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Ecological risk assessment of surface sediments of Çardak Lagoon along a human disturbance gradient

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Abstract Lagoons are the hotspot ecosystems whose sustainability should be secured using the ecological assessment indicators. This study aimed to quantify the surface sediment metal distributions of Çardak Lagoon in the Marmara region of Turkey, to characterize their natural and anthropogenic sources and transport mechanisms and to assess their potential ecological risks. The surface sediment samples were collected from 11 stations using Van Veen grab, while for the background values to be determined, core sampling was used from two stations. The analyses of multiple elements, total organic carbon, carbonate, and chlorophyll degradation by-products were carried out to characterize sediments. Enrichment factor and the indices of potential ecological and toxic risks were applied to assess the ecological status of the surface sediments. The operation of the gold mine in the close vicinity was found to be responsible for the enrichment of Au and Hg in the lagoon sediments. Cd, Tl, Sb, and Sr were the other elements responsible for the enrichment. The potential risk levels of the lagoon varied between the low and significant levels. The riskiest elements were found to be Hg and Cd which in turn pointed to the mining and agricultural activities as the most dominant human disturbance. The toxic risk index of Çardak Lagoon was estimated to range from 5.21 to 11.00, with a low mean value of 7.98. The C:N ratio range of 8.52 to 134.93 (a mean of 29.07) indicated that the organic C source was mostly of the terrestrial origin, in particular, from the surrounding agricultural lands.

Keywords Modified potential ecological risk assessment · Enrichment factor · Toxic risk index · Gold mining · C: N ratio

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Introduction

Coastal wetlands are the ecotones between the marine and terrestrial ecosystems permanently or temporarily inundated with freshwater or saltwater with a water depth up to six meters below sea level (Botello et al. 2018; Maanan et al. 2015). The coastal wetlands are the biologically most productive ecosystems of the world and include mangroves, coral reefs, seagrass beds, and lagoons (Botello et al. 2018). The river-mouth deltas and the associated lagoons are the hotspots under the intensive human disturbances such as the excessive use of chemicals in agricultural areas, industrialization, urban sprawl, global climate change, and water pollution (Hu et al. 2018; Ustaoğlu et al. 2020; Zonta et al. 2019). These anthropogenic drivers cause adverse

environmental impacts on their morphology, water/sediment quality, water quantity, and ecosystem health which in turn call for the preventive and mitigative actions to secure their conservation and sustainable management such as continuous monitoring and ecosystem rehabilitation (Zonta et al. 2019).

The accumulation of pollutants including metals in the lagoon ecosystems poses a severe threat to the human and ecosystem health through the food chain (Maanan et al. 2015). The sources of metals accumulated in lagoon sediments vary in that municipal and industrial waste streams are considered the anthropogenic sources, while the weathering and erosion of rocks are regarded as the natural sources (Ochieng et al. 2007). Both point sources (e.g., fossil fuel burning and wastewater discharges of plants) and non-point sources (e.g., runoffs, erosions and acid depositions) also contribute to this process (Rippey et al. 2008; Hu et al. 2011; Nriagu and Pacyna 1988). Therefore, the main target of the studies about the pollution of the aquatic sediments is not only to determine the levels of metals but also to distinguish between the human-induced versus natural sources of sediment metal accumulation and their ecological risks. In so doing, various approaches have been devised such as geoaccumulation index, enrichment factor, sediment quality guidelines, potential ecological risk index, and pollution load index (Bing et al. 2013). The enrichment factor and geoaccumulation indices compare the background and current values to determine the presence of anthropogenic effect, while the sediment quality guidelines and potential ecological risk index detect the level of possible environmental impacts (Kükrer 2017). In recent years, toxic risk index has been developed, based on threshold values obtained from ecotoxicological experiments (Zhang et al. 2016).

Suspended particles play a key role in the metal dynamics since the metals can be easily adsorbed onto fine particles and accumulate in the sediment (Strady et al. 2017). The metals that have reached the aquatic sediments are considered the conservative pollutants and damage the ecosystems under certain conditions (Yi et al. 2011). For example, the metals stored in the sediments are released to the water matrix depending on changes in dissolved oxygen and organic-inorganic carbon concentrations, pH, and oxidation/reduction conditions (Çevik et al. 2009; Wang et al. 2012).

The majority of the metals poses a risk to organisms, while some in certain quantities are required for the living. For example, Cu and Zn in the natural water bodies and sediments are the micronutrients required by the aquatic biota; however, their high concentrations exhibit toxicity (Bai et al. 2011). Hence, the ecological state and risk assessments mentioned above are required to signal the present and future health threats and to devise the preventive and mitigative measures. Therefore, the objectives of this study were to (1) quantify the surface sediment metal distributions of Çardak Lagoon in the Marmara region of Turkey, a rare ecosystem, along a human disturbance gradient; (2) characterize their natural and anthropogenic sources and transport mechanisms; and (3) assess their potential ecological risks.

Materials and methods

A total of 11 monitoring stations was used consisting of ten inner-lagoon and one outer-lagoon ones (Fig. 1). A randomized experimental design was adopted in this study in order to ensure both the avoidance of bias (systematic error) in the selection of sampling sites and the spatiotemporal representativeness of the random samples taken along the human disturbance gradient from more pristine sites to more polluted sites. Also, the reference (natural background) samples were gathered for each metal analyzed in order to detect the effect of human disturbances. Our hypotheses about the sources and fates of the metals along the human disturbance gradient were tested using PCA, *K*-means cluster, and Spearman's correlation ($n = 275$).

Form each station, the surface sediments were sampled with the help of Van Veen grab. For the background values to be determined, core sampling was used from stations 1 and 8 (S1 and S8). To determine the background values, the metal concentrations of each level of the core sampling were divided by the reference metal concentration in order to normalize the fraction-induced errors. The concentration of a given metal at the minimum ratio of metal to reference values was determined as the background value of the metal. The reference element in the core sampling was selected as Ti from among the potential reference elements (e.g., Fe and Al) by virtue of its minimum coefficient of variation.

Analysis of chlorophyll degradation by-products (CDP) in the wet sediments of the surface samples was conducted using the acetone extraction method (Lorenzen 1971). The remaining samples were dried at 60 °C and beaten. Total organic carbon (TOC) analysis

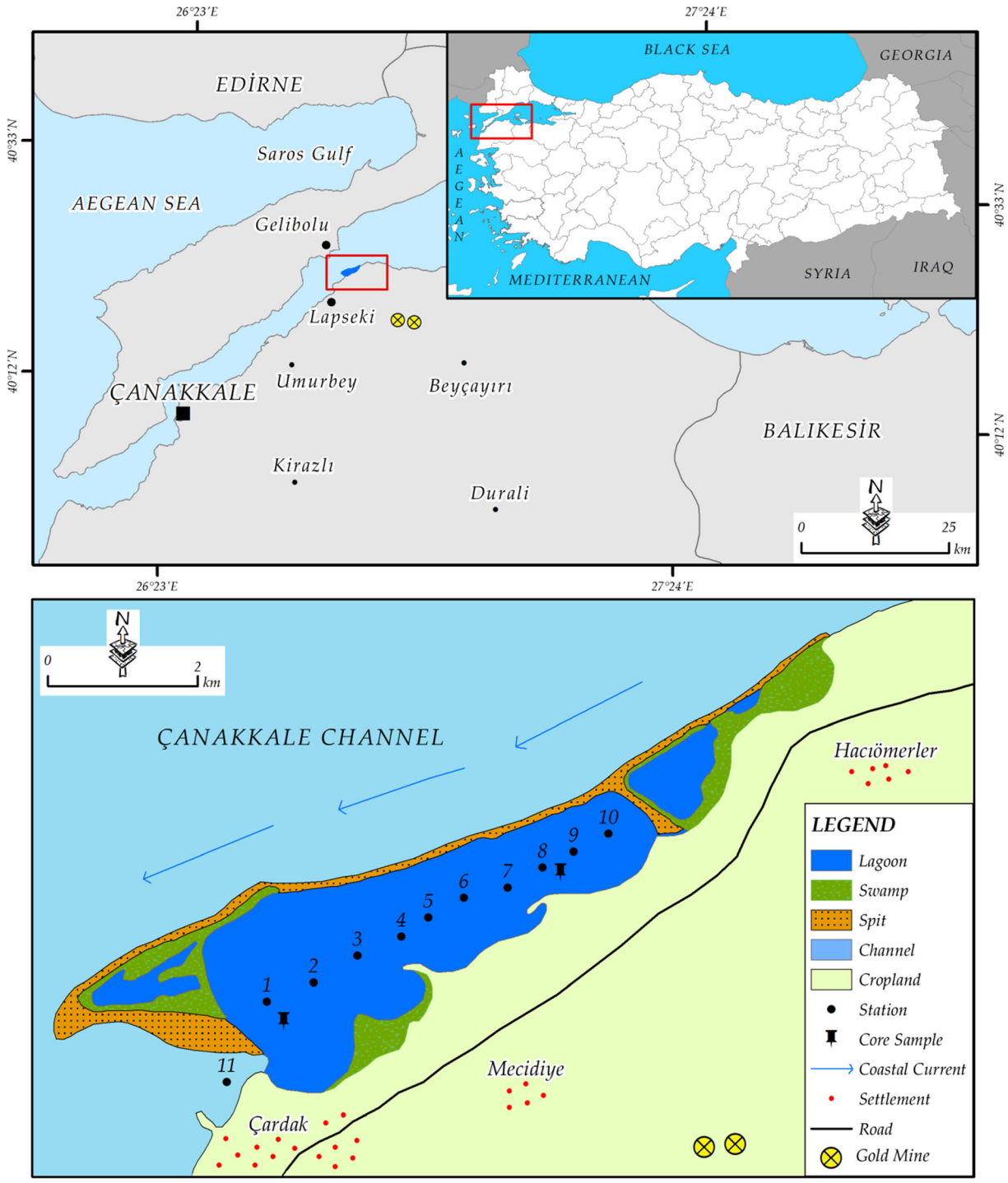


Fig. 1 Location of 11 sampling stations at Çardak Lagoon

was performed using the Walkley-Black method (Gaudette et al. 1974). The samples were dispatched to the Bureau Veritas Laboratory (Canada) for multiple element analysis by an inductively coupled plasma mass spectrometry (ICP-MS). The standard reference measurements for the quality control/assurance procedure were made using the blind sample and duplicate readings. The recoveries of the elements in the standard

reference material (STD DS 11) measured varied between 91.22 and 114.86%.

The enrichment factor (EF) was estimated to distinguish between the anthropogenic versus natural sources of the sediment metal accumulation by dividing the observed metal/reference element ratio by the background metal/reference element ratio (Acevedo-Figueroa et al. 2006; Çevik et al. 2009; Vrhovnik et al. 2013; Yilgor et al. 2012). In this study, the reference element was adopted as Ti since it had the lowest coefficient of variation among Fe, Al, and Ti. According to Sutherland (2000), EF < 2 refers to minimal or no enrichment; EF = 2–5 to a moderate enrichment; EF = 5–20 to a significant enrichment; EF = 20–40 to a very high enrichment; and EF > 40 to an extremely high enrichment.

In the ecological risk assessment, a modified risk index (MRI) was computed separately for each metal (Eq. 1). For a total/integrated assessment, a potential ecological risk index (PERI) was also computed (Eq. 2) (Brady et al. 2015; Hakanson 1980; Zhang et al. 2017):

$$\mathrm{MRI} = \mathrm{EF} \times \mathrm{Tr}^{\mathrm{i}} \tag{1}$$

$$\mathrm{PERI} = \sum \mathrm{MRI} \tag{2}$$

where Tr^{i} is the toxicity release coefficient of metals and assumed thus: Hg = 40, Cd = 30, As = 10, Cu = Pb = Ni = 5, Cr = 2, Zn = 1, Mn = 1, Co = 5, Tl = 10, and V = 2 (Hakanson 1980; Li et al. 2018; Rodríguez-Espinosa et al. 2018). The MRI and PERI values were scaled as follows: MRI < 40 refers to a low potential ecological risk; 40 ≤ MRI < 80 to a moderate potential ecological risk; 80 ≤ MRI < 160 to a significant potential ecological risk; 160 ≤ MRI < 320 to a high potential ecological risk; MRI ≥ 320 to an extremely high potential ecological risk; PERI < 150 to a low potential ecological risk; 150 ≤ PERI <300 to a moderate potential ecological risk; 300 ≤ PERI < 600 to a significant potential ecological risk; and PERI ≥ 600 to an extremely high potential ecological risk.

To determine the toxicity risks of each metal, toxic risk index (TRI_i) was used as follows (Zhang et al. 2016):

$$\mathrm{TRI}_i = \sqrt{\frac{\left((C_i/\mathrm{TEL})^2 + (C_i/\mathrm{PEL})^2\right)}{2}} \tag{3}$$

where C_i is the observed metal concentration, TEL is the threshold effect level, and PEL is the probable effect level *i* (Macdonald et al. 1997). The sum of the individual TRI_i values for the metals yields the integrated TRI thus:

$$\mathrm{TRI} = \sum_{i=1}^{n} \mathrm{TRI_i} \tag{4}$$

The TRI values were scaled for interpretation as follows: TRI ≤ 5: no toxic risk; 5 < TRI ≤ 10: a low toxic risk; 10 < TRI ≤ 15: a moderate toxic risk; 15 < TRI ≤ 20: a considerable toxic risk; and TRI > 20: a very high toxic risk.

The distribution of nitrogen (N) concentration in the sediments as a significant anthropogenic input to the ecosystems was measured using the Dumatherm method by the Application and Research Center for Science and Technology of Mehmet Akif Ersoy University. The sources of total organic carbon (TOC) were determined using the TOC/N ratio.

Results and discussion

Sediment characterization through distributions of metals, and organic carbon

The descriptive statistics are presented for the variables and background values measured in Table 1, while the spatial (station) distributions of the measured variables are illustrated in Fig. 2. The minimum values were observed at S3 for Cu, Pb, Co, Mn, Zn, Ni, Fe, Ag, Tl, Cd, Hg, Al, V, and Cr; at S4 for As and Au; at S11 for Sr; at S9 for Sb; and at S1 for Ti. The maximum values were observed at S1 for Cu, Pb, Zn, Ag, Cd, and V; at S2 for Co, Ni, Fe, As, Tl, Hg, Al, and Cr; at S3 for Sb; at S4 for Sr; at S8 for Au; at S9 for Mn; and at S11 for Ti. When compared to the background values of the core sediment samples of Çardak Lagoon, the mean values of the surface sediment metals measured were high.

To make a conclusion about their origin, the EF values were utilized. The strong correlations among the metals are indicative of the similar origins and transport mechanisms (Song et al. 2019; Suresh et al. 2011). In this study, only As did not exhibit any positive correlation with the other elements but a strong negative correlation with Sr. In other words, As significantly differed from the others in terms of its origin, transport mechanism, and deposition process (Table 2). The

Table 1 Descriptive statistics of 25 variables measured in Çardak Lagoon ($n = 275$)

	Cu (ppm)	Pb (ppm)	Zn (ppm)	Ag (ppb)	Ni (ppm)	Co (ppm)	Mn (ppm)	Fe (%)	As (ppm)	Au (ppb)	Sr (ppm)	Cd (ppm)	Sb (ppm)
Mean	32.9	18.6	65.3	75.5	57.9	12.0	327.3	2.5	18.6	9.7	202.6	0.2	0.7
Min	12.1	7.4	33.3	34.0	34.5	7.4	212.0	1.5	13.6	2.7	114.9	0.05	0.4
Max	54.8	27.2	92.2	116	74.3	15.4	401.0	3.3	29.2	48.3	315.0	0.32	1.2
SE	3.8	2.0	5.2	8.3	3.85	0.7	18.8	0.2	1.2	4.0	20.0	0.03	0.08
CV (%)	38.7	35.0	26.7	36.5	22.0	20.5	19.1	23.3	22.3	136.0	32.7	42.6	39.8
Background	29.0	13.3	35.9	55.0	50.5	9.8	260.0	2.0	8.5	1.9	51.1	0.1	0.2

	V (ppm)	Cr (ppm)	Al (%)	Ti (%)	Tl (ppm)	Hg (ppb)	TP (%)	TS (%)	TN (%)	TOC (%)	CDP (μg/g)	$CaCO_3$ (%)
Mean	43.6	55.6	1.6	0.015	0.5	46.4	0.05	1.3	0.3	4.4	134.8	4.3
Min	24.0	34.0	0.8	0.012	0.3	29.0	0.03	0.5	0.005	1.6	50.5	3.5
Max	55.0	70.0	2.1	0.025	0.7	70.0	0.06	1.9	0.6	8.9	280.5	5.03
SE	3.1	3.6	0.1	0.001	0.04	4.0	0.002	0.1	0.1	0.6	25.5	0.1
CV (%)	23.9	21.3	25.7	24.1	26.9	28.6	18.5	35.9	79.4	48.8	62.7	11.9
Background	34.0	45.8	1.3	0.01	0.2	16.0						

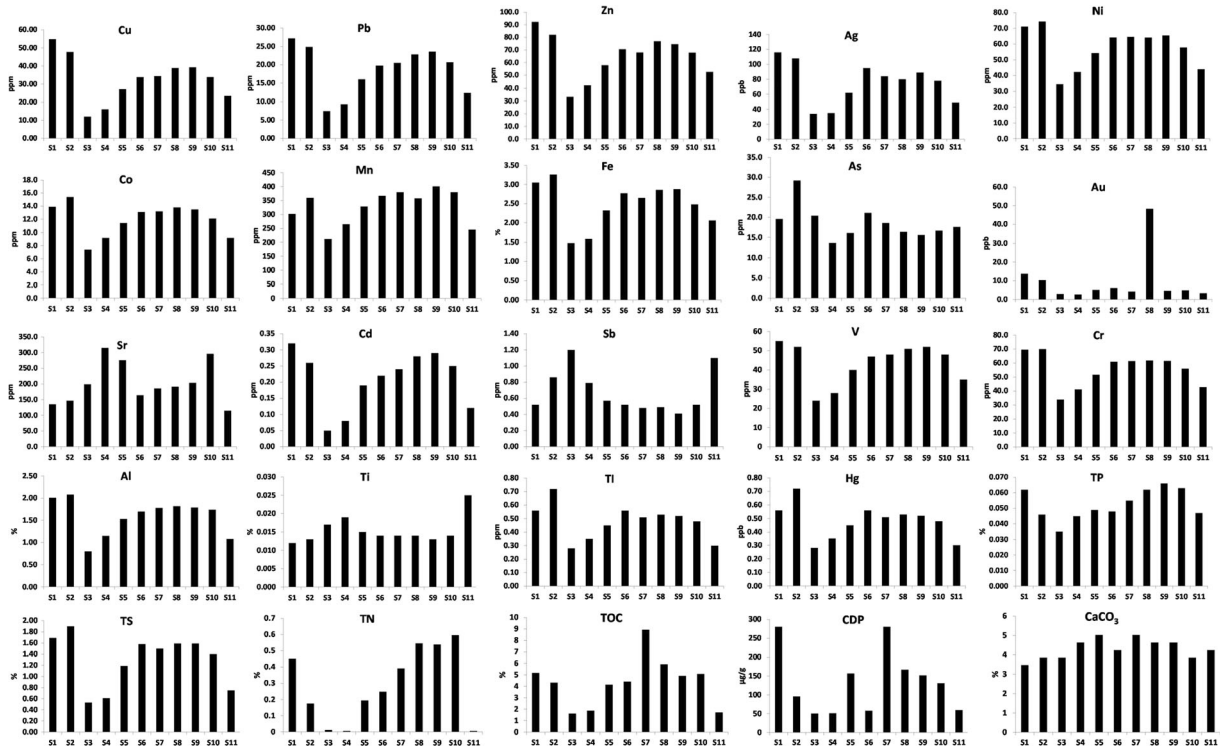


Fig. 2 Spatial distributions of 25 variables measured in the study region

strong correlation of TS with some metals (e.g., Cu, Pb, Zn, Ni, Fe, Ag, Fe, and Th) may be related to the formation of dissolved sulfite (Bai et al. 2016; G. Zhang et al. 2016). The Spearman's correlation matrix analysis showed significant relationships between most elements but appeared to pinpoint their transport and deposition processes rather than their origins when combined with their EF values. For example, the elements of the lithogenic origin such as Cu, Ni, and Co related to the elements of the anthropogenic origin such as Hg, Au, and Cd. This case appeared to result from the study area being a lagoon under the influence of both marine and terrestrial ecosystems.

The TOC content varied between 1.62 and 8.94%, with an average value of 4.38%. The minimum and maximum TOC values were observed at S3 and S7, respectively. TOC had a strong positive correlation with Cu, Pb, Zn, Ag, Ni, Co, Mn, Fe, Cd, V, Cr, Al, and Hg. This indicated that TOC played an important role in the transport process of these elements. Sb and Ti were inversely related to TOC.

$CaCO_3$ varied between 3.48 and 5.03%. Its minimum value was at S1, while the maximum value was at S5 and S7. $CaCO_3$ did not have any significant correlation with the elements, and thus, played no significant role as a carrier in the transport process. The CDP concentrations of the surface sediments were estimated to range from 50.49 to 280.50 μg/g, with a mean of 134.80 μg/g. S3, 4, 6, and 11 had a relatively low CDP value, while S1 and 7 had a CDP value of above 250 μg/g. CDP was positively correlated with Cu, Pb, Zn, Co, Cd, V, Cr, Al, Hg, P, TOC, and total N (TN). The CDP values are indicative of the net primary productivity and the role of plants in the transport of the metals in water to the sediments. The correlation of CDP with the metals signified the transport mechanism by which the metals absorbed into the plant cells ended up buried in the surface sediments through the dead plant residues.

The biogeochemical cycles of N and phosphorus (P) are the basic drivers of the (a)biotic components of the aquatic ecosystems that exert control over the biological productivity, and the water quality. TN was measured at S4 and 11 below the detection limit but peaked at S9. The minimum and maximum TP values were detected at S3 (0.05%) and at S9 (0.066%). The strong correlations among total P (TP), TN, TOC, and CDP pointed to the increase in the plant biomass, and thus, C sequestration depending on the N and P inputs.

Table 2 Spearman's correlation matrix of 25 variables measured for Çardak Lagoon ($n = 275$)

	Cu	Pb	Zn	Ag	Ni	Co	Mn	Fe	As	Au	Sr	Cd	Sb
Pb	*0.99*												
Zn	*0.96*	*0.95*											
Ag	*0.90*	*0.88*	*0.94*										
Ni	*0.95*	*0.92*	*0.93*	*0.96*									
Co	*0.97*	*0.95*	*0.98*	*0.91*	*0.94*								
Mn	0.56	0.56	0.49	0.56	*0.62*	0.53							
Fe	*0.96*	*0.95*	*0.98*	*0.95*	*0.96*	*0.98*	0.56						
As	0.20	0.18	0.29	0.43	0.35	0.27	−0.07	0.30					
Au	*0.75*	*0.76*	*0.85*	*0.74*	*0.66*	*0.80*	0.30	*0.79*	0.30				
Sr	−0.37	−0.33	−0.45	−0.50	−0.45	−0.39	0.17	−0.43	*−0.68*	−0.36			
Cd	*0.96*	*0.97*	*0.93*	*0.83*	*0.85*	*0.91*	0.59	*0.91*	0.04	*0.75*	−0.25		
Sb	−0.59	−0.56	−0.54	−0.51	0.54	−0.54	*−0.80*	−0.52	0.31	−0.37	−0.14	*−0.69*	
V	*1.00*	*1.00*	*0.95*	*0.89*	*0.93*	*0.95*	0.58	*0.95*	0.15	*0.74*	−0.33	*0.98*	−0.61
Cr	*0.97*	*0.95*	*0.98*	*0.91*	*0.95*	*1.00*	0.53	*0.98*	0.29	*0.81*	−0.44	*0.91*	−0.53
Al	*0.97*	*0.96*	*0.95*	*0.86*	*0.92*	*0.99*	0.55	*0.95*	0.20	*0.77*	−0.29	*0.92*	−0.55
Ti	*−0.94*	*−0.94*	*−0.91*	*−0.91*	*−0.92*	*−0.90*	−0.60	*−0.92*	−0.29	*−0.69*	0.25	*−0.91*	0.58
Tl	*0.86*	*0.85*	*0.94*	*0.95*	*0.91*	*0.93*	0.53	*0.94*	0.41	*0.82*	−0.40	*0.78*	−0.47
Hg	*0.95*	*0.93*	*0.88*	*0.85*	*0.92*	*0.91*	0.53	*0.88*	0.28	*0.67*	−0.40	*0.88*	−0.54
TP	*0.63*	*0.66*	0.55	0.47	0.49	0.51	*0.71*	0.52	−0.34	0.46	0.10	*0.78*	*−0.85*
TS	*0.96*	*0.95*	*0.99*	*0.94*	*0.95*	*0.99*	0.54	*1.00*	0.31	*0.82*	−0.44	*0.91*	−0.52
TOC	*0.73*	*0.70*	*0.69*	*0.63*	*0.65*	*0.71*	*0.68*	*0.63*	−0.02	0.57	−0.09	*0.76*	*−0.86*
CDP	*0.71*	*0.67*	*0.63*	0.54	0.59	*0.64*	0.44	0.56	−0.13	0.56	−0.19	*0.72*	*−0.69*
$CaCO_3$	−0.21	−0.28	−0.23	−0.26	−0.17	−0.16	0.26	−0.21	−0.60	−0.21	0.38	−0.19	−0.40
TN	*0.62*	*0.66*	0.58	0.48	0.48	0.55	*0.71*	0.53	−0.12	0.58	0.15	*0.76*	*−0.80*

	V	Cr	Al	Ti	Tl	Hg	TP	TS	TOC	CDP	$CaCO_3$
Pb											
Zn											
Ag											
Ni											
Co											
Mn											
Fe											
As											
Au											
Sr											

Table 2 (continued)

	V	Cr	Al	Ti	Tl	Hg	TP	TS	TOC	CDP	$CaCO_3$
Cd											
Sb											
V											
Cr	*0.95*										
Al	*0.96*	*0.98*									
Ti	*− 0.94*	*− 0.90*	*− 0.90*								
Tl	*0.84*	*0.92*	*0.89*	*− 0.86*							
Hg	*0.94*	*0.92*	*0.92*	*− 0.90*	*0.76*						
TP	*0.69*	0.51	0.54	− 0.60	0.38	0.58					
TS	*0.95*	*0.99*	*0.96*	*− 0.91*	*0.95*	*0.88*	0.51				
TOC	*0.73*	*0.70*	*0.73*	*− 0.67*	0.61	*0.74*	*0.76*	*0.64*			
CDP	*0.70*	*0.65*	*0.66*	− 0.58	0.44	*0.79*	*0.72*	0.58	*0.83*		
$CaCO_3$	− 0.22	− 0.17	− 0.17	0.31	− 0.22	− 0.16	0.12	− 0.21	0.15	0.25	
TN	*0.67*	0.55	0.60	*− 0.65*	0.47	0.58	*0.90*	0.54	*0.82*	*0.64*	− 0.03

The italicized values denote p value < 0.05

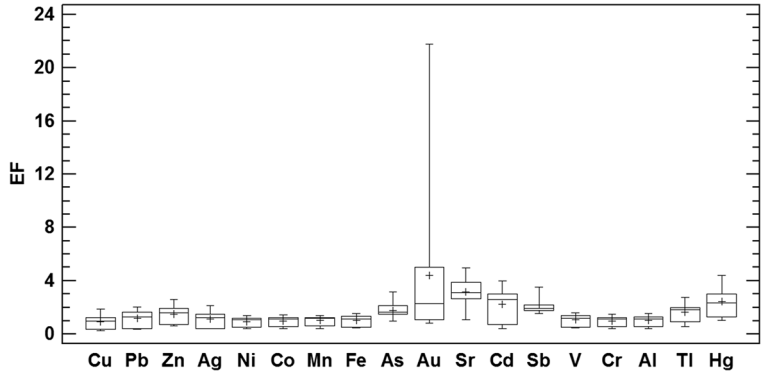


Fig. 3 Box and whisker diagrams of enrichment factor (EF) values

The C:N ratio has been commonly used to determine the origin of organic matter (OM) in the aquatic ecosystems (Faganeli et al. 1988). Despite its importance as an indicator, the isotopic C13/C12 ratio of the planktonic OM production varies too much to be used for the sediments of estuaries and lakes (Sampei and Matsumoto 2001). Naturally, with the increased sediment age, the C:N ratio is expected to rise due to the microbial decomposition of N-rich materials. The newly settled sediments have a plankton-based C:N ratio range of 6 to 8, while the more recalcitrant terrestrial materials have a higher C:N ratio (Gälman et al. 2008). The N concentration of the surface sediments of Çardak Lagoon was below the detection limit at S4 and S11. This was the reason for the exclusion of these two stations in the estimation of the C: N ratios. As a result, the C:N ratios varied between 8.52 and 134.93, with a mean of 29.07. This finding indicated that the C content of the study area was mostly of the terrestrial origin and received from the surrounding agricultural lands. The C:N ratios of S8, 9, and 10 were in the range of 8–10 which in turn showed that the autochthonous C production at these stations was more pronounced.

Assessment of metal accumulation via EF

The mean EF values estimated for the metals were of the following descending order: Au > Sr > Hg > Cd > Sb > As > Tl > Zn > Pb > Ag > V > Fe > Mn > Al > Co > Cr > Ti > Cu > Ni (Fig. 3). The EF values were in the range of 0.29–1.89 for Cu; 0.39–2.04 for Pb; 0.65–2.57 for Zn; 0.40–2.11 for Ag; 0.42–1.41 for Ni; 0.45–1.45 for Co; 0.45–1.42 for Mn; 0.50–1.55 for Fe; 0.99–3.17 for As; 0.86–21 for Au; 1.08–4.97 for Sr; 0.44–4.00 for Cd; 1.58–3.53 for Sb; 0.49–1.62 for V; 0.45–1.52 for Cr; 0.40–1.56 for Al; 0.60–2.77 for Tl; and 1.02–4.38 for Hg. Cu, Ni, Co, Mn, Fe, V, Cr, and Al were not enriched at any station and of the natural origin. Pb and Ag at S1, Zn at S1 and 2, As at S12 and 6, and Tl at S1, 2, 6 and 9 were enriched at a moderate level, while the other stations exhibited an enrichment at the minimal level. Ag is considered a modern pollutant due to its association mostly with the effluents of the treated sewage discharges (Hornberger et al. 1999) as well as with mining lands and smelters (Yoo et al. 2004).

Though rarely evaluated in the related literature, Tl is more toxic than Cu, Pb, Zn, Cd, and Hg in terms of public health (Peter and Viraraghavan 2005). The high EF value of Tl was most likely to stem from the fossil fuel burning (Liu et al. 2018). Au exhibited the minimal enrichment at S3, 4, 7, and 11 and the moderate enrichment at the other stations except for S1 and 8. S1 and 8 had the significant and extremely significant enrichments, respectively. Sr showed the moderate enrichment at all the stations except for S11. The enrichment and distribution patterns of Sr were reported to follow the main route of sea water into estuaries (Zhou et al. 2004). The source of the enriched Sr in Çardak Lagoon appeared to be the sea water.

Cd was enriched at the minimal level at S3, 4, 5, and 11 and at the moderate level at the other stations. Sb was enriched at the minimal level at S5 to 10 and at the moderate level at the other stations. Hg was enriched at the moderate level at all the stations except for S3, 4, and 11 with the minimal enrichment. The strong correlation between Au and Hg, and their high EF values indicated that these elements originated from the gold mines operating close to the lagoon (Pinedo-Hernández et al. 2015; Song et al. 2019). As, Cd, Hg, Pb, and Zn were reported to exist in fertilizers and pesticides (Cai et al.

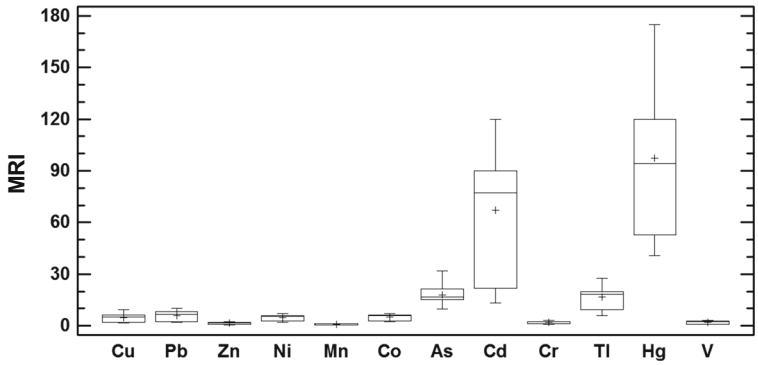


Fig. 4 Box and whisker diagrams of modified risk index (MRI) values

2015; Huang et al. 2007). For example, since Cd is abundant in phosphatic rocks, its concentration is high in phosphate fertilizers (Cai et al. 2015). The most probable origin of Sb was attributed to the atmosphere to which Sb appeared to be released from the fossil fuel burning and urban traffic (Shotyk et al. 2005). Given the EF value distribution of the atmospheric elements, all the metals except for Sb exhibited the minimal enrichment at S11 outside of the lagoon, that is, the maritime environment. In other words, the inner section of the lagoon served as the sink for the most elements.

MRI- and PERI-based ecological risk assessment

The mean MRI values for the potential risk estimation of the metals were of the following descending order: Hg > Cd > As > Tl > Pb > Co > Cu > Ni > V > Cr > Zn > Mn (Fig. 4). According to the risk scale, Hg was not found to be at a low-risk level in any station. Hg posed a moderate-risk level at S11, a high-risk level at S1, and a moderate-to-significant-risk level at the other stations. In terms of the ecological risk, another element that exceeded the threshold was Cd. The moderate-risk level

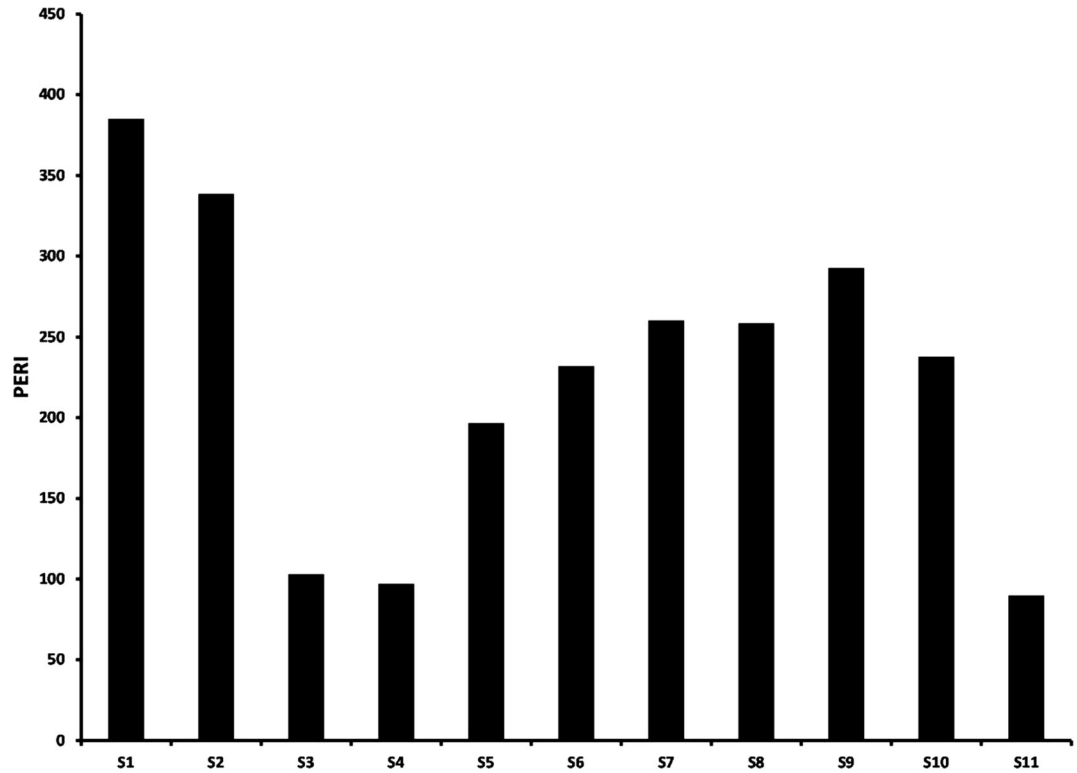


Fig. 5 Spatial distributions of potential ecological risk index (PERI) values

Table 3 Component weights from PCA

Element	Component 1	Component 2	Component 3
Cu	*0.23*	0.12	0.14
Pb	*0.24*	0.03	0.08
Zn	*0.23*	0.07	0.13
Ag	*0.23*	0.14	− 0.01
Ni	*0.23*	0.06	− 0.10
Co	*0.23*	0.04	− 0.13
Mn	0.19	− 0.19	*− 0.32*
Fe	*0.23*	0.10	− 0.02
As	0.08	*0.48*	− 0.28
Au	0.10	− 0.07	*0.40*
Sr	− 0.07	*− 0.38*	− 0.33
Cd	*0.23*	− 0.05	0.11
Sb	− 0.18	*0.33*	0.09
V	*0.24*	− 0.01	0.06
TP	0.18	− 0.28	*0.32*
Cr	*0.24*	0.06	− 0.05
Ti	− 0.19	0.06	*0.22*
Al	*0.24*	0.01	− 0.09
Tl	0.22	0.13	*− 0.27*
TS	*0.23*	0.06	− 0.11
Hg	*0.22*	0.15	0.06
TOC	0.18	*− 0.20*	− 0.09
CDP	0.16	− 0.17	*0.24*
$CaCO_3$	− 0.02	*− 0.38*	− 0.32
TN	0.19	*− 0.26*	0.20
Eigenvalues	17.50	3.16	1.23
Percent of variance	70.01	12.65	4.90

Italicized values denote the maximum loadings (characteristic elements) of each component

as the mean value rose to the significant level at S1, 2, 8, 9, and 10. The stations with the low-risk level for Cd were S3, 4, and 11.

The MRI values of all the other elements were low. The ecological risks were lower in the maritime environment than the lagoon. Based on the PERI values, S3, 4, and 11 had the low-risk level. S1 and 2 were under the significant risk level, while the rest of the stations was under the moderate-risk level (Fig. 5).

TRI-based ecotoxicological risk assessment

Unlike the EF-based MRI and PERI values, TRI was based on the thresholds derived from the ecotoxicological laboratory experiments of some biota groups living in sediments. The use of indices from different viewpoints provides a wider perspective to and diverse insights into the ecological risk assessment of the metals. The TRI estimates of Çardak lagoon sediments ranged from 5.21 to 11.00, with a mean of 7.98. The ecotoxic risk level of the lagoon sediments is low except for S2 with the moderate-risk level. The biggest contribution to TRI was made by Ni followed by As and Cu. The higher contributions of the elements with the low EF value to TRI appeared to result from the possibility of their concentrations exceeding the threshold of the toxic effect even if these elements were of the natural origin.

Assessment of probable origins of elements

Based on the PCA analysis, the three principal components (PCs) were determined with the eigenvalues > 1 and accounted for 87.56% of the total variation (Table 3). PC1 explained 70.01% of the variation and consisted of Cu, Pb, Zn, Ag, Ni, Co, Fe, Cd, V, Cr, Al, TS, Hg, and Au. PC2 elucidated 12.65 of the variation and consisted of positively charged As and Sb, and negatively charged Sr, TOC, $CaCO_3$, and TN. PC3 accounted for 4.90 of the variation and consisted of positively charged Au, TP, Ti, and CDP, and negatively charged Mn and Tl. PC1 was composed of the elements with the low EF values. Due to the presence of the lithophil elements such as Fe and Al, PC1 presented the weathering of the terrestrial rocks.

The presence of Cd and Hg in PC1 whose concentrations were elevated in the lagoon due to the anthropogenic effect pointed to the influence of another factor. Under the influence of both maritime and terrestrial ecosystems, the lagoon sediments may receive these elements from different sources but may immobilize them under the similar hydrogeochemical processes (Karthikeyan et al. 2018). In PC2, As and Sb appeared to possess the similar origins and transport processes. TOC, TN, and $CaCO_3$ were found to represent the terrestrial inputs. The C:N ratios of the sediments pointed to C as the terrestrial origin. TOC and TN appeared to arrive at the lagoon from the surrounding intensive agricultural activities. Au, TP, and Ti in PC3 had the transport process in common. The lithophil nature of Ti made it possible that Au and TP reached the lagoon by accompanying the terrestrial weathering materials. The probable source of Au with the high EF was the gold

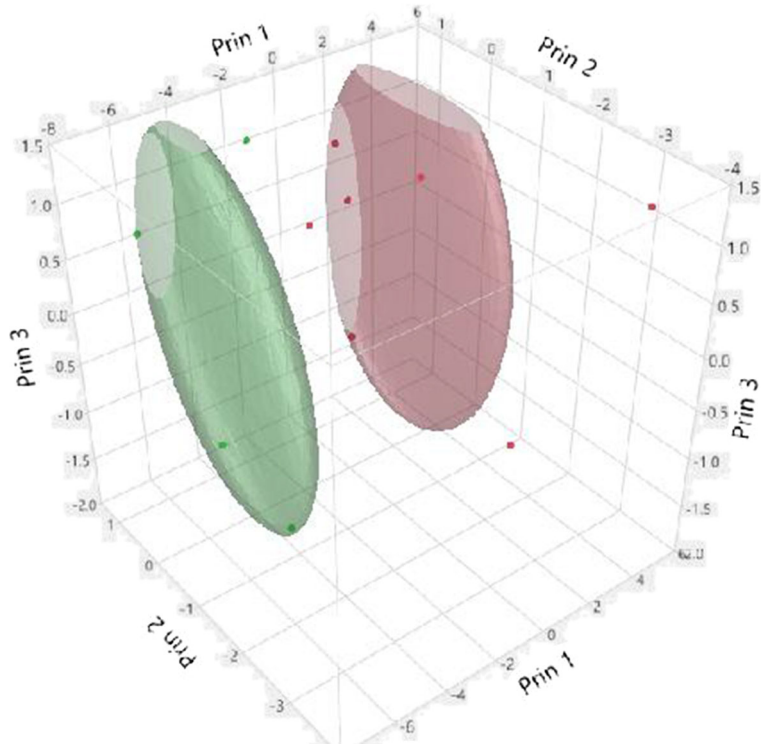


Fig. 6 *K*-means clustering results ($n = 7$ and 4 for clusters 1 and 2, respectively), and the two clusters (S1, 2, and 6 to 10 versus S3 to 5 and 11)

mine in the vicinity. TP seemed to come from the municipal wastes. Mn and Tl of the natural origin had a different transport process from the other elements.

The *K*-means cluster algorithm was used to aggregate observations with similar values of the 25 variables measured across the 11 stations in this study. This method uses an iterative algorithm called *k*-means that partitions the observations so as to minimize distances to cluster centroids. Our results showed that the best fit to the data occurred with the 2 clusters ($n = 7$ and 4 for clusters 1 and 2, respectively) as determined by the highest value of cubic clustering criterion (CCC) (−0.2759) (Fig. 6). The two clusters (S1, 2, and 6 to 10 versus S3 to 5 and 11) can be considered to represent the separation of the human-induced (the stations with the significant-to-moderate PERI values) versus natural (the stations with the low PERI values) disturbances of the lagoon-monitoring sites.

Conclusions

In this study, the metal concentrations of the surface sediments of Çardak Lagoon under the urbanization and industrialization pressures were monitored and pointed to its significant human-induced disturbance. The operation of the gold mine in the close vicinity was found to be responsible for the enrichment of Au and Hg in the lagoon sediments. The agricultural activities were the anthropogenic stress source in that phosphate fertilizers appeared to enrich Cd. The wet and dry depositions of particulate matters emitted to the atmosphere from the intensive urbanization and industrialization onto the lagoon may be the origin of Tl and Sb. The Sr enrichment of the lagoon sediments was related to the sea water. The TOC content was caused mostly by the terrestrial ecosystems. The potential risk level of the lagoon changed between the low and significant levels. The riskiest elements were found to be Hg and Cd which in turn pointed to the mining and agricultural activities as the most dominant human disturbance. The pollution control measures against the terrestrial and atmospheric inputs of the elements are the necessary condition to be met for the health and sustainable management of the lagoon. The challenges of sustaining the human and ecosystem health can be met through the rapid transition to the use of the cleaner and eco-friendly energy technologies, the continuous monitoring of industrial, agricultural and mining-related pollutants, and the widespread adoption of the best management practices in each sector.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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