, H., 2015. Toxic metal (Pb, Cd, Cr, and Hg) levels in Rapana venosa (Valenciennes, 1846), Eriphia verrucosa (Forskal, 1775), and sediment samples from the Black Sea littoral (Thrace, Türkiye). Mar. Pollut. Bull. 95, 215–222.
Mutlu, T., 2021. Heavy metal concentrations in the edible tissues of some commercial fishes caught along the eastern Black Sea coast of Türkiye and the health risk assessment. Spectrosc. Lett. 54, 437–445.
Nazneen, S., Patel, P., 2016. Distribution and fractionation of heavy metals in surface sediments of Chilika lagoon, east coast of India. IOSR J. Environ. Sci. Toxicol. Food Technol. 10, 63–71.
Ocakoğlu, N., İşcan, Y., Kılıç, F., Özel, O., 2018. Morphologic and seismic evidence of rapid submergence offshore Cide-Sinop in the southern Black Sea shelf. Geomorphology 311, 76–89.
Oksanen, J., Blanchet, F.G., Friendly, M., Kindt, R., Legendre, P., McGlinn, D., Minchin, P.R., O'Hara, R.B., Simpson, G.L., Solymos, P., Stevens, M.H.H., Szoecs, E., Wagner, H., 2020. vegan: Community Ecology Package.
Ozkan, E.Y., Buyukisik, B., 2012. Geochemical and statistical approach for assessing heavy metal accumulation in the southern Black Sea sediments. Ekoloji 11–24.
Özşeker, K., 2019. Investigation of sediment pore water heavy metal (Cu and Pb) geochemistry in Deriner Dam Lake. Acta Aquat. Turc. 15, 60–67.
Ozseker, K., 2021. Toxic metal pollution and ecological risk estimation in the sediment around Hopa Harbor, Türkiye (SE). Clean Soil Air Water 49 (3), 1–10. https://doi.org/10.1002/clen.202000269.
Ozseker, K., Eruz, C., 2016. Ecological pathways of heavy metal pollution in Solakli River Basin (river bed, uzungol lake and estuary) sediment of southeastern Black Sea region, Türkiye. Indian J. Geo-Mar. Sci. 45.
Ozseker, K., Eruz, C., Ciliz, S., 2013. Determination of copper pollution and associated ecological risk in coastal sediments of Southeastern Black Sea Region, Türkiye. Bull. Environ. Contam. Toxicol. 91.
Ozseker, K., Seyhan, K., Eruz, C., 2016. Ecological risk assessment and spatial distribution of heavy metals in sediment and pore water around Trabzon harbor, Türkiye. Fresenius Environ. Bull. 25.
Özsoy, E., Ünlüata, Ü., 1997. Oceanography of the Black Sea: a review of some recent results. Earth Sci.Rev. 42, 231–272.
Parween, M., Ramanathan, A.L., Raju, N.J., 2021. Assessment of toxicity and potential health risk from persistent pesticides and heavy metals along the Delhi stretch of river Yamuna. Environ. Res. 202, 111780.
Peycheva, K., Stancheva, M., Georgieva, S., Makedosnki, L., 2017. Heavy metals in water, sediments and marine fishes from Bulgarian Black Sea.
R Core Team, 2021. R: A Language And Environment for Statistical Computing.
Raykov, V., Zlateva, I., Ivanova, P., Dimitrov, D., Golumbeanu, M., 2020. Stratified seafloor marine litter assessment. Bulgarian Black Sea waters case. J. Environ. Prot. Ecol. 21, 463.
Rudnick, R.L., McLennan, S.M., Taylor, S.R., 1985. Large ion lithophile elements in rocks from high-pressure granulite facies terrains. Geochim. Cosmochim. Acta 49, 1645–1655.
Saiful, I., Kawser, A., Mohammad, R., Habibullah, A., Muhammad, K., 2015. Heavy metal pollution in surface water and sediment: a preliminary assessment of an urban river in a developing country. Ecol. Indic. 48, 282–291.
Sarı, E., Çağatay, M.N., Acar, D., Belivermiş, M., Kılıç, Ö., Arslan, T.N., Tutay, A., Kurt, M.A., Sezer, N., 2018. Geochronology and sources of heavy metal pollution in sediments of Istanbul Strait (Bosporus) outlet area, SW Black Sea, Türkiye. Chemosphere 205, 387–395.
Selvaraj, K., Ram Mohan, V., Szefer, P., 2004. Evaluation of metal contamination in coastal sediments of the Bay of Bengal, India: geochemical and statistical approaches. Mar. Pollut. Bull. 49, 174–185.
Sezgin, M., Bat, L., Ürkmez, D., Arıcı, E., Öztürk, B., 2017. Black Sea Marine Environment: The Turkish Shelf. Turkish Marine Research Foundation (TUDAV), Istanbul.
Sharma, R., Ngangbam, Singh, S., Dileep, Singh, K., 2020. Impact of heavy metal contamination and seasonal variations on enzyme's activity of Yamuna river soil in Delhi and NCR. Appl. Water Sci. 103 (10), 1–8.
Shaw, J.B., 1990. A cognitive categorization model for the study of intercultural management. Acad. Manag. Rev. 15, 626.
Sinem Atgin, R., El-Agha, O., Zararsiz, A., Kocataş, A., Parlak, H., Tuncel, G., 2000. Investigation of the sediment pollution in Izmir Bay: trace elements. Spectrochim. Acta Part B At. Spectrosc. 55, 1151–1164.
Soliman Alshami, A., A, S.D., 2018. Mineralogy and digenetic impacts on chemical composition of paleozoic mudrocks, southwestern Sinai, Egypt. Al Azhar Bull. Sci. 29, 93–107.

Sreenivasulu, G., Nadimikeri, J., Chinnapolla, S.R.R.B., Ballari, L., Madiga, R., Nirmala, K., Tella, L.P., 2018. Assessment of heavy metal pollution from the sediment of Tupilipalem Coast, southeast coast of India. Int. J. Sediment Res. 33, 294–302.

Stan, M.-I., Aivaz, K.-A., Ioniţiu, I., 2019. Projects to reduce the coastal erosion of the Romanian Black Sea area. Ovidius Univ. Ann. Ser. Civ. Eng. 21.

Staneva, J.V., Dietrich, D.E., Stanev, E.V., Bowman, M.J., 2001. Rim current and coastal eddy mechanisms in an eddy-resolving Black Sea general circulation model. J. Mar. Syst. 31, 137–157.

Sur, M., Sur, H.İ., Apak, R., Erçağ, E., 2012. In: The pollution status of bottom surface sediments along the Turkish coast of the Black Sea, 460, pp. 453–460.

Terzi, Y., Erüz, C., Özşeker, K., 2020. Marine litter composition and sources on coasts of south-eastern Black Sea: a long-term case study. Waste Manag. 105, 139–147.

Terzi, Y., Gedik, K., Eryaşar, A.R., Öztürk, R.Ç., Şahin, A., Yılmaz, F., 2022. Microplastic contamination and characteristics spatially vary in the southern Black Sea beach sediment and sea surface water. Mar. Pollut. Bull. 174, 113228.

Tomlinson, D.L., Wilson, J.G., Harris, C.R., Jeffrey, D.W., 1980. Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Helgoländer Meeresuntersuchungen 33, 566–575.

Topcuoğlu, S., Ergül, H.A., Baysal, A., Ölmez, E.K., Kut, D., 2003. Determination of radionuclide and heavy metal concentrations in biota and sediment samples from Pazar and Rize stations in the eastern Black Sea. Fresenius Environ. Bull. 12, 695–699.

Tuncer, G., Karakas, T., Balkas, T.I., Gökçay, C.F., Aygnn, S., Yurteri, C., Tuncel, G., 1998. Land-based sources of pollution along the Black Sea coast of Türkiye: concentrations and annual loads to the Black Sea. Mar. Pollut. Bull. 36, 409–423.

Turekian, K.K., Haven, N., Hans, K., Universitat, W.M.Der, 1961. In: KARL K. TUREKIAN Dept. Geology, Yale University, New Haven, Conn. KARL HANS WEDEPOHL Mineralogische-Institut der Universitat, Gottingen, Germany Distribution of the Elements in Some Major Units of the Earth's Crust. America (NY), pp. 175–192.

Üniversitesi, O., Deniz Bilimleri Fakültesi, F., Sorumlu Yazar, T., Makalesi, A., 2019. In: Acta Aquatica Turcica Karadeniz'e Kıyısı Bulunan Ülkelerin Karadeniz'deki Balıkçılık Yetki Alanları ve Balıkçılık Faaliyetleri İsmet BALIK, 15, pp. 117–125.

Wickham, H., 2016. ggplot2: Elegant Graphics for Data Analysis. Springer-Verlag, New York.

Yeşim Özkan, E., Bir Körfezde İzmir İç Körfez, E., Ağır Metal Kontaminasyonlarına Yeni Bir Yaklaşım Özet, T., 2012. A new assessment of heavy metal contaminations in an eutrophicated bay (Inner Izmir Bay, Türkiye). Turk. J. Fish. Aquat. Sci. 12, 135–147.

Yevgenevich Dyatlov, S., 2015. Heavy metals in water and bottom sediments of Odessa region of the Black Sea. J. Shipp. Ocean Eng. 5, 51–58.

Yiğiterhan, O., Murray, J.W., 2008. Trace metal composition of particulate matter of the Danube River and Turkish rivers draining into the Black Sea. Mar. Chem. 111, 63–76.

Yücesoy Eryılmaz, F., Ergin, M., Yijcesoy, F., 1992. Heavy-metal geochemistry of surface sediments from the southern Black Sea shelf and upper slope Sakarya-Karasu Project View project Patara Project View project heavy-metal geochemistry of surface sediments from the southern Black Sea shelf and upper slope. Artic. Chem. Geol. 99, 265–287.

Zahran, M.A.E.-K., El-Amier, Y.A., Elnaggar, A.A., Mohamed, H.A.E.-A., El-Alfy, M.A.E.-H., Zahran, M.A.E.-K., El-Amier, Y.A., Elnaggar, A.A., Mohamed, H.A.E.-A., El-Alfy, M.A.E.-H., 2015. Assessment and distribution of heavy metals pollutants in Manzala Lake,Egypt. J. Geosci. Environ. Prot. 3, 107–122.

Zárate, A., Dorador, C., Valdés, J., Molina, V., Icaza, G., Pacheco, A.S., Castillo, A., 2021. Benthic microbial diversity trends in response to heavy metals in an oxygen-deficient eutrophic bay of the Humboldt current system offshore the Atacama Desert. Environ. Pollut. 286.

Zhang, C., Yu, Z.gang, Zeng, G.ming, Jiang, M., Yang, Z.zhu, Cui, F., Zhu, M.ying, Shen, L.qing, Hu, L., 2014. Effects of sediment geochemical properties on heavy metal bioavailability. Environ. Int. 73, 270–281.

Zhang, Y., Li, H., Yin, J., Zhu, L., 2021. Risk assessment for sediment associated heavy metals using sediment quality guidelines modified by sediment properties. Environ. Pollut. 275, 115844.

Ziyath, A.M., Mahbub, P., Goonetilleke, A., Adebajo, M.O., Kokot, S., Oloyede, A., 2011. Influence of physical and chemical parameters on the treatment of heavy metals in polluted stormwater using zeolite—a review. J. Water Resour. Prot. 03, 758–767.