

# Ecological Risk Assessment and Seasonal-Spatial Distribution of Trace Elements in the Surface Sediment of Trabzon Harbour, Turkey

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**How to cite this paper:** Kucuk, Y.K. and Topcu, A. (2017) Ecological Risk Assessment and Seasonal-Spatial Distribution of Trace Elements in the Surface Sediment of Trabzon Harbour, Turkey. *Open Journal of Ecology*, 7, 348-363.

<https://doi.org/10.4236/oje.2017.75025>

**Received:** April 20, 2017

**Accepted:** May 23, 2017

**Published:** May 26, 2017

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## Abstract

A seasonal-spatial distribution and ecological risk assessment of the surface sediment are provided for Trabzon Harbour, located in the Eastern Black Sea Region. Sediments were collected from three stations, one of which was a control station, and a total of nine heavy metals were analyzed. In the sediment samples, concentrations of iron (Fe:  $57.972 \pm 1.226 - 116.250 \pm 0.554 \mu\text{g}\cdot\text{g}^{-1}$  DW), copper (Cu:  $5.790 \pm 0.250 - 14.770 \pm 0.270 \mu\text{g}\cdot\text{g}^{-1}$  DW), cadmium (Cd:  $0.070 \pm 0.016 - 0.232 \pm 0.005 \mu\text{g}\cdot\text{g}^{-1}$  DW), lead (Pb:  $55.100 \pm 0.540 - 4.652 \pm 0.066 \mu\text{g}\cdot\text{g}^{-1}$  DW), chrome (Cr:  $9.232 \pm 0.046 - 28.640 \pm 0.377 \mu\text{g}\cdot\text{g}^{-1}$  DW), zinc (Zn:  $4.592 \pm 0.300 - 54.322 \pm 0.437 \mu\text{g}\cdot\text{g}^{-1}$  DW), arsenic (As:  $2.702 \pm 0.233 - 6.332 \pm 0.186 \mu\text{g}\cdot\text{g}^{-1}$  DW), manganese (Mn:  $21.175 \pm 0.374 - 41.465 \pm 0.410 \mu\text{g}\cdot\text{g}^{-1}$  DW), nickel (Ni:  $9.272 \pm 0.042 - 54.230 \pm 0.158 \mu\text{g}\cdot\text{g}^{-1}$  DW), total phosphorus (TP:  $0.160 \pm 0.003 - 0.250 \pm 0.001 \mu\text{g}\cdot\text{g}^{-1}$  DW), total nitrogen (TN:  $0.111 \pm 0.001 - 0.161 \pm 0.001 \mu\text{g}\cdot\text{g}^{-1}$  DW), organic matter (OM:  $0.767 \pm 0.010 - 1.750 \pm 0.009 \mu\text{g}\cdot\text{g}^{-1}$  DW), total organic carbon (TOC:  $1.450 \pm 0.001 - 4.407 \pm 0.002 \mu\text{g}\cdot\text{g}^{-1}$  DW), clay ( $10.845 \pm 0.347 - 40.545 \pm 0.830$ ; %), sand ( $25.330 \pm 0.700 - 58.237 \pm 0.047$ ; %), and silt ( $17.180 \pm 0.289 - 41.990 \pm 0.116$ ; %) contents were determined. Dissolved oxygen ( $\text{O}_2$ :  $9.100 \pm 0.115 - 14.530 \pm 0.047 \text{ mg}\cdot\text{L}^{-1}$ ), water temperature ( $9.025 \pm 0.095 - 24.975 \pm 0.051^\circ\text{C}$ ), pH ( $8.130 \pm 0.047 - 8.905 \pm 0.041$ ), and electrical conductivity (EC:  $756.242 \pm 0.050 - 780.655 \pm 0.213 \text{ mmhos}\cdot\text{cm}^{-1}$ ) were measured in the sampling stations. Based on the concentration relationships, the SQGs (practical, reliable and predictive tools for assessing sediment quality), enrichment factor (EF) and Igeo analyses, the results indicated that the harbour has been contaminated by heavy metals to varying degrees, and organic material plays a key role in controlling the distribution of these heavy metal concentrations in the sediment. The spatial distribution pattern of heavy metals in the surface sediments of Trabzon Harbour is a basis for undertaking and providing monitoring studies

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of heavy metal contamination with regard to marine traffic, river input and anthropogenical effects around the port.

### Keywords

Heavy Metals, Sediment, Sediment Quality Guidelines, EF, Igeo, Trabzon Harbour

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## 1. Introduction

Sediments in aquatic ecosystems are home to many benthic and epibenthic organisms. They also affect the behavior of chemicals in these ecosystems. Moreover, they host and act as an important nutrient source for aquatic organisms, which in turn have an important effect on the pollution patterns in the aquatic systems. Sediments in marine environments serve as the ultimate sink of heavy metals [1]. They are also important for the transport and storage of potentially hazardous metals [2]. These metals enter into the aquatic system as a consequence of soil erosion, weathering of rocks, volcanic eruptions and human activities such as mining, dredging, and metal processing and use. Sediment analysis has an important part in determining the pollution status of marine environments [3].

Trace metals in aquatic environments accumulate primarily in the upper sections of sediment due to biological-geochemical mechanisms. These metals are toxic to marine organisms, and may cause death, impaired growth and reproduction capacity, and thus result in lower diversity of species [4] [5]. These metals also occur naturally in rock and can be introduced into aquatic environments through natural processes [6]. When heavy metals are present in aquatic ecosystems in concentrations exceeding the natural background load, they may accumulate to toxic levels without visible signs. This has become a problem of increasing concern.

It is important to determine whether sediment heavy metal concentrations pose a threat to aquatic organisms. The extent of metal pollution is determined by comparing metal concentrations in surface sediments to the TEL (threshold effects level) and PEL (probable effects level) of the SQGs (Sediment Quality Guidelines) established by [7] [8] and [9]. The extent of metal pollution in marine sediment can be assessed in a number of ways, such as USEPA, Igeo and Enrichment Factor (EF) [10] [11] [12] [13].

According to Turkey's foreign trade transport data from 2009, 72% of the country's export and 94% of its import goods were transported by sea. Therefore, marine transportation is an important dynamic not only for the global economy, but also for Turkey's economy. The shipping trade is developing rapidly in parallel to advances in technology. In addition, as it is a safer and more economic means of transport, maritime transport is gradually increasing. However, these developments in maritime transport also bring about problems such

as marine pollution caused by ships. The discharge of oil to the sea, the use of anti-fouling and anti-corrosive paints, oil spills during shipping and terminal transfers and effluent discharges from refineries probably comprise the anthropogenic sources of Pb, Cr, Fe, Cu, Zn, and Cd into the oceans. Major ecological impacts have also increased in areas remote from the shoreline.

Although there are limited number of studies regarding heavy metal concentrations in the sediment of the Black Sea coastline [14] [15] [16] [17], to date there has been no research revealing the anthropogenic effects of metals and the environmental risk associated with their concentrations at Trabzon Harbour. The objectives of this research paper were to make the first records of: (1) the seasonal and spatial concentrations of the metals iron (Fe), copper (Cu), cadmium (Cd), lead (Pb), chromium (Cr), zinc (Zn), arsenic (As), manganese (Mn) and nickel (Ni) in the surface sediments of Trabzon Harbour; (2) the seasonal and spatial concentrations of the total phosphorus (TP), total nitrogen (TN), organic matter (OM), total organic carbon (TOC) with clay, sand and silt contents of the surface sediment; (3) the correlation between heavy metals and surface sediment chemical parameters; and (4) the environmental risk associated with the metal contents of the sediments using available SQGs.

## 2. Materials and Methods

### 2.1. Site Description

Trabzon is located on the coastline of the Black Sea, the world's largest inland sea, which has a link to the world's greatest seas and a place at the beginning of the transit route used by the Russian Federation and the Republics of Iran, Iraq, and Turkey. Trabzon Harbour plays a critical role in linking these countries to the European and world markets. Trabzon Harbour, having a length of 1.525m docl, a three million ton storage capacity, a ship acceptance of 2.000 and a 250.000 passenger capacity, provides service to container ships, Ro-ro casting and shiploading [18]. Trabzon Harbour is located at 40 57'30"N - 41 06'36"N latitude and 40 02'30"E - 39 25'00"E longitude [19]. According to the Ship Trade General Management statistics for 2013, the number of sea vessels visiting Trabzon Harbour was 92 in January, 76 in February, 87 in March, 90 in April, 90 in May, 30 in June, 107 in July, 104 in August, 104 in September, 96 in October [20].

### 2.2. Study Site

The present research was conducted in Trabzon Harbour. Sediment and water samples were collected from three stations, of which the second (located in a dock with a depth of 9.5 m and a length of 400 m) and third (located in a dock with a depth of 9.5 m and a length of 580 m) stations in the port were selected to represent the Trabzon Harbour Maritime Authority, and the first station was the control station, located 1.530 m from the second and third stations (**Figure 1**). Sampling was carried out in April, July and October 2013 and January 2014, seasonally, with four renewals.



**Figure 1.** Trabzon Harbour and sampling stations.

### 2.3. Sampling and in Situ Analyses

Sediment samples were collected from the three stations using an Ekman-Birge grab and transferred to the laboratory in polyethylene bottles preserved in darkness to block the effect of sunlight. The dissolved oxygen and the temperature of the water were measured using an oxygen meter at the site. The pH of the water was estimated in situ with a pH-meter.

Sediment samples were air-dried for a period of 20 days, homogenized by grinding, and finally passed through a 1.0 mm sieve for texture analyses in laboratory conditions. Organic matter (%) was determined by the loss of weight during ignition at 550°C for 2 hours [21]. The water content of the sediment samples was specified by considering the difference between the samples before and after drying at 110°C for 16 hours according to [22]. Total organic carbon in the sediment samples was evaluated with an Organic Carbon Analyzer Unit where total nitrogen values were determined using the Dumas Method. Total phosphorus of the dried sediments was analysed spectrophotometrically after digestion in a mixture of oxidizing acids with reference to [21].

Surficial sediment samples for Fe, Cu, Cd, Pb, Cr, Zn, As, Mn, and Ni were dried at 60°C for 24 hours and then sieved and measured after wet digestion with an atomic absorption spectrophotometer (Perkin-Elmer 2380) operating on flame mode. The exchangeable fraction of metals was determined after extraction with a hydrofluoric/perchloric/sulfuric acid mixture. Detection of these metals was performed using the F-AAS technique [21].

### 2.4. Statistical Analyses

Statistical analyses were performed using Minitab and MStat software for Windows. ANOVA was used to evaluate the statistically significant differences between the sampling periods and sampling sites of the surface sediment [23].

## 3. Results

During the study, water temperature values at all stations ranged between 9.03 and 24.98°C, while dissolved oxygen and pH values changed between 9.10 and

14.53 mg·L<sup>-1</sup> and 8.13 and 8.91, respectively. The differences in mean EC values were found to be significant at all stations in all seasons ( $p < 0.05$ ) (Table 1).

The differences in total phosphorus concentrations among the stations were found to be significant in all seasons ( $p < 0.05$ ) except for the third station. The highest total phosphorus value ( $0.25 \pm 0.003 \mu\text{g}\cdot\text{g}^{-1}$  DW) was measured at the third station in January, whereas the lowest value ( $0.16 \pm 0.003 \mu\text{g}\cdot\text{g}^{-1}$  DW) was measured at the first station in April. The differences in total nitrogen concentrations between the seasons for the third station was found to be insignificant during the whole study period ( $p > 0.05$ ), whereas the differences between the seasons for this parameter were found to be insignificant for the first and second stations except for January. The highest mean concentration of total nitrogen was found in April at the third station ( $0.161 \pm 0.001 \mu\text{g}\cdot\text{g}^{-1}$  DW). Total organic carbon values were between 1.45 and 4.41  $\mu\text{g}\cdot\text{g}^{-1}$  DW at all stations. Sediment TOC concentrations among the stations were found to be significant during the study period ( $p < 0.05$ ) and the minimum value for this parameter was determined at the first station, whereas the maximum value was found at the third station. The differences in the sediment's mean LOI values between April 2013 and January 2014 were found to be statistically significant at all the stations for the entire research period ( $p < 0.05$ ). In this study, water content values were between 56.86 and 68.70% (Table 2). The sediment texture values are shown in Table 2.

**Table 1.** Seasonal and spatial variations of water physico-chemical parameters in Trabzon Harbour (Mean value  $\pm$  standard deviation, N = 4).

Parameters	Stations Months	I	II	III
O <sub>2</sub> (mg·L <sup>-1</sup> )	April 2013	11.700 $\pm$ 0.091 <sup>A*c**</sup>	11.220 $\pm$ 0.024 <sup>Bc</sup>	11.262 $\pm$ 0.025 <sup>Bc</sup>
	July 2013	9.875 $\pm$ 0.170 <sup>Ad</sup>	9.350 $\pm$ 0.288 <sup>Bd</sup>	9.100 $\pm$ 0.115 <sup>Bd</sup>
	October 2013	13.475 $\pm$ 0.050 <sup>Ab</sup>	13.150 $\pm$ 0.057 <sup>Bb</sup>	12.150 $\pm$ 0.057 <sup>Cb</sup>
	January 2014	14.530 $\pm$ 0.047 <sup>Aa</sup>	13.475 $\pm$ 0.050 <sup>Ba</sup>	12.975 $\pm$ 0.095 <sup>Ca</sup>
Water temperature (°C)	April 2013	19.920 $\pm$ 0.053 <sup>Ab</sup>	19.930 $\pm$ 0.053 <sup>Ab</sup>	19.582 $\pm$ 0.053 <sup>Bb</sup>
	July 2013	24.225 $\pm$ 0.287 <sup>Ba</sup>	24.922 $\pm$ 0.051 <sup>Aa</sup>	24.975 $\pm$ 0.051 <sup>Aa</sup>
	October 2013	17.825 $\pm$ 0.050 <sup>Bc</sup>	18.227 $\pm$ 0.032 <sup>Ac</sup>	18.492 $\pm$ 0.032 <sup>Ac</sup>
	January 2014	9.025 $\pm$ 0.095 <sup>Cd</sup>	9.167 $\pm$ 0.039 <sup>Bd</sup>	9.275 $\pm$ 0.039 <sup>Ad</sup>
pH	April 2013	8.420 $\pm$ 0.021 <sup>Ab</sup>	8.337 $\pm$ 0.047 <sup>Bb</sup>	8.337 $\pm$ 0.025 <sup>Bc</sup>
	July 2013	8.322 $\pm$ 0.033 <sup>Ab</sup>	8.345 $\pm$ 0.031 <sup>Ab</sup>	8.212 $\pm$ 0.015 <sup>Bb</sup>
	October 2013	8.130 $\pm$ 0.047 <sup>Ac</sup>	8.180 $\pm$ 0.040 <sup>Ac</sup>	8.175 $\pm$ 0.028 <sup>Aa</sup>
	January 2014	8.905 $\pm$ 0.041 <sup>Aa</sup>	8.837 $\pm$ 0.025 <sup>Ba</sup>	8.832 $\pm$ 0.015 <sup>Bd</sup>
EC (mmhos·cm <sup>-1</sup> )	April 2013	778.835 $\pm$ 1.150 <sup>Ba</sup>	780.410 $\pm$ 0.430 <sup>Aa</sup>	780.655 $\pm$ 0.213 <sup>Aa</sup>
	July 2013	757.252 $\pm$ 1.349 <sup>Ac</sup>	756.765 $\pm$ 0.231 <sup>Ad</sup>	756.242 $\pm$ 0.050 <sup>Ad</sup>
	October 2013	761.250 $\pm$ 0.957 <sup>Ab</sup>	761.250 $\pm$ 1.50 <sup>Ac</sup>	761.250 $\pm$ 0.50 <sup>Ac</sup>
	January 2014	756.882 $\pm$ 0.174 <sup>Cd</sup>	769.337 $\pm$ 0.942 <sup>Bb</sup>	774.540 $\pm$ 0.50 <sup>Ab</sup>

\*The different upper-case letters in the same row show the differences between stations ( $p < 0.05$ ), \*\*The different lower-case letters in the same column show the differences between months ( $p < 0.05$ )

**Table 2.** Seasonal and spatial variations of sediment organic material (OM), total organic carbon (TOC), total phosphorus (TP), total nitrogen (TN), water content and sediment texture in Trabzon Harbour (Mean value  $\pm$  standard deviation, N = 4).

Parameters	Stations Months	I	II	III
OM ( $\mu\text{g}\cdot\text{g}^{-1}$ DW)	April 2013	0.902 $\pm$ 0.170 <sup>C<sup>b</sup>**</sup>	1.340 $\pm$ 0.035 <sup>Bb</sup>	1.660 $\pm$ 0.014 <sup>Ab</sup>
	July 2013	1.262 $\pm$ 0.030 <sup>Ca</sup>	1.420 $\pm$ 0.024 <sup>Ba</sup>	1.750 $\pm$ 0.009 <sup>Aa</sup>
	October 2013	0.892 $\pm$ 0.010 <sup>Cb</sup>	1.180 $\pm$ 0.022 <sup>Ac</sup>	1.092 $\pm$ 0.009 <sup>Bd</sup>
	January 2014	0.767 $\pm$ 0.010 <sup>Cc</sup>	1.447 $\pm$ 0.050 <sup>Aa</sup>	1.340 $\pm$ 0.014 <sup>Bc</sup>
TOC ( $\mu\text{g}\cdot\text{g}^{-1}$ DW)	April 2013	1.500 $\pm$ 0.004 <sup>Cb</sup>	2.198 $\pm$ 0.002 <sup>Bd</sup>	4.407 $\pm$ 0.002 <sup>Aa</sup>
	July 2013	1.850 $\pm$ 0.002 <sup>Ca</sup>	3.114 $\pm$ 0.002 <sup>Ba</sup>	4.225 $\pm$ 0.002 <sup>Ab</sup>
	October 2013	1.450 $\pm$ 0.001 <sup>Cd</sup>	2.400 $\pm$ 0.002 <sup>Bc</sup>	2.520 $\pm$ 0.002 <sup>Ad</sup>
TP ( $\mu\text{g}\cdot\text{g}^{-1}$ DW)	January 2014	1.464 $\pm$ 0.002 <sup>Cc</sup>	2.530 $\pm$ 0.007 <sup>Bb</sup>	2.720 $\pm$ 0.003 <sup>Ac</sup>
	April 2013	0.160 $\pm$ 0.003 <sup>Bd</sup>	0.220 $\pm$ 0.002 <sup>Ac</sup>	0.220 $\pm$ 0.001 <sup>Ac</sup>
	July 2013	0.184 $\pm$ 0.001 <sup>Cc</sup>	0.210 $\pm$ 0.002 <sup>Bd</sup>	0.220 $\pm$ 0.001 <sup>Ac</sup>
	October 2013	0.210 $\pm$ 0.001 <sup>Cb</sup>	0.223 $\pm$ 0.002 <sup>Bb</sup>	0.230 $\pm$ 0.001 <sup>Ab</sup>
TN ( $\mu\text{g}\cdot\text{g}^{-1}$ DW)	January 2014	0.214 $\pm$ 0.001 <sup>Ca</sup>	0.241 $\pm$ 0.001 <sup>Ba</sup>	0.250 $\pm$ 0.001 <sup>Aa</sup>
	April 2013	0.122 $\pm$ 0.001 <sup>Cc</sup>	0.131 $\pm$ 0.009 <sup>Bb</sup>	0.161 $\pm$ 0.009 <sup>Aa</sup>
	July 2013	0.120 $\pm$ 0.009 <sup>Cc</sup>	0.128 $\pm$ 0.006 <sup>Bb</sup>	0.156 $\pm$ 0.002 <sup>Aa</sup>
	October 2013	0.112 $\pm$ 0.001 <sup>Cc</sup>	0.124 $\pm$ 0.001 <sup>Bb</sup>	0.137 $\pm$ 0.006 <sup>Aa</sup>
Water Content (%)	January 2014	0.145 $\pm$ 0.011 <sup>Aa</sup>	0.145 $\pm$ 0.010 <sup>Aa</sup>	0.141 $\pm$ 0.001 <sup>Aa</sup>
	April 2013	67.31 $\pm$ 0.50 <sup>Ab</sup>	64.38 $\pm$ 0.63 <sup>Ba</sup>	60.05 $\pm$ 0.83 <sup>Ca</sup>
	July 2013	65.13 $\pm$ 1.13 <sup>Ac</sup>	60.15 $\pm$ 0.51 <sup>Bb</sup>	56.86 $\pm$ 0.55 <sup>Cb</sup>
	October 2013	68.70 $\pm$ 0.43 <sup>Aa</sup>	58.67 $\pm$ 1.09 <sup>Bc</sup>	57.72 $\pm$ 0.41 <sup>Bb</sup>
Clay (%)	January 2014	67.60 $\pm$ 0.49 <sup>Ab</sup>	59.10 $\pm$ 0.44 <sup>Bc</sup>	59.37 $\pm$ 0.73 <sup>Ba</sup>
	April 2013	13.412 $\pm$ 0.123 <sup>Cc</sup>	30.330 $\pm$ 0.472 <sup>Bc</sup>	35.317 $\pm$ 0.407 <sup>Ac</sup>
	July 2013	17.590 $\pm$ 0.416 <sup>Ca</sup>	24.830 $\pm$ 0.578 <sup>Bd</sup>	37.422 $\pm$ 0.179 <sup>Aa</sup>
	October 2013	14.940 $\pm$ 0.463 <sup>Cb</sup>	35.730 $\pm$ 0.552 <sup>Ab</sup>	31.980 $\pm$ 0.749 <sup>Bd</sup>
Silt (%)	January 2014	10.845 $\pm$ 0.347 <sup>Cd</sup>	40.545 $\pm$ 0.830 <sup>Aa</sup>	36.305 $\pm$ 0.375 <sup>Bb</sup>
	April 2013	35.920 $\pm$ 0.204 <sup>Bd</sup>	25.105 $\pm$ 0.392 <sup>Cc</sup>	37.812 $\pm$ 0.245 <sup>Aa</sup>
	July 2013	39.800 $\pm$ 0.576 <sup>Ab</sup>	17.180 $\pm$ 0.289 <sup>Cd</sup>	37.485 $\pm$ 0.969 <sup>Ba</sup>
	October 2013	39.155 $\pm$ 0.370 <sup>Ac</sup>	38.110 $\pm$ 0.408 <sup>Ba</sup>	30.972 $\pm$ 0.713 <sup>Cc</sup>
Sand (%)	January 2014	41.990 $\pm$ 0.116 <sup>Aa</sup>	37.010 $\pm$ 0.619 <sup>Bb</sup>	33.502 $\pm$ 0.278 <sup>Cb</sup>
	April 2013	51.452 $\pm$ 1.025 <sup>Aa</sup>	45.302 $\pm$ 0.106 <sup>Bb</sup>	27.345 $\pm$ 0.065 <sup>Cc</sup>
	July 2013	42.675 $\pm$ 0.452 <sup>Bd</sup>	58.237 $\pm$ 0.047 <sup>Aa</sup>	25.292 $\pm$ 0.042 <sup>Cd</sup>
	October 2013	46.690 $\pm$ 0.638 <sup>Ac</sup>	26.502 $\pm$ 0.415 <sup>Cc</sup>	37.337 $\pm$ 0.594 <sup>Ba</sup>
	January 2014	47.750 $\pm$ 0.091 <sup>Ab</sup>	25.330 $\pm$ 0.700 <sup>Cd</sup>	29.715 $\pm$ 0.507 <sup>Bb</sup>

\*The different upper-case letters in the same row show the differences between stations ( $p < 0.05$ ), \*\*The different lower-case letters in the same column show the differences between months ( $p < 0.05$ )

The mean concentrations and standard deviations of the studied heavy metals in the sediment from Trabzon Harbour are presented in **Table 3**. Based on their maximum content, the components of the surface sediment were arranged in the following decreasing order: Fe > Pb > Zn > Ni > Mn > Cr > Cu > As > Cd.

Significant positive and negative correlations between certain sediment chemical properties and heavy metals were established in the summer period, keeping

in mind that generally, heavy metal toxicity has the greatest effect on aquatic organisms in summer months (Tables 4-6).

**Table 3.** Seasonal and spatial variations of sediment heavy metal concentrations in Trabzon Harbour (Mean value  $\pm$  standard deviation, N = 4).

Parameters	Stations Months	I	II	III
Fe ( $\mu\text{g}\cdot\text{g}^{-1}$ DW)	April 2013	57.972 $\pm$ 1.226 <sup>C<sup>c</sup>**</sup>	116.250 $\pm$ 0.554 <sup>Aa</sup>	101.800 $\pm$ 0.481 <sup>Bb</sup>
	July 2013	71.040 $\pm$ 0.581 <sup>Ba</sup>	110.170 $\pm$ 0.750 <sup>Ab</sup>	111.017 $\pm$ 0.793 <sup>Aa</sup>
	October 2013	56.600 $\pm$ 0.921 <sup>Cd</sup>	95.815 $\pm$ 0.370 <sup>Ac</sup>	82.762 $\pm$ 0.913 <sup>Bc</sup>
	January 2014	61.942 $\pm$ 0.467 <sup>Cb</sup>	96.160 $\pm$ 0.550 <sup>Ac</sup>	82.915 $\pm$ 0.853 <sup>Bc</sup>
Cu ( $\mu\text{g}\cdot\text{g}^{-1}$ DW)	April 2013	6.180 $\pm$ 0.730 <sup>Cb</sup>	13.000 $\pm$ 0.046 <sup>Bb</sup>	14.437 $\pm$ 0.520 <sup>Aa</sup>
	July 2013	7.102 $\pm$ 0.311 <sup>Ca</sup>	10.520 $\pm$ 0.581 <sup>Bc</sup>	14.017 $\pm$ 0.160 <sup>Aa</sup>
	October 2013	5.790 $\pm$ 0.258 <sup>Cb</sup>	14.740 $\pm$ 0.300 <sup>Aa</sup>	11.447 $\pm$ 0.358 <sup>Bb</sup>
	January 2014	6.050 $\pm$ 0.150 <sup>Cb</sup>	14.770 $\pm$ 0.270 <sup>Aa</sup>	14.222 $\pm$ 0.255 <sup>Ba</sup>
Cd ( $\mu\text{g}\cdot\text{g}^{-1}$ DW)	April 2013	0.120 $\pm$ 0.082 <sup>Cb</sup>	0.152 $\pm$ 0.095 <sup>Bc</sup>	0.232 $\pm$ 0.005 <sup>Aa</sup>
	July 2013	0.074 $\pm$ 0.001 <sup>Cc</sup>	0.112 $\pm$ 0.050 <sup>Bd</sup>	0.142 $\pm$ 0.005 <sup>Ad</sup>
	October 2013	0.160 $\pm$ 0.005 <sup>Ca</sup>	0.230 $\pm$ 0.082 <sup>Aa</sup>	0.177 $\pm$ 0.005 <sup>Bc</sup>
	January 2014	0.070 $\pm$ 0.016 <sup>Cc</sup>	0.170 $\pm$ 0.050 <sup>Bb</sup>	0.192 $\pm$ 0.005 <sup>Ab</sup>
Pb ( $\mu\text{g}\cdot\text{g}^{-1}$ DW)	April 2013	4.652 $\pm$ 0.066 <sup>Cd</sup>	6.442 $\pm$ 0.160 <sup>Ad</sup>	5.702 $\pm$ 0.102 <sup>Bd</sup>
	July 2013	6.625 $\pm$ 0.119 <sup>Cb</sup>	12.325 $\pm$ 0.087 <sup>Bb</sup>	14.245 $\pm$ 0.052 <sup>Aa</sup>
	October 2013	7.212 $\pm$ 0.164 <sup>Ca</sup>	10.275 $\pm$ 0.130 <sup>Ac</sup>	8.640 $\pm$ 0.126 <sup>Bc</sup>
	January 2014	5.420 $\pm$ 0.024 <sup>Cc</sup>	55.100 $\pm$ 0.540 <sup>Aa</sup>	11.822 $\pm$ 0.026 <sup>Bb</sup>
Cr ( $\mu\text{g}\cdot\text{g}^{-1}$ DW)	April 2013	9.232 $\pm$ 0.046 <sup>Bd</sup>	13.372 $\pm$ 0.204 <sup>Ab</sup>	9.422 $\pm$ 0.120 <sup>Bd</sup>
	July 2013	11.892 $\pm$ 0.197 <sup>Bc</sup>	16.100 $\pm$ 4.985 <sup>Bb</sup>	28.640 $\pm$ 0.377 <sup>Aa</sup>
	October 2013	12.395 $\pm$ 0.031 <sup>Cb</sup>	12.780 $\pm$ 0.059 <sup>Ab</sup>	12.602 $\pm$ 0.020 <sup>Bc</sup>
	January 2014	16.205 $\pm$ 0.117 <sup>Ca</sup>	20.050 $\pm$ 0.067 <sup>Aa</sup>	17.212 $\pm$ 0.165 <sup>Bb</sup>
Zn ( $\mu\text{g}\cdot\text{g}^{-1}$ DW)	April 2013	4.592 $\pm$ 0.300 <sup>Cb</sup>	27.572 $\pm$ 0.300 <sup>Bb</sup>	54.322 $\pm$ 0.437 <sup>Aa</sup>
	July 2013	4.925 $\pm$ 0.080 <sup>Cb</sup>	20.262 $\pm$ 0.470 <sup>Bc</sup>	39.372 $\pm$ 0.314 <sup>Ab</sup>
	October 2013	4.902 $\pm$ 0.127 <sup>Cb</sup>	29.950 $\pm$ 0.210 <sup>Aa</sup>	27.090 $\pm$ 0.344 <sup>Bd</sup>
	January 2014	5.365 $\pm$ 0.300 <sup>Ca</sup>	29.470 $\pm$ 0.453 <sup>Ba</sup>	30.710 $\pm$ 0.423 <sup>Ac</sup>
As ( $\mu\text{g}\cdot\text{g}^{-1}$ DW)	April 2013	2.762 $\pm$ 0.101 <sup>Bc</sup>	2.702 $\pm$ 0.233 <sup>Bd</sup>	3.527 $\pm$ 0.305 <sup>Ac</sup>
	July 2013	3.107 $\pm$ 0.071 <sup>Cb</sup>	6.160 $\pm$ 0.048 <sup>Aa</sup>	5.715 $\pm$ 0.338 <sup>Bb</sup>
	October 2013	3.532 $\pm$ 0.041 <sup>Ca</sup>	3.937 $\pm$ 0.017 <sup>Ab</sup>	3.807 $\pm$ 0.043 <sup>Bc</sup>
	January 2014	3.222 $\pm$ 0.181 <sup>Bb</sup>	3.332 $\pm$ 0.132 <sup>Bc</sup>	6.332 $\pm$ 0.186 <sup>Aa</sup>
Mn ( $\mu\text{g}\cdot\text{g}^{-1}$ DW)	April 2013	28.840 $\pm$ 0.448 <sup>Ba</sup>	28.780 $\pm$ 0.255 <sup>Bc</sup>	31.625 $\pm$ 0.327 <sup>Ab</sup>
	July 2013	27.370 $\pm$ 0.310 <sup>Cb</sup>	28.101 $\pm$ 0.545 <sup>Bd</sup>	29.757 $\pm$ 0.327 <sup>Ac</sup>
	October 2013	21.175 $\pm$ 0.374 <sup>Cc</sup>	41.465 $\pm$ 0.410 <sup>Aa</sup>	29.982 $\pm$ 0.578 <sup>Bc</sup>
	January 2014	23.652 $\pm$ 0.398 <sup>Cb</sup>	40.670 $\pm$ 0.420 <sup>Ab</sup>	35.235 $\pm$ 0.590 <sup>Ba</sup>
Ni ( $\mu\text{g}\cdot\text{g}^{-1}$ DW)	April 2013	9.272 $\pm$ 0.042 <sup>Cd</sup>	11.565 $\pm$ 0.147 <sup>Bd</sup>	13.535 $\pm$ 0.068 <sup>Ac</sup>
	July 2013	11.470 $\pm$ 0.073 <sup>Cc</sup>	11.407 $\pm$ 0.073 <sup>Bb</sup>	47.372 $\pm$ 0.453 <sup>Aa</sup>
	October 2013	13.310 $\pm$ 0.105 <sup>Bb</sup>	15.240 $\pm$ 0.251 <sup>Ac</sup>	13.515 $\pm$ 0.030 <sup>Bc</sup>
	January 2014	20.112 $\pm$ 0.137 <sup>Ca</sup>	54.230 $\pm$ 0.158 <sup>Aa</sup>	24.740 $\pm$ 0.048 <sup>Bb</sup>

\*The different upper-case letters in the same row show the differences between stations ( $p < 0.05$ ), \*\* The different lower-case letters in the same column show the differences between months ( $p < 0.05$ )

**Table 4.** Pearson correlation matrix for the heavy metals and major elements, OM, TP, TN, TOC in first station in July 2013.

	OM	TP	TN	TOC	Fe	Cu	Cd	Pb	Cr	Zn	As	Mn	Ni
<b>Ni</b>	0.943	0.698	-0.442	-0.595	-0.611	-0.265	0.895	-0.720	-0.286	-0.954*	-0.591	-0.291	-
<b>Mn</b>	-0.593	-0.691	-0.606	-0.439	-0.575	-0.232	-0.011	0.795	-0.832	0.093	0.856	-	-
<b>As</b>	-0.800	-0.965*	-0.461	-0.287	-0.231	-0.414	-0.479	0.741	-0.538	0.512	-	-	-
<b>Zn</b>	-0.838	-0.683	0.463	0.580	0.716	0.107	-0.987*	0.494	0.442	-	-	-	-
<b>Cr</b>	0.050	0.321	0.890	0.813	0.933	0.444	-0.481	-0.359	-	-	-	-	-
<b>Pb</b>	-0.879	-0.651	0.000	0.196	-0.016	0.290	-0.366	-	-	-	-	-	-
<b>Cd</b>	0.761	0.674	-0.426	-0.522	-0.722	0.008	-	-	-	-	-	-	-
<b>Cu</b>	-0.131	0.436	0.787	0.807	0.490	-	-	-	-	-	-	-	-
<b>Fe</b>	-0.313	0.016	0.912	0.907	-	-	-	-	-	-	-	-	-
<b>TOC</b>	-0.342	0.155	0.980*	-	-	-	-	-	-	-	-	-	-
<b>TN</b>	-0.155	0.316	-	-	-	-	-	-	-	-	-	-	-
<b>TP</b>	0.834	-	-	-	-	-	-	-	-	-	-	-	-
<b>OM</b>	-	-	-	-	-	-	-	-	-	-	-	-	-

\*Correlation is statistically significant according to 0.05 level (two way). \*\*Correlation is statistically significant according to 0.01 level (two way).

**Table 5.** Pearson correlation matrix for the heavy metals and major elements, OM, TP, TN, TOC in second station in July 2013.

	OM	TP	TN	TOC	Fe	Cu	Cd	Pb	Cr	Zn	As	Mn	Ni
<b>Ni</b>	0.268	-0.946	-0.507	-0.293	-0.452	0.430	0.293	0.507	0.112	0.267	0.202	0.924	-
<b>Mn</b>	0.595	-0.844	-0.191	-0.181	-0.076	0.583	0.636	0.798	0.215	0.611	0.542	-	-
<b>As</b>	0.789	-0.218	0.717	-0.138	0.717	0.293	0.966*	0.877	0.595	0.984*	-	-	-
<b>Zn</b>	0.884	-0.225	0.625	0.004	0.719	0.460	0.997**	0.943	0.452	-	-	-	-
<b>Cr</b>	-0.018	-0.381	0.598	-0.845	0.160	-0.534	0.383	0.243	-	-	-	-	-
<b>Pb</b>	0.937	-0.391	0.333	0.115	0.540	0.686	0.962*	-	-	-	-	-	-
<b>Cd</b>	0.917	-0.225	0.577	0.067	0.713	0.530	-	-	-	-	-	-	-
<b>Cu</b>	0.804	-0.130	-0.223	0.694	0.277	-	-	-	-	-	-	-	-
<b>Fe</b>	0.702	0.514	0.850	0.389	-	-	-	-	-	-	-	-	-
<b>TOC</b>	0.437	0.586	-0.115	-	-	-	-	-	-	-	-	-	-
<b>TN</b>	0.367	0.391	-	-	-	-	-	-	-	-	-	-	-
<b>TP</b>	-0.080	-	-	-	-	-	-	-	-	-	-	-	-
<b>OM</b>	-	-	-	-	-	-	-	-	-	-	-	-	-

\*Correlation is statistically significant according to 0.05 level (two way). \*\*Correlation is statistically significant according to 0.01 level (two way).

It is important to determine whether concentrations of heavy metals in sediment pose a threat to aquatic organisms. The extent of metal pollution was assessed by comparing metal concentrations in the surface sediments at the stations in this study to the TEL/PEL and Target Limit values of some SQGs (MacDonald 2000) (Table 7 and Table 8). As shown in Table 8, in general, metal concentrations were lower than the average continental crust and average shale values except for Pb and Cd concentrations. The results of the calculation of Enrichment Factor and Igeo in Trabzon Harbour sediments are shown in Table 9.



**Table 6.** Pearson correlation matrix for the heavy metals and major elements, OM, TP, TN, TOC in third station in July 2013.

	OM	TP	TN	TOC	Fe	Cu	Cd	Pb	Cr	Zn	As	Mn	Ni
<b>Ni</b>	0.540	-0.501	-0.181	-0.793	-0.380	-0.792	-0.592	-0.308	0.816	0.927	-0.395	-0,922**	-
<b>Mn</b>	-0.438	0.491	0.273	0.822	0.270	0.864	0.514	0.183	-0.884	-0.968*	0.468	-	-
<b>As</b>	0.499	-0.437	-0.009	0.097	-0.629	0.687	0.305	-0.466	-0.644	-0.598	-	-	-
<b>Zn</b>	0.213	-0.435	-0.421	-0.832	-0.035	-0.963*	-0.345	0.072	0.973*	-	-	-	-
<b>Cr</b>	0.018	-0.406	-0.569	-0.823	0.157	-0.998**	-0.141	0.269	-	-	-	-	-
<b>Pb</b>	-0.894	0.232	-0.575	0.000	0.920	-0.337	0.697	-	-	-	-	-	-
<b>Cd</b>	-0.522	-0.174	-0.683	0.000	0.456	0.135	-	-	-	-	-	-	-
<b>Cu</b>	0.038	0.352	0.556	0.788	-0.213	-	-	-	-	-	-	-	-
<b>Fe</b>	-0.984*	0.585	-0.217	0.293	-	-	-	-	-	-	-	-	-
<b>TOC</b>	-0.426	0.853	0.717	-	-	-	-	-	-	-	-	-	-
<b>TN</b>	0.153	0.663	-	-	-	-	-	-	-	-	-	-	-
<b>TP</b>	-0.636	-	-	-	-	-	-	-	-	-	-	-	-
<b>OM</b>	-	-	-	-	-	-	-	-	-	-	-	-	-

\*Correlation is statistically significant according to 0.05 level (two way). \*\*Correlation is statistically significant according to 0.01 level (two way).

**Table 7.** Comparison between metal concentrations (in  $\mu\text{g}\cdot\text{g}^{-1}$  DW) determined in sediments from studied stations and the TEL, PEL and Target-Limit values of some SQGs [9].

Heavy metal Content	Stations	As	Cd	Cr	Cu	Pb	Ni	Zn
<b>Trabzon Harbour</b>	I	2.8 - 3.5	0.07 - 0.16	9.2 - 16.2	5.8 - 7.1	4.7 - 7.2	9.3 - 20.1	4.6 - 5.4
	II	2.7 - 6.2	0.11 - 0.23	12.8 - 20.1	10.5 - 14.8	6.4 - 55.1	11.4 - 54.2	20.3 - 30.0
	III	3.5 - 6.3	0.14 - 0.23	9.4 - 28.6	11.5 - 14.4	5.7 - 14.3	13.5 - 47.4	27.1 - 54.3
<b>SQGs</b>		<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Pb</b>	<b>Ni</b>	<b>Zn</b>
<b>Canadian</b>								
TEL		7.2	0.7	52.3	18.7	30.2	15.9	124
PEL		41.6	4.2	160	108	112	-	271
<b>Wisconsin</b>								
TEL		9.8	0.99	43	32	36	23	120
PEL		33	5.0	110	150	130	49	460
<b>Flemish</b>								
Target value		20	2.5	60	20	70	70	160
Limit value		100	7	220	100	350	280	500

**Table 8.** Comparison between metal concentrations (in  $\mu\text{g}\cdot\text{g}^{-1}$  DW) determined in sediments from studied stations and the TEL and PEL-SQGs, Average Continental Crust, Average Shale and SQGs (Low-High).

Heavy metal Content	Stations	As	Cd	Cr	Cu	Pb	Ni	Zn
<b>Trabzon Harbour</b>	I	2.8 - 3.5	0.07 - 0.16	9.2 - 16.2	5.8 - 7.1	4.7 - 7.2	9.3 - 20.1	4.6 - 5.4
	II	2.7 - 6.2	0.11 - 0.23	12.8 - 20.1	10.5 - 14.8	6.4 - 55.1	11.4 - 54.2	20.3 - 30.0
	III	3.5 - 6.3	0.14 - 0.23	9.4 - 28.6	11.5 - 14.4	5.7 - 14.3	13.5 - 47.4	27.1 - 54.3
<b>SQGs</b>		<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Pb</b>	<b>Ni</b>	<b>Zn</b>
TEL <sup>1</sup>		7.24	0.68	52.3	18.7	30.2	15.9	124
PEL <sup>1</sup>		41.6	4.21	160.0	108.0	112.0	42.8	271.0
<b>Average Continental Crust<sup>2</sup></b>		-	0.1	35	25	20	-	71
<b>Average Shale<sup>3</sup></b>		-	0.8	90	45	20	68	95
<b>SQGs (Low-High)<sup>4</sup></b>		20 - 70	1.5 - 10	80 - 370	65 - 270	50 - 220	21 - 52	200 - 400

<sup>1</sup>TEL, threshold effect level, <sup>2</sup>PEL, probable effect level [12]; <sup>2</sup>Average Continental Crust; <sup>3</sup>Average Shale; <sup>4</sup>SQGs (Low-High) [24].

**Table 9.** Seasonal and spatial variations of EF and Igeo values in Trabzon Harbour.

Parameters	Stations	I		II		III	
	Months	EF	Igeo	EF	Igeo	EF	Igeo
Fe	April 2013	14.49	3.27	29.06	4.28	25.45	4.09
	July 2013	17.76	3.57	27.67	4.21	27.77	4.21
	October 2013	14.13	3.24	23.95	4.00	20.70	3.79
	January 2014	15.49	3.37	24.04	3.79	20.73	3.79
Cu	April 2013	0.16	-3.28	0.33	-2.21	0.36	-2.10
	July 2013	0.18	-3.08	0.26	-2.51	0.35	-2.10
	October 2013	0.15	-3.37	0.37	-2.03	0.29	-2.39
	January 2014	0.15	-3.31	0.37	-2.02	0.36	-2.08
Pb	April 2013	0.27	-2.46	0.38	-1.99	0.34	-2.16
	July 2013	0.39	-1.94	0.73	-1.05	0.84	-0.84
	October 2013	0.42	-1.82	0.60	-1.31	0.51	-1.56
	January 2014	0.32	-2.23	3.24	-1.11	0.70	-1.10
Zn	April 2013	0.07	-4.41	0.42	-1.83	0.84	-0.84
	July 2013	0.08	-4.31	0.31	-2.27	0.61	-1.31
	October 2013	0.08	-4.31	0.46	-1.70	0.42	-1.85
	January 2014	0.08	-4.18	0.45	-1.73	0.47	0.32
Mn	April 2013	0.042	-5.14	0.042	-5.15	0.47	-5.01
	July 2013	0.040	-5.22	0.041	-5.18	0.044	-5.10
	October 2013	0.031	-5.59	0.061	-4.62	0.044	-5.09
	January 2014	0.035	-5.43	0.060	-4.65	0.052	-4.86
Cr	April 2013	0.13	-3.59	0.18	-3.05	0.13	-3.56
	July 2013	0.16	-3.22	0.22	-2.79	0.39	-1.95
	October 2013	0.17	-3.16	0.17	-3.12	0.17	-3.14
	January 2014	0.22	-2.78	0.27	-2.47	0.23	-2.69

#### 4. Discussion

In marine ecosystems, sediments act not only as carriers but also as a sink for contaminants, and they reflect the history of pollution in aquatic systems. The accumulation of certain trace metals generally occurs in the surface portion of the sediment by means of biological-geochemical mechanisms and becomes toxic to living aquatic organisms. Along the coastline of the Black Sea, industry has been developing intensively and quickly. In other words, there are many plants (iron and steel), power stations and oil refineries. The waste-water from plants, atmospheric deposition, the metallurgical industry, the discharge of pollutants from shipping vehicles and transport, and especially mining waste, are possible anthropogenic sources of metals in the sediment. As there are only a limited number of studies [14] [15] [16] [17] on heavy metal concentrations in the sediment of the Black Sea coastline, this research conducted in Trabzon Harbour aims to reveal the anthropogenic effects of metals and the environmental risk associated with metal concentrations. The concentration of heavy metals in the surface sediment had the trend Fe > Pb > Zn > Ni > Mn > Cr > Cu > As > Cd.

The maximum concentration values for Fe, Cd, Pb and Ni in the sediment samples at the Trabzon Harbour stations were higher than the findings that reported by the researchers above. On the other hand, the sediment Cu, Cr, Zn, and Mn concentrations determined in this study were generally lower than the results of [14] [15] [25] [26]. Trabzon Harbour seems to be affected by the heavy atmospheric rains in the Eastern Black Sea Region, the mining facilities and the sediment's geological structure as well. The magmatic rocks of the northern part of Turkey, rich in mineral deposits, contribute significant amounts of Cr, Ni, Cu, Pb and Zn to this region's sediment.

In estuaries, where, in addition to natural inputs, concomitant activities such as harbour activities and industrial, agricultural and residential activities can cause heavy metal release from the sediment to the environment. In the Eastern Black Sea Region, residents and the industrial sector generally use coal or fuel oil for heating. It is well known that ash particles occur as a result of fossil fuel consumption, and this ash is a potential effective source for the atmospheric discharge of many metals. The higher concentrations of Zn, Cu, Mn, Ni, As and Pb, especially in the fall and winter, show that fossil fuel consumption plays a major role in metal composition management in this study.

Chlorophyll-a concentrations reached their maximum levels in the spring and fall periods [27]. The higher concentrations of Mn in the sediment in this study were found at the first and second stations in April and October, revealing that there was a relation between the water column and the sediment. This coincides with the association of the phytoplankton bloom in fall and spring with the maximum levels of manganese in the sediment.

Sediment metal concentrations were evaluated as Cd:  $0.58 \text{ mg}\cdot\text{kg}^{-1}$  and Zn:  $596 \text{ mg}\cdot\text{kg}^{-1}$  in Taiwan Kaohsiung Port between 2002 and 2005 [8]. The maximum concentrations of Cd and Zn were determined in October as  $0.23 \text{ mg}\cdot\text{kg}^{-1}$  at the second station and  $54 \text{ mg}\cdot\text{kg}^{-1}$  at the third station. The maximum Zn concentration in Trabzon Harbour was found to be lower, whereas the highest Cd concentration was close to the above researcher's findings. It is a well-known fact that Zn, a key and essential element for all living things, has a lower toxicity when compared to other metals. Therefore, Zn concentrations were not found to be high enough to pose a threat to the aquatic organisms in the Trabzon Harbour.

The distribution of some heavy metals (Cu, Zn, Cd, Pb, Fe, Ni, Cr and Mn) in the sediment of the coastline of southwestern Spain was investigated by [28]. The maximum concentrations of certain heavy metals there were (Zn:  $649 \text{ mg}\cdot\text{kg}^{-1}$ , Cu:  $336 \text{ mg}\cdot\text{kg}^{-1}$ , Pb:  $197 \text{ mg}\cdot\text{kg}^{-1}$ , and Cd:  $2.5 \text{ mg}\cdot\text{kg}^{-1}$ ), evaluated over a 35-km length along the coastline close to the region where the mouths of the Tinto and Odiel rivers combine. According to our study conducted in Trabzon Harbour, contrary to the sediment Ni concentration, Fe, Cr, Cu and Pb concentrations were found to be much lower than the researches indicated above. This could be a result of the lower number of industrial facilities near Trabzon Harbour. A positive correlation was assessed between Fe and Cd in Trabzon Har-

bour in April, October and January, and Zn and Cd in July and January. This positive correlation triggers the flux of Zn into the aquatic system moving with the effluents following the industrial production of Zn, Cu, Pb and Fe.

Organic matter in colloidal form plays an important role in the exchange capacity of sediment, whereas in the presence of iron, organic matter adsorbs greater amounts of phosphates, as these carry negative surface charges. A high sediment organic material content ensures a fractional humic material context; therefore, this can play a critical role in the phosphorus retention mechanism [29]. The sediment organic material concentration was detected as <20% spatially and seasonally at Trabzon Port, and the positive correlation between TP and TOC indicated phosphorus retention in the sediment.

In aquatic ecosystems, total organic carbon is an important factor in controlling the abundance of some heavy metals [30]. A positive correlation was established between TOC and TP and also between TOC and some heavy metals (Pb, Cu and Fe) in July at Trabzon Port. The positive correlation between the sediment total organic carbon and the heavy metals in Trabzon Port was compatible with [5] [30] [31], who stated that TOC is the key element in controlling the abundance of heavy metals in sediment.

The degree to which the heavy metal load from the sediment is toxic and harmful to the aquatic environment depends on the geochemical conditions of the sediment. Furthermore, the assessment of contamination status is based mainly on SQGs or quantitative indices such as the geo accumulation index (Igeo) and Enrichment Factor. According to the Canadian and Wisconsin SQGs, there are three ranges for TEL and PEL values as follows: There is no adverse biological effect if the concentrations of metals in the sediment are lower than the TEL values. When the values are between TEL and PEL values, this may occasionally be associated with an adverse biological effect. If the concentrations are higher than PEL values, there is an association with adverse biological effects [32].

According to Flemish SQGs for dredged materials [33]: 1) The dredged sediment may be dumped at sea when metal concentrations are lower than the target value. 2) Further investigation is needed when the concentrations are between the target and limit values. 3) Dumping the dredged sediment into the sea is forbidden if the concentrations are higher than the limit value. The comparison results of Trabzon Port and the Flemish SQGs are given in **Table 4**. Sediment heavy metal values of Trabzon Port are all lower than the target values, indicating that the dredged sediment may be dumped at sea [9].

TEL/PEL SQGs are applied to determine the degree to which the sediment-associated chemical status might adversely affect the aquatic organisms. The threshold effects level is intended to present chemical concentrations below which adverse biological effects rarely occur, and the probable effects level is intended to present chemical concentrations above which adverse biological effects frequently occur [12]. The heavy metal concentrations in this study were compared with the TEL and PEL values, and the results are presented in **Table 7** and

**Table 8** [9]. Among the investigated elements, Pb and Ni most often exceeded the TEL and PEL values, and so were expected to have occasional adverse biological effects. Therefore, the contamination ranking of the Pb and Ni loads in the sediment compared with regional background levels seems to be reliable, and this result is in agreement with [34]. The sediment Pb (second station) value exceeded the values with respect to the Average Continental Crust, Average Shale and SQGs (Low-High) [24], and Ni (second and third stations) values only exceeded the SQGs (Low-High) value.

Concentrations of eight heavy metals in the surface sediment of the western part of the Egyptian Mediterranean Coast were assessed to evaluate the concentration levels and spatial distributions with the Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) by [35]. There was not an adverse biological effect when sediment heavy metal concentrations were lower than the TEC, whereas there was a significant risk if the concentrations were greater than the PEC level. Sediment heavy metals (Cd, Cr, Pb, Cu and Zn) in Trabzon Port were in line with the findings of [35], who stated that there is no risk to aquatic organisms at these levels. However, Ni, the main source of minerals, reached its maximum value ( $54.2 \text{ mg}\cdot\text{kg}^{-1}$ ) at the second station in January. With the increase of heavy rain in this period, river discharge and erosion also increase, and this leads to increasing amounts of Ni in Trabzon Port. To assess the metal contamination in the surface sediment of Trabzon Port, the concentrations of the most toxic metals (As, Cd, Cr, Cu, Pb, Ni and Zn) were compared with USEPA data. According to the USEPA sediment guideline [10] [11], the maximum sediment As concentration ( $2.7 - 6.3 \text{ }\mu\text{g}\cdot\text{g}^{-1}$  DW) was considered moderately polluting (3 - 8), the Cr concentration (max value  $28.6 \text{ }\mu\text{g}\cdot\text{g}^{-1}$  DW) was evaluated as moderately polluting (25 - 75) and Pb ( $55 \text{ }\mu\text{g}\cdot\text{g}^{-1}$  DW) was also at the same pollution level (40 - 60). Ni (max  $54.2 \text{ }\mu\text{g}\cdot\text{g}^{-1}$  DW) was moderately polluting at the third station, but heavily polluting at the second station. The maximum Cu concentration ( $5.8 - 14.8 \text{ }\mu\text{g}\cdot\text{g}^{-1}$  DW) at  $<25$  was non-polluting, and Zn ( $4.6 - 54.3 \text{ }\mu\text{g}\cdot\text{g}^{-1}$  DW)  $<90$  values were non-polluting as well. Possible anthropogenic sources of metals in the sediment of Trabzon Port are likely the discharge of untreated waste, commonly industrial and municipal, sewage run-off and petroleum contamination in the port. Especially Ni, Cu, Pb, Zn and Cr have been found to be associated with petroleum contamination in coastal environments, as [5] indicated.

According to [13] [36], contamination levels may be classified in the following order:  $I_{geo} \leq 0$  = unpolluted,  $I_{geo} < 1$  = unpolluted to moderately polluted,  $I_{geo} < 2$  = moderately polluted,  $I_{geo} < 3$  = moderately to strongly polluted,  $I_{geo} < 4$  = strongly polluted,  $I_{geo} < 5$  = strongly to very strongly polluted,  $I_{geo} > 5$  = very strongly polluted. The results of the geoaccumulation index revealed that Trabzon Port,  $I_{geo}$  values for Cu, Pb, Cr, Zn and Mn were lower than zero, indicating that sediment pollution level remained at a very low degree. In contrast, the Fe concentrations of between 3 and 4 at the control station shows moderate to strong pollution however, at the second and third stations, pollution levels were

found to be strongly to very strongly polluted (between 4 and 5) in Trabzon Port.

According to [8],  $EF < 1$  indicates no enrichment,  $EF < 3$  is minor enrichment,  $EF = 3 - 5$  is moderate enrichment,  $EF = 5 - 10$  is moderately severe enrichment,  $EF = 10 - 25$  is severe enrichment,  $EF = 25 - 50$  is very severe enrichment, and  $EF > 50$  is extremely severe enrichment. The calculation of enrichment factors in Trabzon Port for the three stations showed that: EF values for Cu, Pb, Cr, Zn, Mn and Cr were  $< 1$ , showing low pollution levels, whereas EF values for Fe concentration at the three stations demonstrated a moderately severe enrichment pollution level at  $> 6$ .

## 5. Conclusion

Although there are a limited number of existing studies on the sediment of the Black Sea coastline, there has been no research revealing the anthropogenic effect of metals in Trabzon Port. This study investigated the magnitude and ecological relevance of anthropogenic heavy metal pollution in Trabzon Port by means of sediment quality assessment methods. Comparison with sediment quality guidelines revealed that Fe and Pb in the Port sediment are the two main threats causing adverse biological effects. In general, relatively higher ecotoxicological potentials were found at the port stations than at the control station. In conclusion, in addition to natural inputs, concomitant activities such as harbour activities within the port and nearby industrial, agricultural and mining activities can release heavy metals, which could soon pose a threat to the environment due to their accumulation in the sediment. The data from this study regarding metal levels should be used as a baseline reference for future metal pollution monitoring programs in Trabzon Port, which will be a useful tool for authorities in charge of sustainable management.

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