Accumulation of essential and toxic metals in sediment from the Marmara Sea along Tekirdağ coast: risk assessment for ecological health

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A B S T R A C T

In our study, sediment samples were collected from four different stations in the spring of 2018 to reveal the presence of essential and toxic metals in the Marmara Sea along the coast of Tekirdağ. Concentrations of essential and toxic metals in sediments of Cd, Ni, Cu, Pb, Cr, Mn, Hg, Fe, As and Zn were measured with an inductively coupled plasma optical emission spectroscopy device. The mean essential and toxic metal contents of sediment samples were determined as Fe (10,646.65 mg/kg) > Mn (265.03 mg/kg) > Ni (20.46 mg/kg) > Zn (18.63 mg/kg) > Cr (16.34 mg/kg) > As (11.94 mg/kg) > Pb (5.22 mg/kg) > Cu (3.8 mg/kg) > Cd (2.3 mg/kg). Hg could not be determined because it is in the below detection limits. The potential ecological risk index was calculated for all the metals, except for Hg, in four locations. In the sample SDM1 considerable risk for Cd was detected, moderate risk was found in SDM2 sample and low risk was detected in SDM3 and SDM4 samples. No other ecological risk was found for other metals. The reason for the very high ecological risk was calculated for cadmium might be that cadmium has high toxicity coefficient compared to other metals and due to the use of phosphorous fertilizer containing cadmium in agricultural activities and activities in the field of industry affecting natural water flows, erosion or discharges passing through the Marmara Sea along the coast of Tekirdağ province.

Keywords: Marmara Sea; Tekirdağ; Sediment; Essential and toxic metals; Ecologic risk assessment

1. Introduction

Toxic metals were continued to be in the worrying pollutant class in parallel with the industrial developments [1]. A variety of factors cause pollution with toxic metals especially pipeline construction, wastewater treatment and disposal, mining, industrial and agricultural activities [2]. These metals tend to accumulate in the sediment and move through the food chain. Toxic metals cause pollution in the sediment layer due to their toxicity, persistence and bioaccumulation and constitute significant risks in the marinal environment [3,4]. Studies proved that the ecological risks of toxic metals in sediment have reached serious levels to threat the health of the marine ecosystem [5–8].

Tekirdağ province, located in the Ergene basin, is one of the rare cities in Turkey with two separate seashores and a maximum length of the coast (135 km). Urbanization along the coast of Tekirdağ province continues to increase rapidly because it is a coastal city where industry is widespread. The coastal area of Tekirdağ province is strongly influenced by intense industrial and agricultural activities since 1960, heavy ship traffic to Asia-port the first transit container port
in Turkey which started to operate in 2015, and pollution resulting from atmospheric deposition. Many studies have been completed about toxic and essential metal pollution in sediment in the study area and these studies have revealed the state of toxic metals in the region [9–11]. But there is no ecological risk assessment for the existing toxic metal concentrations.

The main objectives of these studies were:

- Determine the distribution of essential and toxic (Zn, Cr, Cu, Ni, Mn, Pb, Cd, Hg, As and Fe) metals in sediments collected from the Tekirdağ area on the coast of the Marmara Sea
- Assess potential risks associated with toxic metal toxicity using EPA sediment quality guidelines (EPASQG) and potential ecological risk index (RI).
- Determine the differences between essential and toxic metals in sediment samples with Spearman sequence correlation coefficients

2. Materials and methods

2.1. Study area

In this study, sediment samples were collected from four different places along the Tekirdağ provincial coastline of the Marmara Sea in the spring of 2018. The first of these places was Şarköy which was awarded with the international blue flag. The rest of the three places were the center of Tekirdağ, Yenice town where one of the branches of the Ergene River enters the Marmara Sea and the town of Marmara Ereğlisi (Fig. 1).

Presently, there are 1081 industrial organizations in Tekirdağ province. Along the basin, the quality of the surface waters begins to decrease due to the increase in the textile facilities, leather, paper and chemical sectors and the intensive agricultural activities [12]. Contaminated surface waters, leakage discharges, floods or erosion exposes the Marmara Sea to all sort of negative effects, along in the shore of Tekirdag.

2.2. Sediment collection and preparation

In this study, the top 20 cm of the bottom sediment was collected using a grab sampler and protected in glass bottles (1 kg) (Table 1). Sediment samples collected from four different places were brought in the laboratory in ice boxes.

The sediment samples were air-dried for 3 d in the laboratory. Once air-drying was completed, sediment samples were powdered and passed through a 160 μm sieve. Before the analysis the samples were packed in polyethylene bags and stored below −4°C.

2.3. Analysis of essential and toxic metals

As in the first phase, all glass and polyethylene materials were kept in dilute nitric acid solution (1/9, v/v) for 48 h and they were rinsed with distilled de-ionized water prior to use. In order to prepare the reagents and standard solutions analytical grade HNO₃ and HCl (Merck, Darmstadt, Germany) were used. After sediment samples reached room temperature, they were dried at 105°C for 24 h until they reached stable weight. Samples of 0.5 g were taken from the dried sediment samples and disintegrated in a mixture of 3 ml HCl and 9 ml HNO₃ in a microwave oven (CEM, Inc. Mars 6, Matthews, NC, USA) (power:1800; ramp time:20 min; hold time: 18 min; temperature:190) [13].

The samples were filtered (Whatman No. 41, pore size 20–25 μm) and diluted with Milli-Q water to 25 mL. A blank digest was carried out in the same way. All the reagents used were of ultrapure grade (Merck Suprapur, Darmstadt, Germany). Water was deionized and further purified using a Milli-Q system (18 MW cm, Millipore, Milford, Ma., USA) and used to prepare all the reagents and standard solutions. Measurement of essential and toxic metal in sediment of Cd, Ni, Cu, Pb, Cr, Mn, Hg, Fe, As, and Zn was performed with an inductively coupled plasma optical emission spectrocope (SPECTRO brand Spectroblue model ICP-OES) [14,15]. The recoveries of the elements ranged from 95% to 104%. All elements of toxic metals were expressed in mg kg⁻¹ dry weight. Data were expressed as mean ± standard deviation, and each was performed in triplicate.

2.4. Assessment of sediment quality

Concentrations of Cd, Ni, Cu, Pb, Cr, Mn, Hg, Fe, As and Zn elements were compared with US EPASQG to assess the possible risks of metal pollution in sediment cooled to room temperature (Table 3).
To assess the characteristics and environmental behavior of toxic metal pollutants in coastal sediments, the potential ecological RI method was proposed to be used by Håkanson [16] from a sedimentological perspective. To assess the degree of toxic metal pollution in sediment, the potential ecological RI was defined according to the toxicity of metals and the response of the environment. RI is used to calculate the two equations below.

\[ RI = \sum E_r \]

\[ E_r = T_r C_f \]

\[ C_f = \frac{C_i}{C_o} \]

Toxic response factors for As, Cr, Pb, Cu, Cd and Zn were 10, 2, 5, 5, 30 and 1, respectively, according to Hakanson [16]. Potential ecological RI values in Table 2 are classified as potential toxicity [16].

In the evaluation of the metal contents of the marine bottom sediments, in cases that the anthropogenic inputs are not involved, the average shale metal concentrations are taken as the basis to represent the upper level of the earth’s crust. Therefore, in the evaluation of the sediment analysis results, the data obtained for each metal were compared with the shale average values. The reference values for As, Cr, Pb, Cu, Cd and Zn are 13, 90, 20, 45, 0.3 and 95 mg/kg, respectively [17].

### 2.6. Statistical analysis

The data were statistically analyzed using the statistical package, SPSS 16.0 (SPSS, USA). Spearman’s rho correlation analysis was performed to determine the interrelationships between essential and toxic metals in sediment.

### 3. Results and discussion

#### 3.1. Assessment of toxic metals in sediment samples

Metal concentrations can be high in coastal ecosystems of regions where industrial and agricultural activities are...
intensive. These metals sink to sea bottom and affect all the species of that place. In this study, essential and toxic metal concentrations were determined in sediment samples collected from 4 different places on the Marmara Sea coast of Tekirdağ province (Table 3). Toxic metal levels of sediments obtained from different sources such as sea, river and lake were indicated in Table 4.

The Fe concentration measured in sediment samples was measured 3783.9 mg/kg in Çorlu Yenice, and the maximum was measured as 19,789 mg/kg in Şarköy. According to some studies in the literature, Fe concentrations were 973.389 μg/g, 49,921 mg/kg, 12,587 mg/kg and 17.17 mg/kg in sediment samples obtained from the Hydro River in India [18], Iskenderun Bay [19], Atatürk Dam Lake [20], Çıldır Lake [21], respectively. In the study conducted in the Gediz River, Fe concentration was determined as 3,072 mg/kg [22]. The most abundant element in the earth’s crust is Fe, and the concentration of Fe can be high in sediments. Fe concentrations at the four different places in our study were moderately polluted according to sediment quality concentrations determined by the EPA.

Cu concentration was determined as 1.2–8 mg/kg in the sediment samples. As Yenice had the lowest amount of Cu, Şarköy sediment samples had the highest. In the literature, Cu concentrations were 37.053 mg/kg in Iskenderun Bay [19], 14.5–22.7 mg/kg in sediment samples taken from Atatürk Dam Lake [20] and 0.61 mg/kg in sediment samples taken from Çıldır Lake [21]. Cu amounts of eastern London and Port Elizabeth ports were found between 12.7–183.0 and 8.6–82.3 mg/g, respectively [25]. Cu concentrations measured in our study proved that based on sediment quality standards they were not contaminated.

Mn concentration was measured between 73.9 and 395.5 mg/kg in the sediment samples. In the literature, Mn concentrations were measured 1,304.5 mg/kg, 73.6–512.07 mg/kg, 331–552 μg/g, 16.34 mg/kg, 87.4–549.0 mg/g, 103.0–499.0 mg/g and 145 mg/kg in sediment samples collected from Iskenderun Bay [19], Atatürk Dam [20], Evokes Bay in the Aegean Sea [26], Çıldır Lake [21], East London [25], Port Elizabeth [25] and Gediz River [22], respectively. Our results were similar with sediment samples obtained from Atatürk Dam [20]. According to the sediment quality standards determined by the EPA, Tekirdağ Merkez, Şarköy and Marmara Ereğlı are classified to be partially polluted.

As shown in Table 3, Zn concentrations of sediment samples were determined 26.5, 23.4, 8.6 and 16 mg/kg in Şarköy, Tekirdağ, Yenice and Marmara Ereğli, respectively. In some studies, Zn amounts of sediment samples of Iskenderun Bay [19], Atatürk Dam [20] and Çıldır Lake [21] were 232.87, 59.4–60.79 and 82.31 mg/kg, respectively. Additionally, in the other study it was measured 26.1–332.0 mg/g (Ports of East London) and 18.8–126.0 mg/g (Port Elizabeth) [25]. In our study, Zn concentrations in four different places were not considered to be polluted according to the sediment quality standard determined by the EPA.

Whereas (total) concentration was measured the lowest in the Marmara Ereğli sediment samples (0.18 mg/kg), it was the highest in Şarköy samples (35.41 mg/kg). In the literature, the concentrations in sediment samples taken from the Mediterranean Sea around the shores of Turkish Republic of Northern Cyprus were 3.3–55.4 mg/kg [27]. In the Nigeria

<table>
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<tr>
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<tr>
<td>Fe</td>
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<td>Cu</td>
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<td>Mn</td>
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<td>Cr</td>
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<td>Ni</td>
<td>Ni</td>
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<td>Pb</td>
<td>Pb</td>
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Lagos lagoon sediment samples, it was 1.27–2.67 mg/kg [28]. In the other study, as the values of sediment samples taken from Nance lake in China were between 0.05 and 0.10 mg/kg [29]. Concentration measured in Şarköy is excessive based on sediment quality standards determined by the EPA.

Cd concentrations of the sediment samples were measured between 0.04 and 5.45 mg/kg. In the literature, Cd concentrations were measured 4.4725 and 1.6–3.6 mg/kg in sediment samples taken from Iskenderun Bay [19] and Nador lagoon (Mediterranean coast) [30], respectively. In our study, the Cd concentration in Tekirdağ exceeded the limit value of 2 mg/kg determined by the FAO, while the sediment samples taken from Şarköy highly exceeded this ratio. According to the EPASQG, the Şarköy is over-polluted in terms of Cd.

Cr values of samples were measured 0.12 mg/kg (minimum) in the Marmara Ereğlisi and 38.91 mg/kg (maximum) in Tekirdağ. In the literature, Cr concentration was determined as 1,419.8 mg/kg in sediment samples taken from Iskenderun Bay [19]. In this study, the Cr concentrations measured in Tekirdağ were found to be moderately polluted based on the EPASQG.

Ni amount of the sediment samples were 31.44, 23.42 and 7.49 mg/kg in Şarköy, Tekirdağ and Yenice, respectively. However, it was not determined in the sediment samples of Marmara Ereğlisi. In the literature, the concentration of Ni in sediment samples taken from Atatürk Dam was determined between 43.69–139.69 mg/kg [20]. These values were higher than the levels obtained in the current study. The Ni concentrations were found to be considered in the moderately contaminated class based on sediment quality standards determined by the EPA in Şarköy and Tekirdağ.

Pb concentrations of samples were found between 2.22 and 8.54 mg/kg. However, it was not determined in the Marmara Ereğlisi samples. Pb concentration of sediment sample taken from the Iskenderun Golf was 141.63 mg/kg [19]. In the other study, it was found 1.69 mg/kg in sediment samples obtained from Çıldır Lake [21]. The sediment samples obtained from Mersin port and Karaduvar fishing areas in Mersin Bay were determined to be overall mean 45.61 and 19.02 μg/g in Karaduvar region and Mersin Port, respectively [31]. In our study, Pb concentrations are not polluted according to EPASQG. Mercury concentrations were not determined because they are below the detection limits.

3.2. Statistical analysis

Spearman’s rho correlation analysis is one measure to discover the links between toxic metals in the study area. Correlation among the toxic metals can provide information about the sources and pathways of toxic metal pollution [32]. The Spearman sequence difference correlation coefficients, which show the relationship between concentrations of toxic metal and trace elements found in sediment samples, are shown in Table 5. The Spearman sequence differences were found with correlation method; Cu (R = 0.964; p < 0.01) and Zn (R = 0.952; p < 0.01) had significantly higher correlation in positive direction. There was a significant correlation between Mn (R = 0.786; p < 0.05), Cd (R = 0.795; p < 0.05) and Ni (R = 0.778; p < 0.05). In addition, there was a significant positive correlation between Cu and Zn (R = 0.988; p < 0.01), Mn (R = 0.795; p < 0.05), Cd (R = 0.768; p < 0.05) and Ni (R = 0.776; p < 0.05). It was found that there was a significant correlation between Mn and Zn (R = 0.786; p < 0.05). There was a significant positive correlation between Zn and Cd (R = 0.771; p < 0.05) and Ni (R = 0.778; p < 0.05). There was a significant correlation between Cd and Ni (R = 0.982; p < 0.01) and Cr and Pb (R = 0.922; p < 0.01), and Cd and Cr (R = 0.747; p < 0.05). There was a significant correlation between Cd and Pb (R = 0.788; p < 0.05), Cr and Ni (R = 0.755; p < 0.05) and Ni and Pb (R = 0.755; p < 0.05). However, no relationship was found between other toxic metal values.

The high correlation coefficients between toxic metals can indicate release from the same source of pollution, which is interdependent and has the same behavior [33]. The absence of any correlation between them indicates that pollution sources are not connected to a factor [34,35]. In this study, there were relatively strong positive correlations between Cd, Pb, Cr, Ni, Mn, Cu and Zn, but As and Fe did not show significant correlations with these metals (see Table 5). It can be said that Cd, Pb, Cr, Ni, Mn, Cu and Zn elements with high correlation are closely related to anthropogenic sources. The fact that Fe and As were not significantly correlated with other metals indicates that

<table>
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<td>0.952**</td>
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<td>0.795*</td>
<td>0.571</td>
<td>0.778*</td>
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<td>0.988**</td>
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<td>0.768*</td>
<td>0.602</td>
<td>0.776*</td>
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*Correlation is significant at the 0.05 level.

**Correlation is significant at the 0.01 level.
3.3. Assessment of ecological risk

The potential ecological RI has been proven to be a highly effective tool to assess the overall contamination of sediments in an aquatic ecosystem [36]. RI of toxic metals in all four sampling sites was calculated in Table 6. The order of potential ecological risk for essential and toxic metals were Cd > As > Pb > Cr > Cu > Zn. In this study, $E_i$ for all sampling sites was below 40, except Cd, suggesting that the sediments from Tekirdağ coastline pose a low risk. Cd was categorized to have quite high ecological risk criteria with $E_i$ value of 544.8 ($E_i \geq 320$). Cd has higher ecological RIs due to high toxicity response factors. Whilst other toxic metals had low ecological risk criteria (low risk), Cd may cause significant ecological effects in the sediment surface.

In terms of spatial distribution, regions with moderate or significant potential ecological RIs for Cd are Şarköy and Tekirdağ, respectively. These two regions demonstrated moderate and significant ecological risk rates. Potential ecological RIs for other metals (Pb, Cu, Cr, as and Zn) are found in all regions.

In our study, the potential ecological RI for toxic metal pollution levels in sediment on the shores of the Marmara Sea in Tekirdağ province confirmed the results of other studies [6,17,30,37]. Considerable RI values were calculated for cadmium are clearly associated with anthropogenic sources. The intensive agricultural activities in Thrace region and the high Cd content of phosphorous fertilizers used to increase agricultural productivity cause cadmium to reach the sea through stream waters, contaminated rivers and floods.

The absence of updated reference toxic metal and essential metal levels for a particular ecosystem or geographic area may lead to over-estimation or underestimation of the actual pollution burden in sediments and the Ecological RI [38]. Therefore, in order to estimate the ecological risks of toxic metals and essential metals correctly, monitoring studies and reference metal levels should be regularly updated, especially in areas with sensitive ecological habitats. The results will guide the risk assessment work to be completed.

### Table 6

<table>
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<th>Sample</th>
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<th>Pb</th>
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<td>90</td>
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<td>0.17</td>
<td>0.13</td>
<td>0.39</td>
<td>0.003</td>
<td>nd</td>
<td>0.883</td>
</tr>
</tbody>
</table>

Pollution sources were different or that they were connected to a geochemical source.

### 4. Conclusion

In our study, ecological risk assessment of toxic metal trace elements was carried out in sediment samples collected from four different points along the shores of the Marmara Sea in Tekirdağ province. Concentrations of Cd, Ni, Cu, Pb, Cr, Mn, Hg, Fe, As, and Zn were measured in sediment samples collected from four places. Cd and As concentrations determined in samples are highly polluted in accordance with the EPASQG. At the same time, when toxic metal and trace elements detected in sediment samples are evaluated according to the index of ecologic risk, cadmium poses considerable ecological risk. Our water resources and their ecosystems, which have important strategic value, are becoming increasingly unusable or some of them are completely lost each year. Toxic metal and trace elements accumulate in sediments due to human activities such as unplanned industrialization and urbanization, inadequate infrastructure, unconscious and uncontrolled chemical use in agriculture (phosphate fertilizers containing cadmium) and disposal of domestic waste waters or due to natural processes, and pose a risk for health of living organisms by significantly affecting water quality.

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### Disclosure statement

No potential conflict of interest was reported by the authors.

### References

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