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RESEARCH ARTICLE

Evaluation of ecological risk, source, and spatial distribution of some heavy metals in marine sediments in the Middle and Eastern Black Sea region, Turkey

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Abstract

In the present study, the concentration levels of heavy metals such as Mn, Fe, Ni, Cu, Zn, Cr, and Pb in sediment samples collected from 16 sampling locations in the Middle and Eastern Black Sea regions, Turkey, **were** measured using energy dispersive X-ray fluorescence spectroscopy (EDXRF). Various pollution parameters and methods, such as the enrichment factor (EF), geo-accumulation index (I_{geo}), contamination factor (CF), pollution load index (PLI), ecological risk index (RI), and geo-spatial distribution patterns, were used to assess the pollution status, ecological risks, and sources of metals in sediment **in detail.** The mean concentrations of Mn, Fe, Ni, Cu, Zn, Cr, and Pb were found to be 565.38, 46,000, 34.38, 104.06, 109.88, 87.31, and 32.31 mg/kg, respectively. Results showed that the mean concentrations of Cu, Zn, and Pb exceeded the crustal shale value, with the exception of Mn, Fe, Ni, and Cr. According to the calculated pollution parameters, although minimal or moderate pollution was detected in the area investigated, it was determined that there was a very low ecological risk. Multivariate statistical analysis results showed that Cu, Zn, and Pb levels in the investigated region were slightly influenced by anthropogenic inputs such as mining and agricultural practices. In addition, the geo-spatial distributions of Cu, Zn, Fe, and Pb were found to be higher in this region due to the mining activities carried out in the Eastern Black Sea region.

Keywords Middle and Easterm Black Sea · Sediment · EDXRF · Pollution indices · Ecologic risk

Introduction

Human activities and the processes of rocks such as fragmentation, transportation, and sedimentation are increasing the accumulation of heavy metals in sea bottoms. Heavy metals enter aquatic ecosystems through fluvial transport, atmospheric deposition, and/or local sewage discharge. Only a small portion of these metals remains dissolved in the water long enough to be transported into the deep sea, while the greatest majority of heavy metals are deposited in coastal sediments (Wang et al. 2017; Ding et al. 2018). Distribution of heavy metals in sediments is affected by chemical composition of the sediments, grain size (i.e., clay, silt, sand), and content of total organic matter (TOM) (Ali and Khan 2019**).** Sediment is an important accumulation place for heavy metals. Therefore, it is very often used in the determination of metal contamination of the aquatic environment.

The Black Sea is a semi-closed basin and has the largest anoxic water basin (Akyüz et al. 2001; Alkan et al. 2015), and it is enclosed by Bulgaria, Georgia, Romania, Russia,

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Ukraine, and Turkey. Turkish Black Sea has a long coast and the region has developing population, industrialization, and urbanization (Bakan and Büyükgüngör 2000; Ergül et al. 2008). Agricultural surface water and inadequate treatment of urban sewage effluents are the main sources of metal pollution in the Black Sea coast of Turkey (Topcuoglu et al. 2003). In addition, the Black Sea region has a very rich potential in terms of Cu, Zn, and Pb **mine** reserves. For this reason, the wastes of the mentioned **reserves** are transported to the marine environment by means of surface waters, as well as rivers and streams of various sizes (Çevik et al. 2008; Baltas et al. 2017a). Therefore, the sediments in the Black Sea have been negatively suffered by the anthropogenic contaminations (Yiğiterhan and Murray 2008; Mülayim and Balkıs 2015).

The contamination of the marine ecosystem is still an important ecological issue worldwide. There are two main reasons for the pollution associated with natural and anthropogenic sources. The main causes of natural pollution are erosion because of wave action and glaciers, ore-bearing rocks, metals released from sediments by a chemical process, wind-blown dust, forest fires, chemical leaching of bedrock, water drainage basins, runoff from banks, and vegetation in small amounts. The major reasons for the anthropogenic sources are mining operations, industrial waste disposal, burning of fossil fuels in motor vehicles, and the smelting and refining metals (Turekian 1971; Bryan 1976; Fernandez-Leborans and Herrero 2000; Järup 2003; Bat et al. 2015). Anthropogenic sources have great importance for the formation of the metal, particularly near coastal sediment (Alkan et al. 2015). Therefore, sediments in the marine ecosystem can provide information on the heavy metal pollutant for the aquatic system.

Heavy metal pollution has a significant role in the contamination of aquatic systems. It is well known that sediments are one of the main transporters of heavy metals to the marine ecosystem (Chatterjee et al. 2007; Idris 2008; Cukrov et al. 2011). Therefore, sediment has an important role in monitoring the heavy metal pollution in the marine environment (Wardas et al. 1996; Ozkan and Buyukisik 2012).

The various works have pointed out that heavy metal contamination particularly in the aquatic ecosystem **has arisen** for more than a decade on a global scale. There are a few publications on marine ecosystem pollution in the region of the Black Sea using several analysis methods (Akyüz et al. 2003; Görür et al. 2012; Sur et al. 2012; Alkan et al. 2015, 2020; Ozseker et al. 2016; Baltas et al. 2017c; Ozseker and Eruz 2017; Sarı et al. 2018; Ustun Odabaşı et al. 2018). To refrain from the contamination of the aquatic environment, the European Union countries have taken measurements for defining heavy metal pollution.

In the literature, no detailed studies on pollution have been found for the coasts of Samsun, Ordu, Giresun, Trabzon, Rize, and Artvin provinces in recent years. Since pollution is a continuum process, it is necessary to carry out this study based on the coast of the Middle and Eastern Black Sea provinces. The main interest of the current work is to evaluate sources and ecologic risk status of the heavy metal pollution for marine sediments in the Middle and Eastern Black Sea coastal region with various parameters such as enrichment factor (EF), the geo-accumulation index (I_{geo}), contamination factor (CF), pollution load index (PLI), and ecological risk index (RI). Multivariate statistical techniques such as Pearson's correlation and principal component analysis (PCA) were applied to evaluate relationships between metals and to define the input sources of heavy metals in sediment samples, respectively. In addition, geo-spatial distribution patterns of metals in sediments were investigated in the studied area. The results obtained may be utilized as a reference for monitoring possible metal contamination in the future.

Materials and methods

Study area

The Middle and Eastern Black sea regions include vast water valleys, mountain ranges, steppes, and broken zones. Large water currents such as Yeşilırmak, Kızılırmak, İkizdere, Harşit, Batlama, Fırtına, and Çoruh Rivers emerge from the sources of this region and pour into the Black Sea (Dalgic et al. 2018). These sampling points chosen for the study are located on the shores of this region and cover the Turkish provinces of Samsun, Ordu, Giresun, Trabzon, Rize, and Artvin (Fig. 1.). The detailed information related to the sampling points is given in Table S1 (Supplementary Materials).

Sediment sampling and chemical analysis

Marine sediment samples were gathered using a Van Veen grab sampler onboard the R / V speed research ship in August 2013 from 16 different sampling stations of the Middle and Eastern Black Sea coastal region of Turkey. The sediment samples were collected at different depths (10–30 **m**) and different distances (0.2–2.0 **nautical miles**). Three sediment samplings, approximately 1–2 kg, were made at each sampling station. At the same time, the position of each sampling point was recorded by the automatic positioning system (GPS) on the research ship. At the points where the samples were taken, temperature and depth parameters were recorded automatically with the help of the CTD multi-parameter probe. The collected sediment samples were stored in clean polyethylene bags and immediately transferred to the laboratory in the cold chain box for further processing (Şirin 2019). Firstly, impurities such as plant fragments and stones were removed from sediment samples. After the sediment samples were weighed on a precision scale to be about

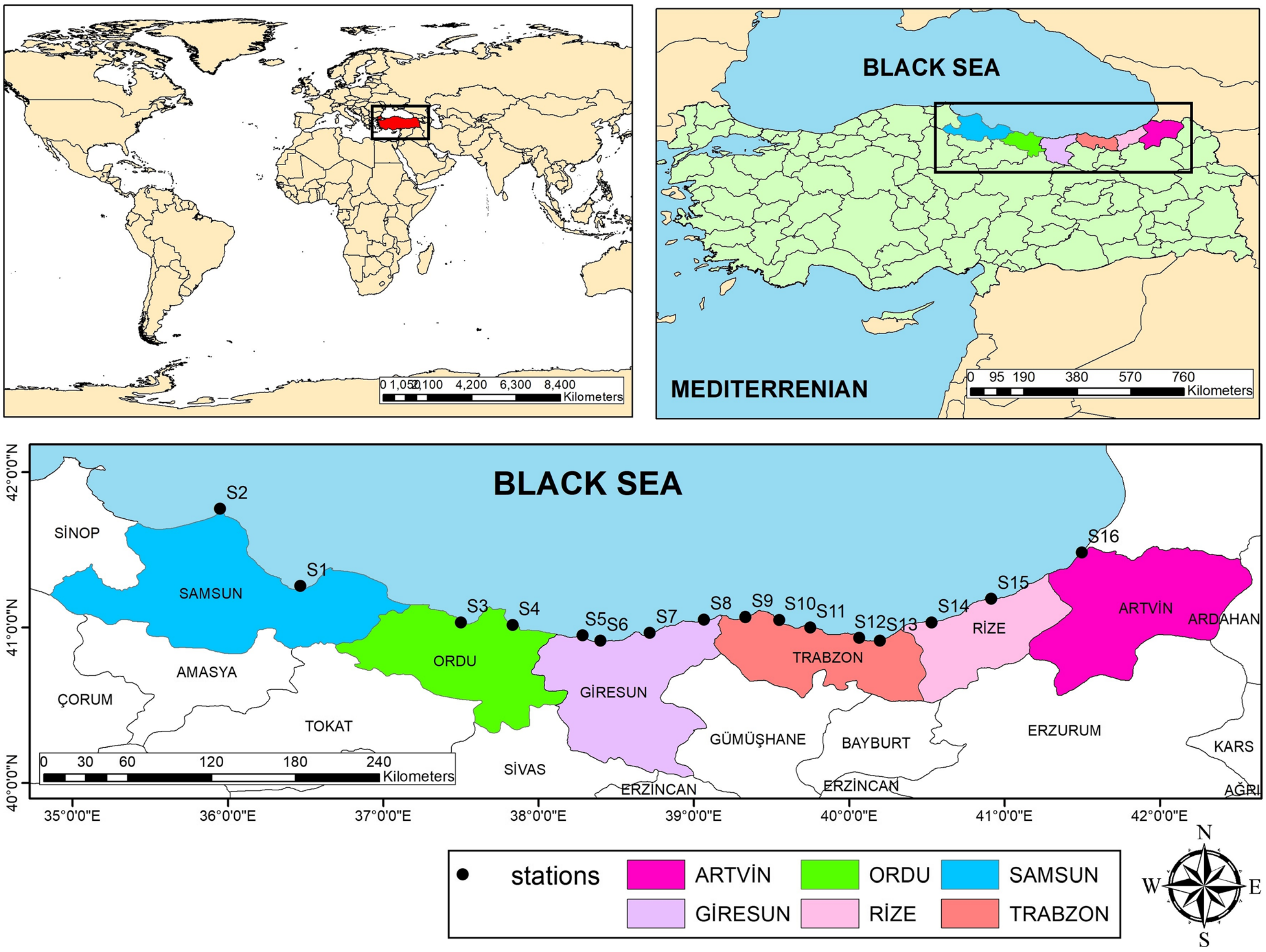


Fig. 1 Map of the study area

100 g, they were left to dry at 105 °C for 48 h until they reached a constant mass (Karbasdehi et al. 2016; Tholkappian et al. 2018) and the samples were ground to a fine powder in a mortar for 15–20 min. The samples were sieved with a 63 μm sieve, as metals accumulated more as a result of the increase in surface area as the particles became smaller in size (Ravisankar et al. 2014; Kumar et al. 2017; Gholizadeh and Patimar 2018; Ni et al. 2018; Ustaoğlu and Islam 2020). Prior to metal analysis, the dried samples were placed in a vacuum-evacuated desiccator. For measurements, after 4 g of pretreated sediment powder and about 0.5 g of Licowax powder were thoroughly mixed in a mortar to ensure homogeneity, it was pressed into a 40-mm diameter disc (pellet) by a 20 ton hydraulic press machine (Specac, Atlas ™ Manual 25 T). The contents of heavy metals such as Mn, Fe, Ni, Cu, Zn, As, and Pb in the sediment were determined using EDXRF spectrometer (Epsilon5, PANalytical, Almelo, the Netherlands). More detailed information about the used EDXRF spectrometer was given in the study by Baltas et al. (2020) (Baltas et al. 2020). Each pellet sample was analyzed in triplicate in the system (Baltas et al. 2017b). The measurement time was taken as 30 min for each pellet sample. As shown in Table S2, quality assurance and control of the method were achieved by using the national certified reference material, the Lake Ontario sediment (NW–WQB–1). The recovery of all metals analyzed in the reference material was between 95.4 and 104.7%.

Assessment of sediment pollution levels

There are many methods to evaluate the size of heavy metal contamination in sediment samples in detail. Various parameters such as the enrichment factor (EF), geo-accumulation index (I_{geo}), contamination factor (CF), pollution load index (PLI), potential ecological risk factor $\left(E_r^i\right)$, and potential ecological risk index (RI) were calculated to determine the level of heavy metal pollution and human input sources in marine sediment samples. Many researchers consider average shale or average crustal abundance values as reference (background) elements (Chandrasekaran et al. 2015; Baltas et al. 2020). For this reason, the values reported for the earth's shale by Krauskopf (1985) (Krauskopf 1985) were used as the reference (background) values for heavy metals and are given in Table 1.

Sediment quality guidelines (SQGs)

It is very important to determine whether the concentration levels of heavy metals in sediments pose an ecological risk to aquatic life. Therefore, risk assessment of heavy metals in sediments was carried out by comparing the heavy metal concentrations with SQGs (Costa-Böddeker et al. 2018; Fakhradini et al. 2019; Tian et al. 2020). According to the quality directive, the indices are the threshold effect level (TEL) and the possible impact level (PEL). Adverse effects rarely occur when metal concentration levels are below TEL and often occur when **they are** above PEL (Macdonald et al. 1996; Gao et al. 2019; Tian et al. 2020). To unify the standards, the potential risks posed by the measured metals were evaluated based on quality guidelines such as TEL and PEL values. TEL and PEL reference values of some of the metals examined are presented in Table 1.

Enrichment factor (EF)

Generally, when the EF values are in the range of $0.5 \leq \mathrm{EF} \leq 1.5$, the metal enrichment is considered to be **arise** from natural weathering processes, **i.e.,** lithogenic sources. If the EF value is greater than 1.5, it is stated that the main source of enrichment is anthropogenic inputs resulting from human activities (Tholkappian et al. 2018). The EF method reduces the influence of granularity and a mineralogical constituent of the investigated environmental medium on assessment results by normalizing heavy metal concentration to conservative element concentration (Lu et al. 2009a, 2009b). In the present work, Fe was taken as a reference because of its high concentration and stability in the earth's shale (Delgado et al. 2010; Varol and Şen 2012; Omwene et al. 2018; Baltas et al. 2020). The EF is calculated by Eq. (1):

$$\mathrm{EF} = \frac{(\mathrm{C_n}/\mathrm{C_{Fe}})_{\mathrm{sample}}}{(\mathrm{B_n}/\mathrm{B_{Fe}})_{\mathrm{Background}}} \tag{1}$$

where $\mathrm{C_n}$ and $\mathrm{C_{Fe}}$ are the concentration of the metal n and Fe in the sample, respectively. $\mathrm{B_n}$ and $\mathrm{B_{Fe}}$ are **the** reference values given by Krauskopf (1985) for the metal n and Fe, respectively (Krauskopf 1985). The pollution level of metals on base of the EF values is summarized in Table S3 (Chen et al. 2007).

Geo–accumulation index ($\mathrm{I_{geo}}$)

$\mathrm{I_{geo}}$, raised by Müller (1969) and extensively used to evaluate heavy metal pollution level in sediment, soil, and dust (Muller 1969; Lu et al. 2017; Tholkappian et al. 2018; Xia et al. 2018), is calculated according to Eq. (2):

$$\mathrm{I_{geo}} = \log_2\left(\frac{\mathrm{C_n}}{1.5 \times \mathrm{B_n}}\right) \tag{2}$$

where $\mathrm{C_n}$ and $\mathrm{B_n}$ are the concentrations of metal n in the sediment sample and its corresponding background value of earth's shale, respectively. Factor 1.5 is used to minimize the effect of possible changes in geogenic background values in sediment (Al-Haidarey et al. 2010). The pollution level of metals in terms of $\mathrm{I_{geo}}$ values is given in Table S3 (Kusin et al. 2018).

Table 1 Descriptive statistics of some properties and heavy metal content in sediments (*n*=48)

Elements	Min (mg/kg)	Max (mg/kg)	Mean (mg/kg)	SD[a] (mg/kg)	K–S test	Skewness	Kurtosis	CV[b] (%)	BGV[c]	TEL[d]	PEL[d]
Mn	326	820	565.38	145.83	0.69	0.28	−0.49	25.79	850	–	–
Fe	34,300	60,000	46,000	7000	0.47	0.18	−0.37	15.22	47,000	–	–
Ni	8	171	34.38	43.79	1.34	2.42	6.15	127.37	80	15.9	42.8
Cu	49	635	104.06	142.09	1.95	3.95	15.73	136.55	50	18.7	108
Zn	54	456	109.88	95.30	1.52	3.61	13.67	86.73	90	124.0	271
Cr	19	306	87.31	83.72	1.29	1.61	1.76	95.89	100	52.3	160
Pb	13	83	32.31	19.27	0.64	0.90	2.20	59.64	20	30.2	112

n: sampling size

[a] Standard deviation (SD)

[b] Coefficent of variation(CV) (%)

[c] Background value (BGV) of chemical elements in the shale (Krauskopf 1985)

[d] *TEL* threshold effect level, *PEL* probable effect level. Sediment quality guidelines (SQG) from Long et al., (1995) (Long et al. 1995)

Contamination factor (CF) and pollution load index (PLI)

The pollution factor (CF) and pollution load index (PLI) were calculated to reveal the level of pollution in the sediments. The pollution factor is a good tool to estimate the pollution levels caused by metals in the environmental environment over a given time period (Ghani 2015). The CF can be calculated depending on Eq. (3) defined by Tomlinson et al. (1980) (Tomlinson et al. 1980), as follows:

$$\mathrm{CF} = \frac{\mathrm{C_{metal}}}{\mathrm{C_{background}}} \tag{3}$$

where $\mathrm{C_{metal}}$ and $\mathrm{C_{background}}$ are the content of metal i in the sediment and its background value in earth's shale, respectively. According to the value of CF, the CF was divided into four categories by Hakanson (1980) (Hakanson 1980) as given in Table S3.

PLI, defined as the geometric average of all individual pollution indexes of heavy metals determined in the sample (Tomlinson et al. 1980; Lu et al. 2014), can identify the comprehensive pollution level of heavy metals. It is calculated according to Eq. (4):

$$\mathrm{PLI} = \sqrt[n]{\mathrm{C_{f1}} \times \mathrm{C_{f2}} \times \mathrm{C_{f3}} \times \ldots \times \mathrm{C_{fn}}} \tag{4}$$

where *n* is the number of heavy metal elements analyzed. The PLI value less than 1 indicates uncontaminated sediment condition, whereas the PLI value greater than 1 indicates a contaminated sediment condition (Chakravarty and Patgiri 2009; Tholkappian et al. 2018; Baltas et al. 2020).

Ecological risk evaluation of metals

To identify the ecological risk of metals in the sediment, sediment quality guidelines (SQGs) and potential ecological risk index (RI) were applied in this study. RI, proposed by Hakanson (1980) (Hakanson 1980) and widely used in the ecological risk analysis of metals in sediment, soil, and surface dust (Yi et al. 2011; Qin et al. 2014), is calculated according to Eq. (5)

$$\mathrm{RI} = \sum_{i} \mathrm{E_r^i} = \sum_{i} \mathrm{T_r^i X C_f^i} \tag{5}$$

where $\mathrm{E_r^i}$ is the potential ecological risk factor of each metal; $\mathrm{T_r^i}$ is the toxic-response factor of metal i, which is 1 for Mn and Zn, 5 for Pb, Ni, and Cu, 2 for Cr (Hakanson 1980; Zhu et al. 2013; Zhang et al. 2014; Pejman et al. 2015); **and** $\mathrm{C_f^i}$ is the contamination factor of metal i. The ecological risk grade on the base of the value of $\mathrm{E_r^i}$ and RI is **shown** in Table S4.

Statistical analysis

Descriptive statistics were used to analyze metals in the sediments of the Middle and Eastern Black Sea. Kolmogorov-Smirnov (K–S) test was applied to analyze whether the metal concentrations were normally distributed (Tian et al. 2017; Cai et al. 2019). Multivariate statistical methods such as correlation and principal component analysis (PCA) were used to judge possible sources of heavy metals. All statistical analyses for the data were performed by using IBM SPSS version 21.0 (SPSS Inc., USA) software. Moreover, spatial distribution maps of metals were visualized using ArcGIS version 10.1 to reveal hot spots of metal contamination. These methods utilized are widely used to investigate possible sources of pollutants in various environmental environments (Zhang et al. 2015; Zhu et al. 2016; Han and Lu 2017; Zhuang and Lu 2020; Yu et al. 2021).

Results and discussion

Heavy metal concentrations in sediment

The descriptive statistics of measured metals in the sediment samples and average shale values reported by Krauskopf (1985) are listed in Table 1. The analysis results showed that the concentration of heavy metals in sediments was in the range of 326–820 mg/kg for Mn; 34,300–60,000 mg/kg for Fe; 8–171 mg/ kg for Ni; 49–635 mg/kg for Cu; 54–456 mg/kg for Zn; 19–306 mg/kg for Cr; and 13–83 mg/kg for Pb. As for the mean concentrations from the whole area, the concentrations of Mn, Fe, Ni, Cu, Zn, Cr, and Pb were found to be 565.38, 46,000, 34.38, 104.06, 109.88, 87.31, and 32.31 mg/kg, respectively. Generally, average metal concentrations were found in the order of Fe > Mn > Zn > Cu > Cr > Ni > Pb. In the case of Mn, Fe, Ni, and Cr, the concentration in all sampling locations was lower than the average shale value reported by Krauskopf (1985), while the mean concentration of Cu, Zn, and Pb was greater than the average shale value due to pedogenic process and human-origin inputs such as mining activities, agricultural runoffs, and traffic emissions.

Since the metal concentrations in the investigated area showed a heterogeneous distribution, the standard deviation (SD) values were found to be high. In order to test the normality of the data, the Kolmogorov-Smirnov test (K–S) was applied to the data obtained, and the distribution of the data was considered normal if the *p* value was above 0.05 (Kelepertzis 2014; Cai et al. 2015). As a result of the K–S test, it was determined that all metals showed a normal distribution. Again, the skewness values were investigated to determine whether the distribution of metals was normal. If the skewness value is between −1 and 1, the distribution of the metal is considered normal, and if it shows a slightly positive skewness value, it is considered abnormal (Chandrasekaran et al. 2015; Baltas et al. 2020). Hence, the concentrations of Ni, Cu, Zn, and Cr were strongly skewed with the skewness higher than 1, and the kurtosis was also higher than 1, caused by the fact that the majority of samples were clustered at relatively low values (Lu et al. 2010; Cai et al. 2019). It **was** indicated that the concentrations of Ni, Cu, Zn, and Cr were not normally distributed. The skewness and kurtosis values of Mn and Fe metals less than 1 indicated that the concentrations of these metals **were** normally distributed.

While the inputs of metals with low coefficient of variation (CV) are expressed by natural resources, the inputs of metals with high coefficient of variation (CV) are expressed mostly by human-induced activities (Marcinkonis et al. 2011; Cai et al. 2015; Mamut et al. 2017; Baltas et al. 2020). **Table 1** shows that the CV of Mn, Fe, Ni, Cu, Zn, Cr, and Pb were 25.79%, 15.22%, 127.37%, 136.55%, 86.73%, 95.89 %, and 59.64%, respectively. In terms of coefficient of variation (% CV), Ni, Cu, Zn, and Cr showed high variability (CV > 75%), while Mn and Pb showed moderate variability (25% < CV < 75%). The CV of Fe showed low variability (CV < 25%). Therefore, the main input sources of Mn, Ni, Cu, Zn, Cr, and Pb except Fe can be explained by anthropogenic activities. It can be said that the main source of Fe is natural resources such as the sediment parent material and topography (Mamut et al. 2017). Topography is a major factor controlling the variation of soil physical-chemical properties due to its effect on runoff, drainage, and soil erosion, which consequently affect soil formation and development (Xiong et al. 2015; Liu et al 2016). Therefore, content and bioavailability of heavy metals in soils may be largely determined by topographic conditions (Du Laing et al. 2009; Liu et al. 2016). As a result, the topography of soils transported as a result of coastal erosion and weathering by rivers and streams is very important in metal accumulation in sediment in the marine environment. Moreover, the results obtained reveal that there are significant variations in heavy metal concentrations, and the spatial distribution of metals in the area under investigation is heterogeneous (Zhang et al. 2018).

The mean concentrations of heavy metals (Mn, Fe, Ni, Cu, Zn, Cr and Pb) in the sediments in the present research were compared with the mean values determined in similar studies, and the results are presented in Table 2. The mean concentrations of Mn and Fe in this study were determined to be lower than the mean values reported in Turkey (Çevik et al. 2008), but it was determined to be higher than the mean values reported in other researches. The mean concentrations of Cu, Zn, and Pb in this study were determined to be lower than the mean values reported in Turkey (Çevik et al. 2008; Alkan et al. 2020; Baltas et al. 2017c), but it was determined to be higher than the mean values reported in other researches. The mean value of Ni and Cr element was higher than all other studies in the literature.

Pollution assessment of heavy metals

Sediment quality guidelines (SQGs)

Compared with the SQGs, the average concentrations of Cr, Pb, Cu, and Ni in the sediments exceeded the TEL values. These results show that the sediments occasionally showed potential ecological risks. Zn was below the TEL value, suggesting that the Zn in the sediment **was** not toxic (Table 1). In particular, the average concentrations of Cr, Pb, Cu, Ni, and Zn were found to be lower than the PEL values. Therefore, metal concentrations detected in sediment samples in the area under investigation **did not** tend to show adverse biological effects.

Enrichment factor (EF)

The calculated EF values for sediments are summarized and presented in Table 3. The average EF values of the metals were found in the order of Cu (1.98) > Pb (1.77) > Zn (1.23) > Cr (0.88) > Mn (0.69) > Ni (0.45). The mean EF values suggest no enrichment for Cr, Mn, and Ni unlike Cu, Pb, and Zn which indicates minimal enrichment. Average EF values were found to be less than 1.5 for Mn, Ni, Cr, and Zn, while it was higher than 1.5 for Cu and Pb. Therefore, although the main sources of Mn, Ni, Cr, and Zn are entirely from crustal materials or natural erosion processes, the main enrichment sources of Cu and Pb are anthropogenic inputs from industrial activities.

Geo-accumulation index (I_{geo})

The calculated I_{geo} values for sediments are summarized and presented in Table 3. The average I_{geo} values of the heavy metals were found in the order of Cu (0.05) > Pb (0.02) > Zn (−0.53) > Fe (−0.63) > Mn (−1.22) > Cr (−1.28) > Ni (−2.20). In general, the average I_{geo} values were found to be less than zero for all metals except Cu and Pb. Based on the Müller classification, the geo–accumulation index shows that the Black Sea region is not contaminated with Zn, Fe, Mn, As, and Ni but uncontaminated to moderately polluted by Cu and Pb.

Contamination factor (CF) and pollution load index (PLI)

The calculated CF and PLI values for metals are summarized and presented in Table 3. CF values decreased in the following descending order: Cu (2.08) > Pb (1.62) > Zn (1.22) > Fe (0.98) > Cr (0.87) > Mn (0.66) > Ni (0.43). The average CF value for Cu, Pb, and Zn indicated the moderate contamination level, whereas the average CF value for Fe, Mn, Ni, and Cr showed a very low pollution level. In addition, the average PLI value was found to be 0.73. Since the average PLI **was**

Table 2 Comparison of heavy metal concentrations (mg/kg) in sediments with the previous studies.

Study area	Mn	Fe	Ni	Cu	Zn	Cr	Pb	References
Turkey (Eastern Black Sea Coast)	446.9	–	23.4	3107.3	4259.5	40.2	208.2	(Alkan et al. 2020)
Turkey (Eastern Black Sea Coast)	399	–	13.8	31.8	70.2	18.5	22.2	(Alkan et al. 2015)
Turkey (Eastern Black Sea Coast)	1,031	94,660	18.75	2,278.4	993.8	27.28	125.18	(Çevik et al. 2008)
Turkey (Eastern Black Sea Coast)	–	–	–	576.31	357.02	–	97.33	(Baltas et al. 2017c)
Iranian (Caspian sea)	–	–	16.6	16.8	29.5	17.9	7.4	(Gholizadeh and Patimar 2018)
Egyptian (Mediterranean coast)	381	13,256	25.93	8.46	22.19	82.74	13.17	(Soliman et al. 2015)
Egyptian (Red sea)	198.76	8451.62	17.52	9.43	44.15	–	11.43	(Nour et al. 2019)
Saudi Arabia (Red sea)	184	3374	14	30	24	39	6.6	(El-Sorogy et al. 2020)
Turkey (Middle and Eastern Black Sea Coast)	565.38	46,000	34.38	104.06	109.88	87.31	32.31	Present study

below 1, no contamination by the metals was detected in the area under investigation.

Ecological risk evaluation

Potential ecological risk index (RI) and ecological risk factor values calculated for heavy metals are given in Table 3. The average risk factors (E_r^i) in sediment samples of the heavy metals were found in the order of Cu (10.41) > Pb (8.08) > Ni (2.15) > Cr (1.75) > Zn (1.22) > Fe (0.98) > Mn (0.66). Since the average E_r^i values for all metals **were** lower than 40, no ecological risk **was** identified in the investigated area as a result of the toxicity factors of the metals. The average value of the RI in the area studied was found to be 31.61. Since the average RI value **was** lower than RI <50, a very low ecological risk **was** identified for all metals in the region. Moreover, Fig. 2 **exhibits** that Cu is the largest contributor (42.87%) to RI, followed by Pb (33.28%), Ni (8.86%), Cr (7.21%), Zn (5.02%), and Mn (2.76%). The contribution rates of metal (loid)s to RI are associated with **not only** their concentrations but also their toxicity response factors.

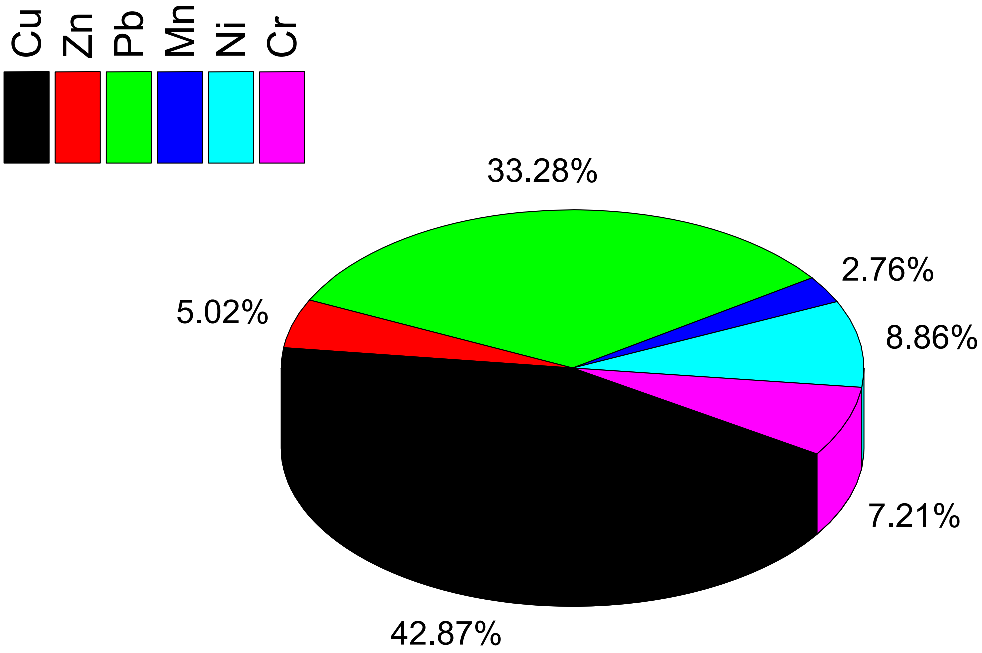
Multivariate analysis of sediment heavy metals

A matrix of Pearson's correlation coefficients was used to assess the degree of correlation among the metals and to distinguish the sources of the metals in the sediments (Table S5). The correlation analysis showed that there was a significantly

Table 3 Calculated pollution indices due to heavy metal concentration.

Elements	EF			I_{geo}			C_f			E_r^i		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Mn	0.69	0.43	1.06	−1.22	−1.97	−0.64	0.66	0.38	0.96	0.66	0.38	0.96
Fe	–	–	–	−0.63	−1.04	−0.23	0.98	0.83	1.28	–	–	–
Ni	0.45	0.08	2.17	−2.20	−3.91	0.51	0.43	0.10	2.14	2.15	0.50	10.69
Cu	1.98	1	9.94	0.05	−0.61	3.08	2.08	0.98	12.70	10.41	4.90	63.50
Zn	1.23	0.62	3.97	−0.53	−1.32	1.76	1.22	0.60	5.07	1.22	0.60	5.07
Cr	0.88	0.20	3.11	−1.28	−2.98	1.03	0.87	0.19	3.06	1.75	0.38	6.12
Pb	1.77	0.59	4.67	0.02	−1.21	1.47	1.62	0.65	4.15	8.08	3.25	20.75
PLI	Mean				Min				Max			
	0.73				0.00				1.21			
RI	Mean				Min				Max			
	24.27				11.79				70.34			

Fig. 2 The contribution of metals to the potential ecological risk



positive relationship between the elemental pairs Cu–Zn ($r = 0.973$), Zn–Cr ($r = 0.960$) and Ni–Cr ($r = 0.845$) at $p < 0.01$. There was also a moderate positive relationship between Fe–Cu ($r = 0.552$), Ni–Distance ($r = 0.615$), and Cr–Distance ($r = 0.529$) at $p < 0.05$ (The expression “Distance” represents the distance of the sampling point to the shore in nautical miles). According to the study published by Thollkappian et al. (2018), if the correlation coefficient between metals is positive, these metals are likely to have a common source, interdependence, and the same behavior in the transportation process. Accordingly, common sources and transport of positively correlated metals may be similar (Wang et al. 2017). But, a moderate negative correlation exists between Fe and Pb ($r = -0.574$, $p < 0.05$). Significant negative correlations between some heavy metals indicated that these heavy metals could originate from different pollution sources (Chabukdhara and Nema 2013; Ahamad et al. 2020). Therefore, negatively correlated Fe and Pb can arise from different sources.

PCA analysis, one of the multivariate statistical methods, was also used to determine the relationships between metals in sediment and the sources of metals. Three main components with eigenvalues greater than 1 were identified, explaining 85.712% of the system variance. The graphical representation of the three components (PC 1, PC 2 and PC 3) where the relationships between heavy metals can be seen is given in Fig. 3. Liu et al. (2003) classified the factor loadings as strong (< 0.75), moderate (0.75–0.50), and weak (0.50–0.30) (Liu et al. 2003; Ustaoğlu and Islam 2020). As reported in Table 4, PC1 (38.503% variance) showed strong positive loading for Cu and Zn and moderate positive loading for Fe. In addition, we found a significant correlation between Cu–Zn and Fe–Cu. The average EF values of Cu and Zn were obtained above 1. Also, the mean concentrations of Cu and Zn in the sediments were more than the background concentrations. The minor enrichment for Cu and Zn in the study area may have resulted from low anthropogenic inputs, including domestic/municipal wastewaters and vehicle emissions (Sun et al. 2019). In addition, fertilizer and pesticide application in agriculture can be considered as the primary source of Cu and Zn, due to the large amount of hazelnut and tea production in the study area (Chen et al. 2018; Song et al. 2019; Ustaoğlu and Islam 2020). Moreover, we can say that these metals are formed as a

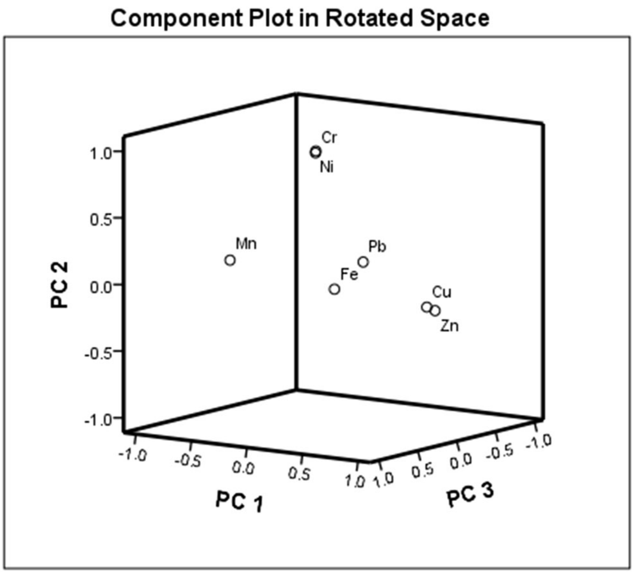


Fig. 3 PCA loading plots for rotated components of heavy metals in sediment

Table 4 Rotated component matrix of metals in sediments in the Middle and Eastern Black Sea

Parameter	PC1	PC2	PC3
Mn	−0.397	0.205	**0.761**
Fe	**0.501**	0.069	**0.701**
Ni	−0.117	**0.951**	0.058
Cu	**0.968**	−0.094	0.180
Zn	**0.948**	−0.142	0.046
Cr	−0.072	**0.951**	0.128
Pb	−0.292	−0.024	**−0.801**
Eigenvalues	**2.695**	**2.206**	**1.099**
% of variance	**38.503**	**31.515**	**15.694**
Cumulative %	**38.503**	**70.018**	**85.712**

result of the mining activities operating intensively in the Eastern Black Sea region (Çevik et al. 2008; Baltas et al. 2017c). The average EF value of Fe was obtained below 1. The concentration of Fe was considered to result from natural sources (Zhu et al. 2013). Therefore, PC1 could be better explained as anthropogenic sources such as agricultural and mining (Kelepertzis 2014; Chandrasekaran et al. 2015; Ma et al. 2016; Baltas et al. 2017c; Lu et al. 2017; Zhu et al. 2019).

PC2 (31.515% variance) showed a high factor loading on Ni and Cr. Additionally, there was a significant positive correlation between Ni and Cr. The average EF values of Ni and Cr were obtained below 1. The mean concentrations of Ni and Cr in the sediments were lower than the background concentrations. In previous studies, it was stated that the main sources of Ni and Cr in sediment are parent materials and pedogenic process (Wang et al. 2016; Cai et al. 2019). Therefore, the high loading factors detected for Ni and Cr in the PC2 component indicate that the levels of these metals can be attributed primarily to lithogenic effects (natural sources) (Jia et al. 2018; Xu et al. 2020).

PC3 (15.694% variance) showed strong positive and negative loading for Mn and Pb, respectively, while it showed moderately positive loading for Fe. In addition, a weak positive correlation was found between Mn and Fe, while a moderately negative correlation was found between Fe and Pb. The average EF value of Pb was obtained above 1. Also, the mean concentration of Pb in the sediments was more than the background concentrations. The minor enrichment for Pb in the study area may have resulted from low anthropogenic inputs, including vehicle emissions and mine reserves (Çevik et al. 2008; Baltas et al. 2017c; Sun et al. 2019). The average EF values of Mn and Fe were obtained below 1. It is known that Fe and Mn metals are naturally occurring metals in the earth's crust. These metals come from natural resources such as coastal erosion and rock weathering (Savitha et al. 2018). The concentrations of Fe and Mn were considered to result from natural sources (Zhu et al. 2013). Therefore, PC3 could be better explained as the natural and anthropogenic sources such as agricultural and mining (Kelepertzis 2014; Chandrasekaran et al. 2015; Ma et al. 2016; Baltas et al. 2017c; Lu et al. 2017; Zhu et al. 2019).

The spatial distribution of heavy metal contents of sediments

The spatial distribution of heavy metal concentration in sediment samples collected from 16 different locations of the Eastern and Middle Black Sea is given in Fig. 4. The spatial distribution patterns of Cu, Fe, and Zn were quite similar. High levels of metals such as Cu, Fe, and Zn were detected in Trabzon, Rize, and Artvin provinces. While the lowest values of Cu and Fe were in Giresun, the lowest value of Zn was found in Samsun. The Eastern Black Sea region is also rich in mine reserves. Among these reserves, the total reserves of 700 million tons of Cu, Zn, and Pb occurrences in the region contribute significantly to the Turkish economy (Çevik et al. 2008; Baltas et al. 2017c). These reserves are considered to be the main sources of high concentrations of Cu and Zn metals in the samples from the Eastern Black Sea region (Otansev et al. 2016; Baltas et al. 2017c; Ustaoğlu and Islam 2020). Moreover, the input sources of Zn into the marine environment are old ships (rust, old metal parts, paint on ship hulls), tourism activities, oil waste, and sewage waste (Ali et al. 2016; Otansev et al. 2016). Besides, feed used for marine farming of animals has also been reported to be a source of Zn and Cu elements (Tian et al. 2020). According to the PCA results, we believe that Cu and Zn can be controlled by human activities, while element Fe can be controlled by both lithogenic/geological sources (natural).

The spatial distribution of Pb concentrations was determined to be highest in Trabzon, Giresun, Ordu, and Samsun provinces. The lowest values were found to be in the province of Artvin. The reason for the higher Pb levels in these sampling provinces can be explained by the fact that these regions have denser populations, **mine** reserve deposits, and large port enterprises. In addition, traffic emissions and industrial, agricultural, domestic, and human-sourced wastes can be interpreted as the reason for the increase in Pb levels in marine sediments in this region (Filzek et al. 2004; Cai et al. 2012). According to the PCA results, it can be said that the input sources of Pb are anthropogenic.

When the spatial distributions for Mn, Cr, and Ni metals were examined, the highest concentrations were found in Samsun. It is thought that the reason for the high determination of these metals regionally is due to municipal wastewater discharges and unprocessed domestic wastes. In addition, the Mn element is used in the production of steel, batteries, and chemicals (Otansev et al. 2016). Ni and Cr concentrations in

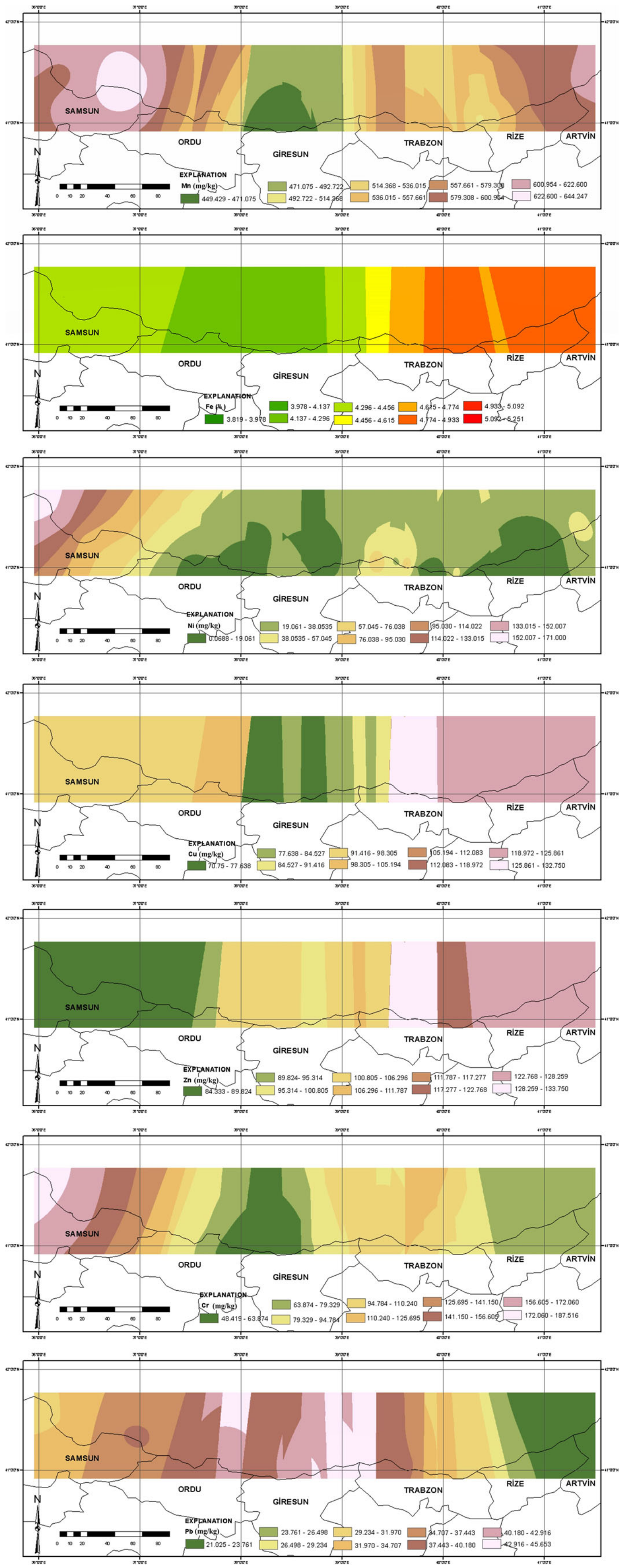


Fig. 4 Spatial distribution of heavy metal contents

sediments may be due to parent rock materials, geogenic origin, or atmospheric deposition of vehicle emissions. In addition, the anthropogenic origin Ni inputs in sediments originate from various fertilizers used in agriculture (Cai et al. 2015; Ungureanu et al. 2017; Tian et al. 2020). **However,** we can **infer** from the PCA results that high Ni, Cr, and Mn values are mainly affected by natural resources such as parent rock materials and coastal erosion.

Conclusions

Heavy metals such as Mn, Fe, Ni, Cu, Zn, Cr, and Pb in sediment samples collected from 16 sampling locations in the Eastern and Middle Black Sea, Turkey, were measured using EDXRF spectrometer. The results showed that Fe was the most abundant metal in all samples due to the abundance of iron in the earth's crust. The average concentrations of Mn, Fe, Ni, and Cr were found to be lower than the crustal shale value, while the average concentrations of Cu, Zn, and Pb were higher due to natural rock erosion as well as anthropogenic inputs such as **mine reserves**, agricultural activities, and traffic emissions. Pollution parameters such as EF, I_{geo}, CF, and PLI were used to reveal the sources and risk status of metal contamination in the sediment in the studied marine region. According to these parameters, the sediment shows a minimal to moderate contamination of pollution of Cu, Zn, and Pb. Since the average pollution load index (PLI) **was** less than one, no contamination by metals was detected in the area under investigation. According to the determined potential ecological risk index (RI) and ecological risk factor $\left(E_r^i\right)$ values, it was revealed that there is a very low risk in the researched area. As a result of the application of multivariate statistical methods used in the identification of the input sources of heavy metals, it was determined that Cu, Zn, and Pb levels in the studied region were slightly affected by anthropogenic and natural inputs. In addition, using the geo-spatial analysis technique, the hot-spot areas of the distribution of metal concentrations were determined. In the geo-spatial distribution map, higher Cu, Zn, Fe, and Pb contents were observed in the Eastern Black Sea region mainly due to the important **mine reserves** that are operated and not operated. Finally, the results of this study will be very useful and informative for future studies as they contain updated data on the levels of metal pollution in the marine environment in the area under investigation.

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Authors' contributions AA, GA, MŞ, ET, OKK: sample collection, analysis, and manuscript preparation. AA, GA, MŞ, EC, HB: data interpretation and editing of the manuscript. AA, OKK, GA, ET: identification of collected samples. AA, GA, MŞ, HB, EC: analysis and data interpretation. HK, MŞ, AA: visualization. MŞ, EC, OKK: manuscript editing.

Data Availability The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests The authors declare that they have no conflict of interest.

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

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