RESEARCH ARTICLE

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An ecological risk investigation of marine sediment from the northern Mediterranean coasts (Aegean Sea) using multiple methods of pollution determination

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Abstract

The aim of this study is an assessment of metal pollution levels in Aegean Sea sediment. Sediment samples collected from 7 different locations (Yeniköy, Edremit, Ayvalık, Dikili, Aliağa, Hekimadası, and Ildır) along the northern Mediterranean region of Turkey were investigated for 11 elements (Cu, Fe, Zn, V, Cd, Ni, As, Pb, Mn, Co, and Cr). Graphite furnace atomic absorption spectrophotometry (GFAAS) and flame atomic absorption spectrophotometry (FAAS) were used for elemental analysis. The findings were evaluated with sediment assessment methods by taking two different values as a reference and then investigating the adverse biological effects of elemental profiles on living organisms. Pb, Mn, As, Cd, and Cr concentrations were within a moderate to significant range in terms of contamination factor (C_f^i), albeit varying according to reference and location. The most problematic region and elements regarding the enrichment factor (EF) was Ayvalık and As, Ni, Cu, Pb, Co, and Cd. However, according to the EF, the anthropogenic effect was not at an alarming level. This was further supported by the results of the geoaccumulation index (Igeo). The findings of the modified degree of contamination (mC_d) and the pollution load index (PLI) suggested that the accumulation was greatest in Ayvalık, and the least in Hekimadası and Ildır. The location with the highest elemental total toxic unit (ΣTU) was Edremit. The effect of the existing element profile on organisms was 21% in this location when the mean effect range–median quotient (m-ERM-q) was considered. As and Ni concentrations in all stations were found to be higher than threshold effect level (TEL) and Effect Range Low (ERL). Ni levels in Edremit exceeded the probable effect level (PEL) and Effect Range Median (ERM). Toxic unit (TU) values of these two elements in all stations ranged from 59.30 to 80.43%.

Keywords Sediment quality guidelines (SQGs) · Cluster analysis (CA) · Toxic metal · Risk factor · Contamination factor · Enrichment factor

Introduction

Urbanization and industrial activities introduce intensive amounts of pollutants, including heavy metals, into the marine ecosystems, and these pollutants directly affect the coastal zones (Xu et al. 2016). The heavy metal pollution resulting from intensive and rapid industrialization threatens the entire ecosystem and has now become a major environmental problem. Trace metals with high concentrations are a significant toxicological threat to fauna and flora in the environment (Hamzeh et al. 2013). They are very important from the environmental perspective due to their high ecological significance, toxic effects, long life, difficult removal from water, and accumulation in the sediment and in living organisms (Hanif et al. 2016, Manasreh et al. 2010). Although Fe, Cu, Zn, Co, Mn, Cr, Mo, V, Se, and Ni are essential for marine organisms, they can show toxic effects above certain threshold levels. In contrast, non-essential metals like Ag, Hg, Cd, and Pb are toxic for the organisms at even very low levels (Saher and Siddiqui 2016). Therefore, Pb, Zn, Cu, Cr, Cd, and some other metals originating from anthropogenic sources are accepted as potentially toxic metals in environmental risk

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assessments (Ma et al. 2016). The accumulation of essential metals occurs through their requirements for continuation of life, whereas those of non-essential metals take place as a result of incorporation into the metabolism via ionic mimicry. Bioavailability of metals is dependent on their partitioning traits and binding strength to the sediment, but the role of exposure to contaminated water or sediment, and the transfer chain of sediment–zoobenthos–carnivores–humans cannot be ruled out (Hamzeh et al. 2016). High metal concentrations in the sediment result in water quality deterioration by creating a resistant barrier against the natural development of aquatic fauna and flora (Yang et al. 2016).

Elemental analysis of the sediment is very important to understand the status of the ecosystem. The reasons are many, including non-instantaneous change in sediment accumulation, the reflection of both natural and anthropogenic accumulations, the comparability of changes between present and former periods, a natural accumulation media in the aquatic environment, and a living and feeding environment for many living organisms.

The sediment, as a potential reservoir, is partitioned from the surrounding water and accumulates higher levels of metals compared to the water in the long term. Metal(loid)s in the water are mostly deposited on the bottom as sediments after reactions with suspended particulate matter (Hwang et al. 2009). Indeed, Salomons and Stigliani (1995) reported that the percentage contaminants remaining in the aquatic environments do not even reach 1% and almost all settle down and are deposited in the sediment. Several complex processes including changes in hydrodynamic conditions, bioturbation and diagenetic factors—as well as physical and chemical conditions—have the potential in sediment to leach metal into the water, and this increases the importance of metals accumulated in the sediment (Alyazichi et al. 2015a, Meng et al. 2016, Zhao et al. 2013). In other words, this situation makes the sediment a second source of water pollutant.

When the background of elemental accumulation of sediment belonging to the Aegean Sea was investigated, it was seen that some research was carried out up to 1975. Smith and Cronan investigated the elemental composition of sediment in the southwestern part of the Aegean Sea in 1975 and found 35,300; 783; 137; 37; 77; and 93 mg/kg of Fe, Mn, Cr, Cu, Ni, and Zn, respectively (Smith and Cronan 1975). In the first study investigating the eastern part of the Aegean Sea, the elements Fe, Mn, Co, Cr, Cu, Ni, and Zn were found in quantities of 24,100; 925; 16; 92; 18; 143; and 39 mg/kg, respectively (Voutsinou Taliadouri and Satsmadjis, 1982). In this study, the first study to be conducted on the Turkish coast covering the area of this study, the elements Fe, Mn, Co, Cr, Cu, Ni, and Zn were found in quantities ranging from 5900 to 57,400; 103 to 2625; 2 to 41; 9 to 312; 3 to 77; 11 to 406; and 19 to 162 mg/kg, respectively (Ergin et al. 1993). Many studies have been carried out since then. These studies have been centered around İzmir,

where industrial activity is high. The results of the one of the first studies focusing on the Gulf of İzmir and its vicinity showed 14 to 500, 0.10 to 10, 2.60 to 478, 21 to 270, 178 to 568, and 2157 to 3771 mg/kg for Hg, Cd, Pb Cr, Cu, and Zn (Kucuksezgin et al. 2011). There have been many other research studies in the area of İzmir and the Gulf of İzmir (Esen et al. 2010; Kara et al. 2014; Pazi 2011; Uluturhan et al. 2011).

Many different methods have been used to investigate the makeup of the sediment. In this study, these methods looked at the following:

1. Understanding how many of the metals that accumulate in the sediment are anthropogenic
2. Understanding the toxic effect of metal deposited on the sediment to the environment
3. Understanding which metal is being accumulated the most
4. Understanding which metal poses the greatest threat to the environment
5. Understanding which locality shows the highest accumulations
6. Understanding in which locality metal accumulation is the biggest threat to the environment.

Within the scope of the study, selected methods were chosen to serve different purposes. Moreover, it was desirable to select them to help confirm each other and to increase the reliability of the results. For this purpose, methods can be grouped under two main headings.

1. Methods that revealed the anthropogenic pollution in the sediment were as follows: contamination factor (C_f^i), contamination degree (Cd), modified degree of contamination (mCd), enrichment factor (EF), geoaccumulation index ($Igeo$) and pollution load index (PLI).
2. Methods that investigated the effect of sediment pollution on the ecosystem: toxic unit (TU), total toxic unit ($\sum TU$), and mean effect range–median quotient (m-ERM-q). The toxic unit is used for comparing the toxic effect of the metals and the total toxic unit is used for comparing the toxic effect on the locations

   Methods that investigate anthropogenic pollution in the sediment can themselves be subdivided into two subheadings:

   a) Methods that identify the metals separately: (C_f^i), (EF), and (I_{geo}). These methods are used to identify which metal is accumulated the most in the locations.
   b) Methods that examine the common effect created by all the metals: (C_d), (mC_d), and (PLI). These methods have been used to compare general metal accumulations without relating the metal to a location.

In addition to these methods, the raw results are also compared with the threshold effect level (TEL), probable effect level (PEL), the effect range low (ERL), and the effect range median (ERM) limit values.

Because of the urbanization and industrialization on the northern Mediterranean Coasts of Turkey (the Aegean Sea), the environmental quality has been decreasing dramatically in recent decades. With this aim, there are two main objectives of this study:

1. determination of some metal concentrations in the surface sediment, and
2. understanding the human pressure on the studied area using multiple methods of pollution determination.

Materials and methods

Study area and sampling

The Aegean Sea is located at the north of the Mediterranean basin and has a border with Turkey and Greece. The Aegean Sea consists of about 7800 islands, mostly small islands, islets, and rocky pinnacles smaller than 1 km^2 (Simaiakis et al. 2017). Owing to rapid urbanization and industrialization, the sea is under the threat of heavy pollution and the threat level is increasing, especially near big industrialized cities like İzmir. This study region hosts both minimum and intensive urbanization and industrialization effects (Fig. 1). There are previous studies dealing with the anthropogenic impacts on the sediment metal accumulations on Greek and Turkish coasts; however, almost all of these have mostly focused on local regions (especially bays and gulfs) where the pollution is relatively intense. This study covers a larger area with a diverse environmental impact. The straight-line distance between the northernmost and southernmost sampling location is more than 170 km, while the coastal distance is more than 500 km. This distance is nearly half of the Turkish coast of the Aegean Sea, which includes three different provinces (Çanakkale, Aydın, and İzmir). The most important point that was considered for choosing the sampling locations was the assessment of the urbanization and industrialization effect on the sediment, along with some areas that have suffered minimal impact from urbanization and industrialization—with the aim of comparing urbanized and industrial areas with areas showing no adverse human influences. Sediment samples include both coastal sediment (Yeniköy, Edremit, Ayvalık, Dikili, and Aliağa) and island sediment (Hekimadası and Ildır).

At each selected location, sampling was replicated three times at 10, 15, and 20 m depths (1 sample at each depth, 3 samples total for each sampling location), during 2015. Surface sediment samples were collected by divers using self-contained underwater breathing apparatus (SCUBA) equipment. These samples were placed in polythene bags and were sent to the Environmental Engineering Department laboratory of Istanbul University on the same day for analysis.

Extraction, analysis, and quality control of metals

A modified version of the microwave digestion method of Hellar-Kihampa et al. (2014) was used in this study; the details of the procedure can be found in Tunca et al. (2016) and Aydın et al. (2017), which were also produced by the same project (acknowledged at the end) based on this research. The analyses were performed by atomic absorption spectrophotometry (GFAAS 600) and flame atomic absorption spectrophotometry (FAAS 400) in which IAEA SL-1 was used as the reference material with recovery ratios from 80 to 107%.

Pollution assessment methods

As reference values, the data from Ildır Station, and the reference and background content values of Turekian and Wedepohl (1961) were used.

Contamination status assessment

- Contamination factor (C_f^i)

C_f^i is the mean of the amount measured compared to the reference value.

$$C_f^i = C^i / C_n^i \tag{1}$$

C^i Concentration of metal in the sediment
C_n^i Pre-industrial reference value of the metal

The results were evaluated against four different scales: $C_f^i < 1$, $1 \leq C_f^i \leq 3$, $3 \leq C_f^i \leq 6$, and $C_f^i \geq 6$, which represent low, moderate, considerable, and very high contamination factors, respectively (Hakanson 1980).

- Degree of contamination (C_d)

C_d is the sum of all contaminants.
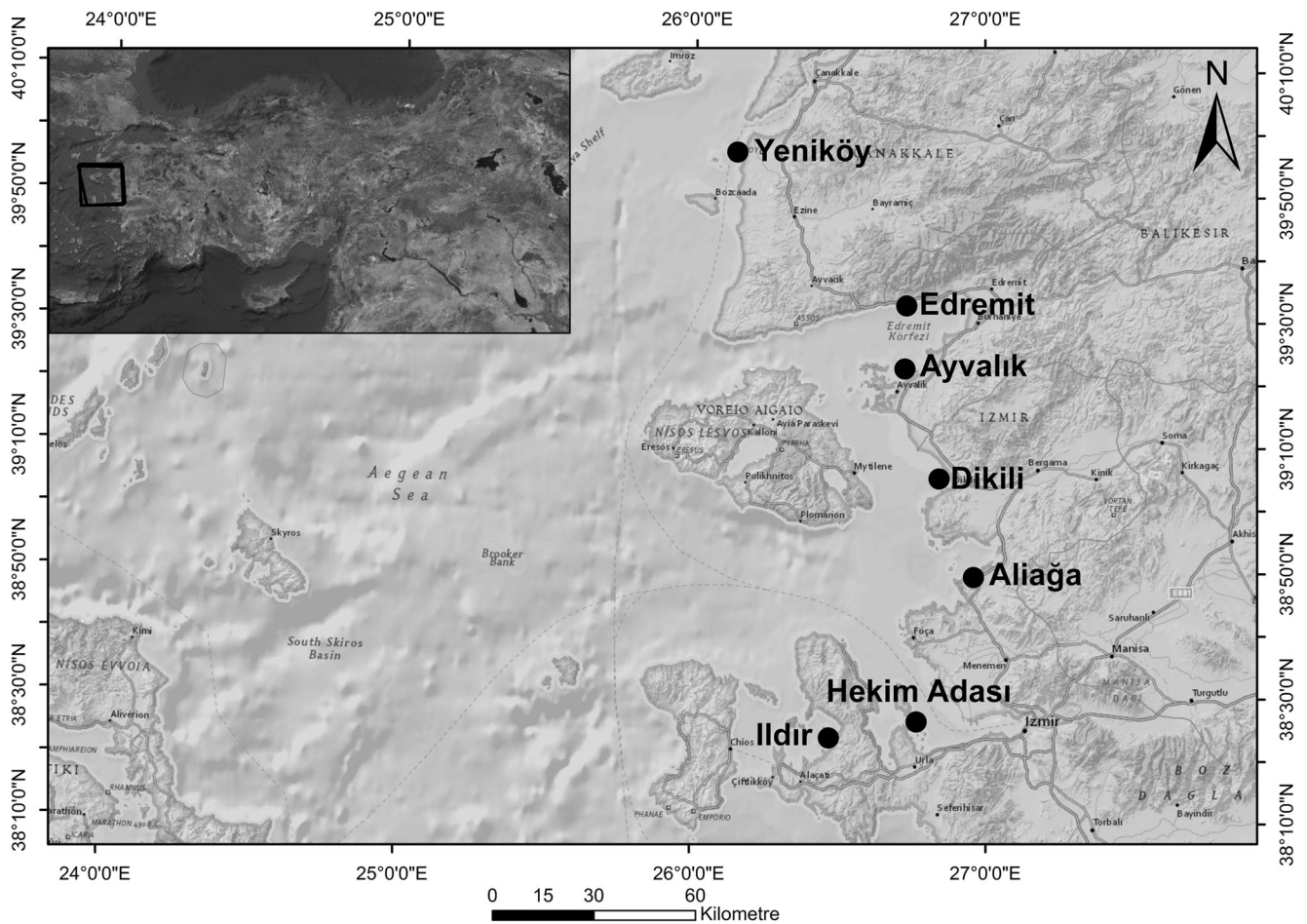
$$C_d = \sum_{i=1}^{n} C_f^i \tag{2}$$

Fig. 1 Sampling stations for this study

C_f^i contamination factor

The C_d ranges covers $C_d \leq 8$, $8 \leq C_d \leq 16$, $16 \leq C_d \leq 32$, and $C_d \geq 32$, which represent low, moderate, considerable, and very high degrees of contaminations, respectively (Hakanson 1980).

• Modified degree of contamination (mC_d)

mC_d is obtained by dividing the contamination factor by the number of studied metals.

$$mC_d = \frac{\sum_{i=1}^{n} C_f^i}{n} \quad (3)$$

C_f^i contamination factor
n number of metals studied

mC_d consists of seven contamination classes: $mC_d < 1.5$, $1.5 \leq mC_d < 2$, $2 \leq mC_d < 4$, $4 \leq mC_d < 8$, $8 \leq mC_d < 16$, $16 \leq mC_d < 32$, and $mC_d \geq 32$, which are nil to a very low degree of contamination, a low degree of contamination, a moderate

degree of contamination, a high degree of contamination, a very high degree of contamination, an extremely high degree of contamination, and an ultra-high degree of contamination, respectively (Abrahim and Parker 2008).

• Enrichment factor (*EF*)

EF is a classification that standardizes the elemental concentrations based on abundant metals like Al, Fe, and Mn, and thereby allows a comparison with the results of other studies. In this study, to normalize the results, we used Fe concentrations.

$$EF = \frac{C_n/C_{\text{ref}}}{B_n/B_{\text{ref}}} \quad (4)$$

C_n metal concentrations measured in the study
C_{ref} reference value of the metal studied (for instance, the Earth's crust)
B_n measured concentration of the reference element in the study (for instance, Fe or Al)
B_{ref} Concentration of the reference element in the reference environment.

There are different approaches to the evaluation of *EF* results. For instance, Zhang and Liu (2002) accepted the values between 0.5 and 1.5 as a natural formation, while above 1.5, it was accepted to be an anthropogenic impact. More detailed classifications than this approach also exist. Haris and Aris (2012) used five classes with < 2, 2 to 5, 5 to 20, 20 to 40, and > 40, which represent depletion to minimal enrichment, moderate enrichment, significant enrichment, very high enrichment, and extremely high enrichment, respectively. A 7-scale grouping (< 1, 1 to 3, 3 to 5, 5 to 10, 10 to 25, 25 to 50, and > 50) was suggested by Hasan et al. (2013), representing no enrichment, minor enrichment, moderate enrichment, moderately severe enrichment, severe enrichment, very severe enrichment, and extremely severe enrichment, respectively.

- Geoaccumulation index (I_{geo})

I_{geo} is a 7-scale classification proposed by Müller (1969).

$$I_{geo} = \log_2 \frac{C_n}{1.5 \times B_n} \tag{5}$$

C_n amount of metal measured in the sediment
B_n background content of metal studied
1.5   constant value for natural fluctuation

The scales are $Igeo \leq 0$, $0 < Igeo < 1$, $1 < Igeo < 2$, $2 < Igeo < 3$, $3 < Igeo < 4$, $4 < Igeo < 5$, and $Igeo \geq 5$, which represent practically uncontaminated, uncontaminated to moderately contaminated, moderately contaminated, moderately to strongly contaminated, strongly contaminated, strongly to extremely contaminated, and extremely contaminated, respectively (Müller 1969).

- Pollution load index (*PLI*)

PLI is the method proposed by Tomlinson et al. (1980).

$$PLI = \left(C_{f1} \times C_{f2} \times C_{f3} \dots \times C_{fn} \right)^{1/n} \tag{6}$$

C_{f1} contamination factor
n number of metals studied.

Two distinct scales are used to evaluate the results. In the first, if *PLI* is < 1, then there is no pollution, but if *PLI* is > 1, then deterioration has begun (Tomlinson et al. 1980). In the second, the index values and meanings are $PLI = 0$ is the background concentration, $0 < PLI < 1$ is unpolluted, $1 < PLI < 2$ is moderately polluted to unpolluted, $2 < PLI < 3$ is moderately polluted, $3 < PLI < 4$ is moderately to highly polluted, $4 < PLI < 5$ is highly polluted, and $5 < PLI$ is very highly polluted (Singh et al. 1999).

Ecological risk assessment

- Toxic unit (*TU*) and total toxic unit (ΣTU)

Toxic unit is related to the toxic effects of elements on living organisms while the total toxic unit looks at which location is the most polluted according to the elements studied.

$$TU = C_i / PEL_{Ci} \tag{7}$$

$$\Sigma TU = \sum_{i=1}^{n} C_i / PEL_i \tag{8}$$

C_i concentration of metal studied
PEL_i probable effect level (*PEL*) value of metal studied
n total number of metals studied

- Mean effect range–median quotient (*m-ERM-q*)

The *m-ERM-q* is a powerful method for understanding the toxic effects on living organisms of the elements in the studied environment.

$$m-ERM-Q = \frac{\sum_{i=1}^{n} C_i / ERM_i}{n} \tag{9}$$

C_i concentration of metal studied
ERM_i effect range median (*ERM*) value of metal studied
n total number of metals studied

According to the method, *m-ERM-q* < 0.1 is a 9% probability of being toxic, $0.11 < m\text{-}ERM\text{-}q < 0.5$ is a 21% probability of being toxic, $0.51 < m\text{-}ERM\text{-}q < 1.5$ is a 49% probability of being toxic, and *m-ERM-q* > 1.50 is a 76% probability of being toxic (Long et al. 2000).

Sediment quality guidelines

The threshold effect level (*TEL*), probable effect level (*PEL*), effect range low (*ERL*), and the effect range median (*ERM*) were used as sediment quality guidelines *(SQGs)*. The *ERL* indicates that below this level, an element or compound has a minimal adverse effect on organisms (< 10% of biota). *ERM* level refers to the concentration which is considered to be toxic and of significant concern. The concentrations which are higher than *ERM* can cause harm to 50% or more of the

population (Long and Morgan 1990; Abrahim et al. 2006). *TEL* and *PEL* represent the concentrations below which adverse effects are expected to occur rarely or frequently, respectively (MacDonald 1994, Rahman et al. 2014a).

Statistical analysis

Cluster analysis (CA) is a categorization method to separate a set of data into similar groups based on a combination of internal variables (Li et al. 2017). The purpose is to explore a system of organizing observations where a number of variables share observed properties (Zhu et al. 2016). CA is one of the most widely used multivariate analysis methods in environmental sediment studies (Chai et al. 2017; Wu et al. 2017; Zhang et al. 2017). In this study, cluster analysis was used to group the sampling localities based on elemental accumulations. The CA results classified the closely related locations within the same or in a similar cluster. The cluster analysis was set using the *Z* score transformation, Euclidean distance, and the Ward method (Tunca et al. 2016). All analyses were performed using SPSS 21.0 software (SPSS v 21.0, IBM, USA).

Results and discussion

Selection of reference values

Previous studies showed that the metal concentrations of the northern Mediterranean were lower than those generally accepted crustal average values determined by Turekian and Wedepohl (1961) or Taylor (1964), for example, by Esen et al. (2010) for the concentrations of Fe; by Uluturhan (2010) for the concentrations of Fe, Al, Hg, Cd, Mn, and Cu; by Demirak et al. (2012) for the concentrations of Cu, Fe, and Zn; by Pazi (2011) for the concentrations of Fe, Mn, Ni, Cu, Cr, and Al. In fact, some locations in this study create problems in terms of the evaluation of the sediment. In all methods of sediment evaluation, an amount of metal in the studied area is associated with a reference value. When the regional concentrations are lower than the crustal averages, then it becomes difficult to understand the existence of an anthropogenic impact. A closer look at the former studies in the region show that some considered the crustal averages as a reference (Balkis et al. 2010) and some formed their own reference values (Aloupi and Angelidis 2001; Pazi 2011). There are also studies that followed both approaches (Christophoridis et al. 2009; Kara et al. 2014; Karditsa et al. 2014). In this study, the least contaminated region was selected as a reference, and the crustal average value was taken as a second reference—as followed by Christophoridis et al. (2009). All findings are shown in Table 1.

We selected Ildır station as the reference because there is no residential or industrial area above the station, and this island is well away from human influences. A similar station is Hekimadası station, which suffers little anthropogenic impact. Indeed, the CA placed these two stations closely with the minimum Euclidean distance (Table 2 and Fig. 2). A closer look at Fig. 2 reveals that in addition to the cluster of Hekimadası and Ildır, there were two other conspicuous clusters: firstly, Dikili and Aliağa and secondly, between Edremit and Yeniköy. Ayvalık appeared to be closer to the cluster of Edremit and Yeniköy. The dendrogram is very consistent with the geographical locations in the study area. This also overlaps with the anthropogenic impacts and will be discussed in the "Geographical cluster" section.

Sediment quality guidelines

Table 1 provides the evaluations of sediment elemental concentrations based on some sediment quality guidelines (*SQG*s). Of these evaluations, the *ERL* and *ERM* were calculated based on toxicity experiments on organisms living in the sediment and the effects of various doses of toxic elements on the sediment (Long et al. 1995). The *ERL* represents the minimal threshold level for a toxic effect. According to this, below that level, the toxic effects are expected to occur in less than 10% of the population. On the other hand, the *ERM* is used for toxic effects on 50% or higher levels of the population, or for more serious contamination levels (Abrahim et al. 2006). Other limit criteria used to understand the toxic effects on living organisms are *TEL* and *PEL*. The toxic effects are expected to occur rarely or frequently at below or above the *TEL* and *PEL* values (Rahman et al. 2014a). In other words, values below the *ERL* and *TEL* represent occasional toxic occurrences in the population, whereas over the *ERM* and *PEL*, values represent more likely toxic occurrences (Bakan and Özkoç 2007). The present findings showed As and Ni were significant at all stations. The concentrations of As exceeded both *TEL* and *ERL* values at these stations, suggesting that even if limited, As had an effect on these areas and could affect 10 to 15% of the benthic population. Since the results were closer to the *ERL* values, the possibility of the population level being affected tended towards 10% rather than 50%. Conversely, the situation was more serious with Ni and its concentrations not only exceeded the threshold of *TEL* and *ERL* in all stations but also *PEL* and *ERL* in Edremit. Moreover, Yeniköy and Ayvalık stations were found to be close to the levels of *PEL* and *ERL*. The sediment organisms in the Edremit region were affected by Ni at a level above 50%, close to 50% in Yeniköy and Ayvalık, and higher than 10% in the other stations. However,

Table 1 Concentrations of the elements studied and compared with sediment quality guidelines (mg/kg)

	As	Pb	Cd	Cu	Zn	Ni	V	Co	Fe	Mn	Cr
Yeniköy	14.01±5.86	13.68±10.77	0.15±0.09	4.49±1.71	32.50±6.96	36.38±3.67	40.53±5.21	8.23±0.79	15,452±12,852	248.99±32.96	24.52±2.67
Edremit	35.50±7.92	9.36±2.15	0.23±0.14	5.05±3.00	43.04±29.27	56.09±36.54	35.04±11.42	7.34±4.34	20,819±10,524	202.13±119.29	29.10±19.87
Ayvalık	36.73±15.25	14.78±9.73	0.47±0.20	8.92±1.38	60.73±3.78	41.42±10.64	53.90±11.72	6.30±2.49	8725±14,429	178.44±67.45	23.24±10.07
Dikili	16.72±6.87	2.23±1.20	0.15±0.19	7.40±5.89	42.38±31.95	21.19±15.48	36.92±16.48	8.88±5.89	27,163±13,676	361.53±375.35	17.73±2.09
Aliağa	13.41±4.43	3.96±1.43	0.27±0.11	8.36±2.45	72.39±18.44	19.84±5.41	35.12±9.28	5.38±0.69	21,271±2999	120.49±17.71	15.11±2.10
Hekimadası	9.84±7.47	3.51±0.93	0.22±0.10	2.96±3.43	33.18±36.59	24.22±31.75	16.04±14.66	4.61±4.63	14,233±12,671	188.00±33.25	11.29±14.94
Ildır	10.85±5.50	3.90±0.83	0.14±0.08	5.66±3.35	29.42±19.29	17.49±10.92	21.74±7.65	2.71±1.71	11,767±5871	88.66±37.72	7.33±4.10
TEL[a]	7.24	30.2	0.68	18.7	124	15.9	–	–	–	–	52.3
PEL[b]	41.6	112	4.21	108	271	42.8	–	–	–	–	160
ERL[c]	8.2	46.7	1.2	34	150	20.9	–	–	–	–	81
ERM[d]	70	218	9.6	270	410	51.6	–	–	–	–	370

[a] Threshold effect level, [b] probable effect level, [c] effect range low, [d] effect range median

concentrations of the other elements studied did not pose a problem.

Contamination status assessment

Contamination factor and degree of contamination

The contamination factor (C_f^i) and degree of contamination (C_d) measures are frequently used in studies related to heavy metals in sediments and provide an evaluation of the existing status. The former allows an individual assessment of elements, while the latter gives a holistic evaluation of elements for all localities. The findings obtained in this study are presented in Fig. 3a, b. When Ildır was taken as a reference, the highest C_f^i values at the third level (considerable) were in Yeniköy for Pb and Cr; in Edremit for Ni, As, and Cr; in Ayvalık for Pb, As, Cd, and Cr; and in Dikili for Mn and Co. Such a high level of elemental contamination was not detected in Aliağa or Hekimadası. The C_d value revealed that all locations except Hekimadası registered at the third level of contamination (considerable) with the highest value in Ayvalık. Hekimadası was at the moderate level (second degree). When crustal average was considered as the reference, the highest C_f^i value was at the second degree (moderate). Element As was found at this level in all stations except Hekimadası and Ildır. In addition to As, Cd was also at this degree in Ayvalık. The highest accumulation occurred in Ayvalık at the moderate level, based on C_d. The other stations were at the cleanest class with a low degree of contamination. The results of a study conducted in 2005 in a nearby location, Gökova, by Balkis et al. (2010), showed that Pb, Cd, Cu, and Mn levels were similar to those of this study, whereas Fe concentrations were higher. A second study in 2006 found similar concentrations for Pb, Cd, Cu, Zn, and Mn, but higher concentrations of Cr, Ni, and Fe compared to this study. Higher concentrations from the inner parts of İzmir Bay compared to ours were reported by Özkan (2012). Compared with this investigation, similar levels of Cd, Pb, Cu, Mn, Zn, and Fe were reported, but higher concentrations of Cr and Ni were reported at Homa Lagoon, İzmir. The C_d findings of Uluturhan et al. (2011) were consistent with ours.

Enrichment factor

Although two different reference values were used in the study, the enrichment factor (EF) results were almost the same. This could be due to the normalizing element used in the calculation of EF (Fe in this case). The EF is used in element-based comparisons. The results of the study are shown in Fig. 4a, b. There are varying classes used in the assessment of EF results. Our findings displayed Ayvalık as the most affected region. In this location,

Table 2 The matrix of Euclidean distance for cluster analysis

	Euclidean distance						
	Hekimadası	Dikili	Aliağa	Ildır	Ayvalık	Edremit	Yeniköy
Hekimadası	.000						
Dikili	4.546	.000					
Aliağa	4.127	3.985	.000				
Ildır	2.223	5.330	4.013	.000			
Ayvalık	6.305	6.059	4.709	6.431	.000		
Edremit	4.782	4.365	4.683	5.633	4.201	.000	
Yeniköy	3.956	3.754	4.641	4.795	4.763	2.960	.000

almost all elemental values for the two references exceeded the threshold value of 1.5 suggested by Zhang and Liu (2002). This means that almost all of the samples were anthropogenic in origin. In Yeniköy, Pb was above the threshold. Hekimadası, Ildır, and Yeniköy appeared to be problematic in terms of As and Cd when crustal average concentrations were used as the reference. Another classification belongs to Haris and Aris (2012) who used a 5-level scale based on cleanness; in accordance with this classification, when Ildır was taken as the reference, in Ayvalık, Pb becomes prominent with a value of 5.12, and As and Cd had values of 15.29 and 8.40, respectively, based on crustal average. In Edremit, As took over with a value of 6.19 based on crustal average. Overall, these values were on the third level of the scale representing a "significant" presence. The 7-level

scale of Hasan et al. (2013) yielded a similar assessment. It can be concluded that there was an anthropogenic presence in some locations, but to a limited extent.

Omar et al. (2015) found the results to be between 1.3 and 0.3 for ten elements on the Moroccan coasts. This range was far below the values of Ayvalık, but slightly lower than those of other locations. On the other hand, the *EF* values obtained from the Cyprus Northern Shelf (eastern Mediterranean) were higher than those of this study (Kontaş et al. 2015). In their study, values of Ni, Cr, Cd, Pb, Cu, and Zn in almost all stations exceeded the limit value of 1.5 (even a value of about 30 was calculated for Ni in Girne) (Kontaş et al. 2015). The mean *EF* values for Cr, Cu, Mn, Ni, Pb, and Zn in Margarita Island, Spain, were recorded as 6, 3, 5, 3, 30, and 10, respectively, by Moukhchan et al. (2013), and were close to our results.
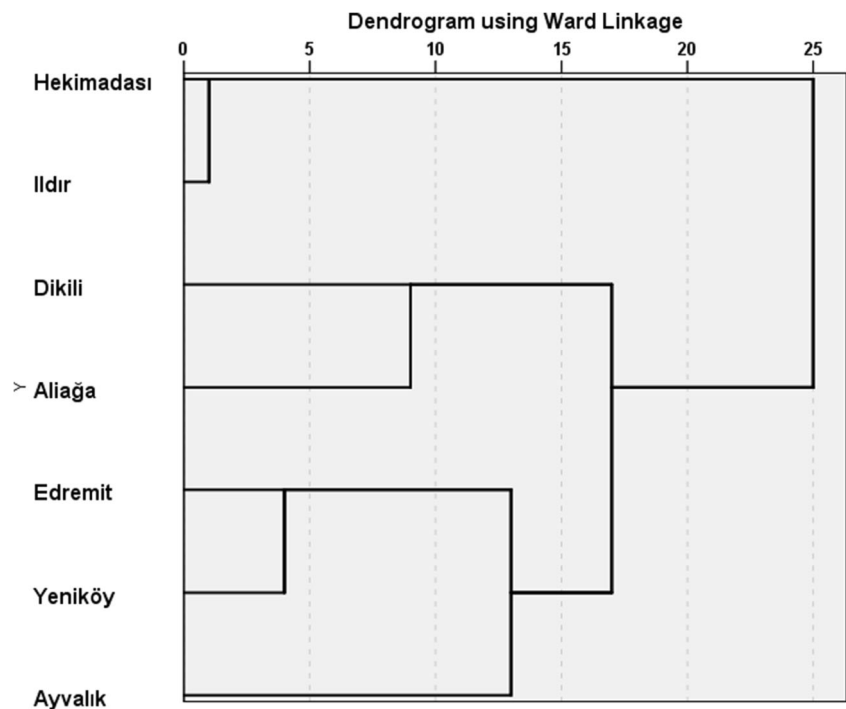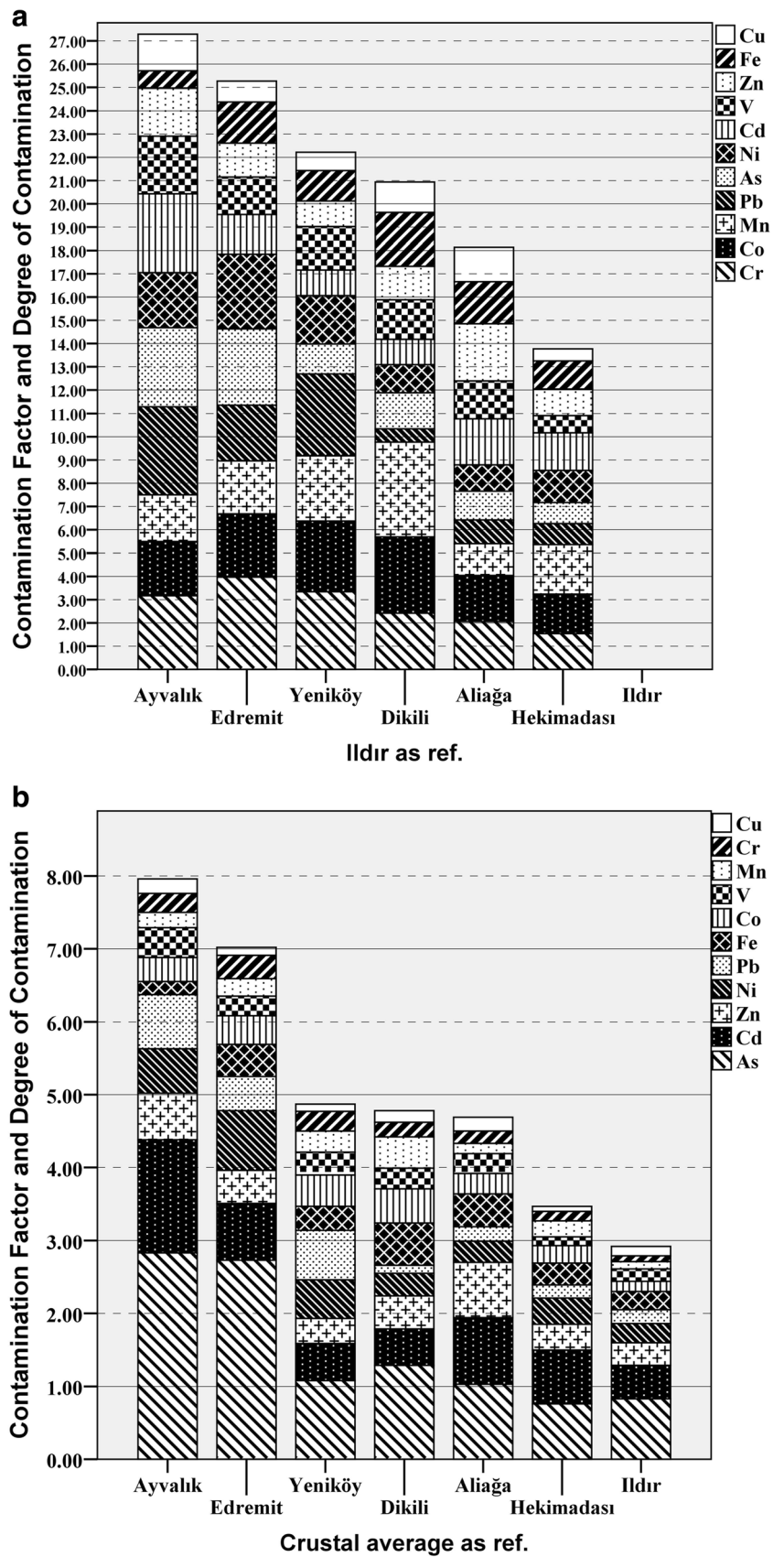
Fig. 2 Distance dendogram of the cluster analysis for the locations

Fig. 3 Values of contamination
factor and degree of
contamination. **a** Ildır as reference
and **b** crustal average as reference

Geoaccumulation index

Another method based on metal comparison is geoaccumulation index (I_{geo}), and the related findings from this study are shown in Fig. 5a, b. Based on Ildır as a reference, the results were distributed within the first three levels "practically uncontaminated," "uncontaminated to moderately contaminated," and "moderately contaminated" on the 7-level scale. Pb, Cr, and Co in Yeniköy; Ni, As, and Cr in Edremit; Pb, As, Cd, and Cr in Ayvalık; and Mn and Co in Dikili were assessed as "moderately contaminated." A change of reference to crustal averages made the results more optimistic, with a classification on the first level of the scale. Exceptions were As in Edremit, and As and Cd in Ayvalık, which were at the second level.

When studies performed in the Mediterranean were considered, the I_{geo} results of Piazzolla et al. (2015) from the northern Tyrrhenian Sea were found to be higher than ours in terms of As and Mn, but similar for Cr, Ni, Pb, and Cu. The I_{geo} values for Cd, Pb, Cr, Cu, and Zn in almost all stations in the Saronic Gulf of Greece were higher than those of this study (Galanopoulou et al. 2009). The I_{geo} values for Pb, Cd, Ni, Co, and As in the Rosetta Region of Egypt appeared to be slightly higher than ours, but similar for Zn, Cr, Mn, Cu, Fe, and V (El-Sorogy et al. 2016).

Modified degree of contamination and pollution load index

Both of these methods help to understand the total effect of all elements determined in the locations, making a comparison of the localities possible. In fact, modified degree of contamination (mC_d) is a modified version of C_d. Due to the formula of C_d, the higher the number of elements that are studied, the bigger the resulting value is. This handicap is eliminated by using the formula for mC_d, and hence, it is possible to make a comparison or classification regardless of the number of elements. The mC_d findings are presented in Fig. 6. There was no difference in the order of locations when both these methods were used with two references. The most contaminated location was determined to be Ayvalık each time. The results were placed in the first three levels of mC_d: between "nil to very low," "low," and "moderate." When the reference was changed to crustal averages, then all station values were below 1.5 at the "nil to very low" level.

The pollution load index (PLI) is assessed with different scales, as in the case of EF. When Ildır was taken as the reference, using the scale used by Tomlinson et al. (1980), the beginning of deterioration was valid for all locations. However, in the case of crustal average, there was no potential problem. Based on the 7-level scale of Singh et al. (1999), the locations were placed on the third and fourth scale level: "moderately polluted to unpolluted" and "moderately polluted" when Ildır was the reference, while they were placed

on the second level "unpolluted" using crustal averages as the reference. El-Bady (2016) found mC_d values to be 0.73 to 1.15, with one exception: five lagoons, Egypt, which was consistent with our findings. However, El-Bady (2016) recorded a value of 7.13 in Barwill Lagoon, well above the present values. A study conducted in Thermaikos Island, Greece, used two different references similar to this investigation. The mC_d was about 1.5, based on crustal averages, but it increased up to about 5 based on their own reference (Christophoridis et al. 2009), and was higher compared to the corresponding mC_d values in this study. Another study performed in Edku Lake, Egypt, which has a connection to the Mediterranean Sea, found mC_d and PLI values within the range of 1.6 to 12.5 and 1.3 to 6.9, respectively (El-Said et al. 2014). These values were higher than those calculated here.

Ecological risk assessment

In this study, we attempted to investigate the effects of metals on the living organisms in the selected locations. For this, toxic unit (TU) values for each element were determined to understand which elements created intensive impacts on the locations. Then, to compare the locations, total toxic unit (ΣTU) values were calculated. Moreover, toxicity of the elements accumulated in the environment was expressed as a percentage by calculating the mean effect range–median quotient (m-ERM-q). The related findings are displayed in Fig. 7.

There were two important results. The first is that although Ayvalık was the most affected region from the perspective of accumulation and contamination, Edremit was the most affected region in terms of the toxic effects on living organisms. The main reason for this is that not all elements have an equal toxicity on organisms. This is obvious from toxicity studies aiming to investigate the toxicity limit values. For example, the ERM value of Cd is 9.6 mg/kg, but this can be up to 410 mg/kg for Zn, meaning that Cd is more toxic compared to Zn. There are a number of factors that affect the toxicity levels of elements. How essential an element is for metabolism is the major factor. Nevertheless, all metals show toxic effects over a certain threshold whether essential or not (Alcorlo et al. 2006). However, the organisms have an ability to regulate the metabolism of more important elements for themselves (Tunca et al. 2013). This mechanism attenuates the toxicity of essential metals such as Zn and Fe, which are highly desirable for metabolism. In other words, more accumulations are required to produce Zn or Fe toxic effects. Another important factor is the structure of the metal, which determines the compounds it will react with and have an affinity for. This is the reason for the high toxicity of elements like Hg and Cd, which can easily react with compounds and block metabolic

Fig. 4 Values of enrichment factor. **a** Ildır as reference and **b** crustal average as reference
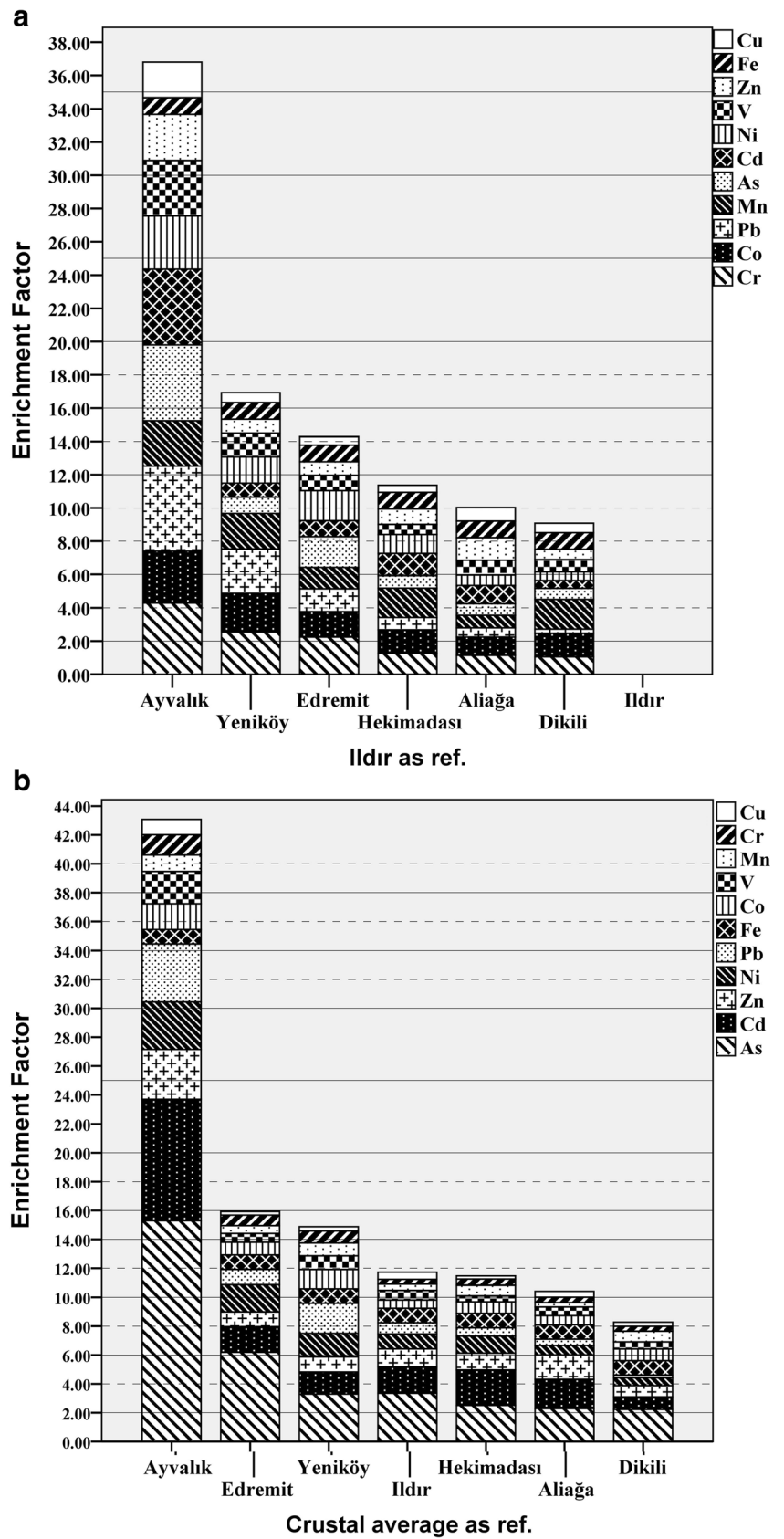
Fig. 5 Values of
geoaccumulation index. **a** Ildır as
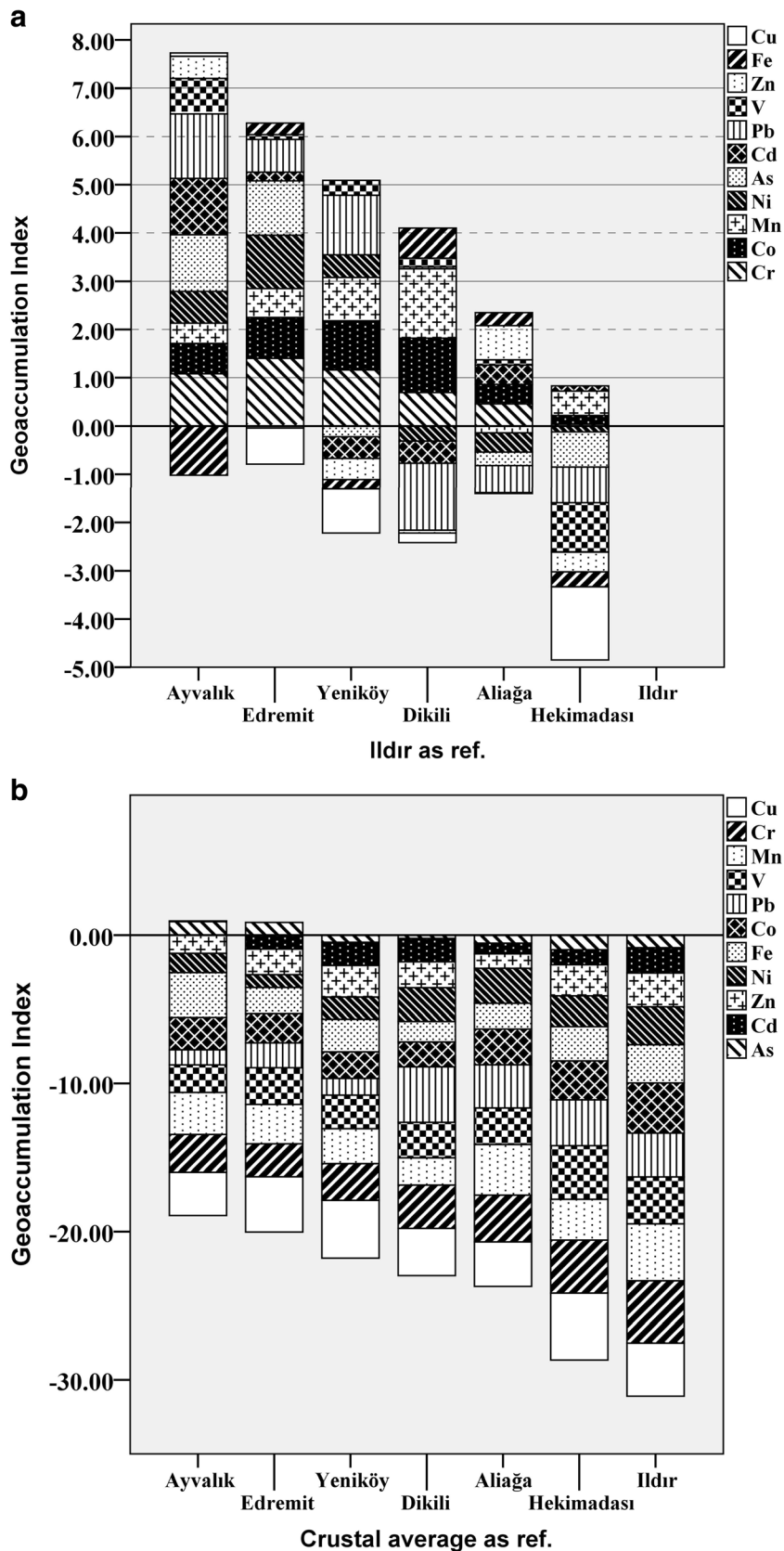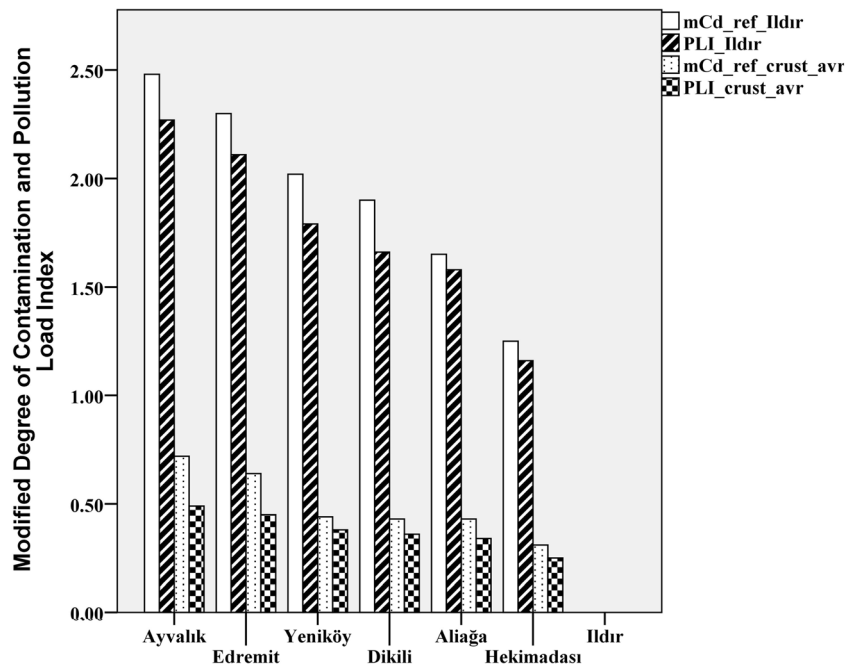reference and **b** crustal average as
reference

Fig. 6 Values of modified degree of contamination and pollution load index

pathways or disrupt the structural components at a cellular level. A metal can show this behavior above a threshold at which it may not be metabolized, even if it is essential.

The second important result of *TU* was that the majority of the toxic effects of the elements studied were caused by As and Ni. The lowest level of *TU* for As and Ni was about 60% in Aliağa, while the highest was in Edremit with over 80%. Actually, Ni is an essential element, but its high concentrations are toxic (Bielmyer et al. 2013). It is a cofactor of some enzymes as well as being involved in metabolic events such as urea metabolism, the hydrogen cycle, and nitrogen fixation (Maleva et al. 2016). Forest fires and volcanic activities are the natural sources of Ni, but coal smoke, diesel and fuel oils, and litter and water incinerations are human contributions (Yahaya Ahmed 2011). Moreover, the waste from mining activities and NiCd batteries represent another anthropogenic Ni source with a total annual amount of 33.1 to 194.2× 10^3 tonnes (Martínez-Ruiz and Martínez-Jerónimo 2015). Ni is known to be hematotoxic, immunotoxic, neurotoxic, genotoxic, and reproductively toxic; shows pulmonary toxicity; and is nephrotoxic and hepatotoxic, and a carcinogenic agent (Das et al. 2008). Conversely, As is not an essential element (Zeneli et al. 2016). Since it has been widely used in medicine, agriculture, livestock, the electronics industry, and metallurgy, it has globally threatened living organisms (He et al. 2016). This metalloid occurs in four different oxidation stages (−III, 0, III, and V) that have different physicochemical traits (Wang et al. 2015). The metalloid is found in nature in two different forms as arsenite (As(III)) and arsenate (As(V)). While As(III) shows a toxic effect on protein metabolism by binding the sulfhydryl groups of cysteine where the resultant reactive

oxygen species (ROS) damage proteins, lipids, and DNA, As(V) inhibits the oxidative phosphorylation by binding in the place of phosphate to ATP thanks to ionic mimicry (Rahman et al. 2014b). The *m-ERM-q* method was used to calculate the total toxic effects of the elements, and the values in Edremit, Ayvalık, Yeniköy, Aliağa, Dikili, Hekimadası, and Ildır were 0.27, 0.24, 0.16, 0.12, 0.12, 0.11, and 0.09, respectively. Although all locations, except Ildır, were classified on the second grade of the 4-level scale with a 21% toxicity level, *m-ERM-q* values yielded parallel results with those of ΣTU, and the most toxic value was recorded for Edremit. The order of other locations was also the same with the lowest level for Ildır at a 9% toxicity level.

Geographical cluster

It was previously mentioned that the CA displayed close locations within the same cluster (Table 2 and Fig. 2). When the CA results were evaluated from the elemental accumulations and contaminations perspective, the geographic proximities were consistent with the accumulations and contaminations calculated using the various methods. The southernmost locations, Hekimadası and Ildır, were placed in the same cluster and the northernmost locations, Edremit and Yeniköy, were the most polluted regions and formed a separate cluster. Neither as polluted as Edremit and Yeniköy nor as clean as Hekimadası and Ildır, Aliağa and Dikili formed a third cluster. Although Ayvalık had the greatest accumulation, it placed close to the cluster of Edremit and Yeniköy.

Fig. 7 Values of toxic unit and
total toxic unit

Fig. 7 Values of toxic unit and total toxic unit
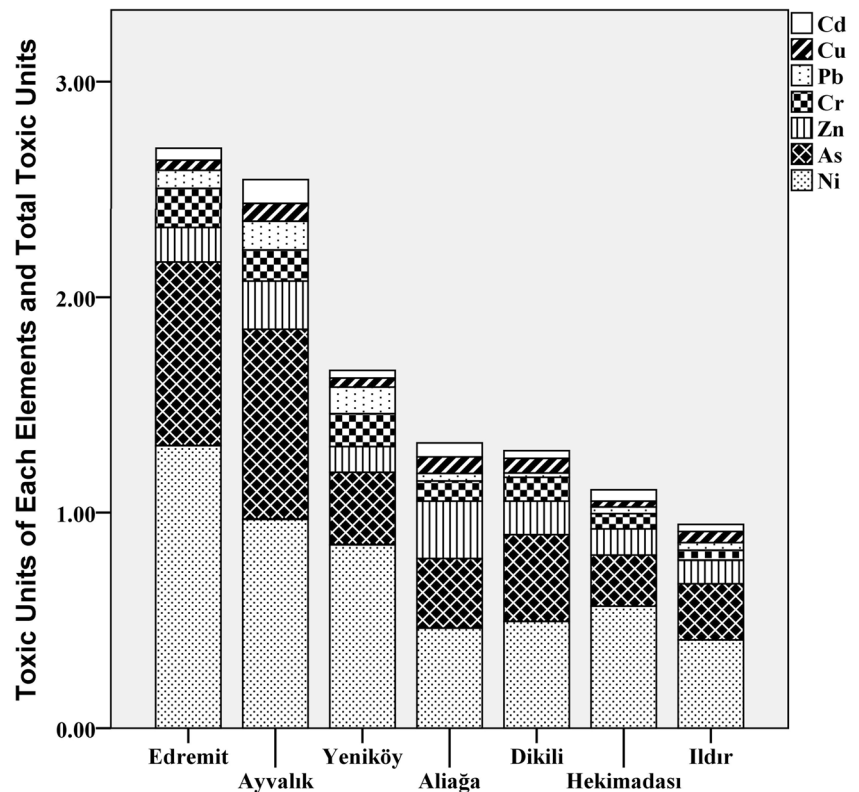
Around the world

These studies have also been compared with studies done in different parts of the world. Single-factor contamination index (SFCI), metal contamination index (MCI), and biota-sediment accumulation factor (BSAF) were all used differently from this study in the Yellow River Delta in China while benefiting from macrobenthic organisms. Like our study, As was found to be high, and As results were found to be 50% above the national standard concentrations and Cd was bioaccumulated by macrobenthic organisms from the sediment (Li et al. 2016) In the study carried out in Qeshm Island, an Iranian island in the Persian Gulf, Zn, Cu, Pb, and Cd were found to be 39.02 to 122.93, 3.23 to 6.01, 1.02 to 2.48, and 0.18 to 0.20 µg g^{-1} in sediment, respectively. These concentrations show great parallels to our study except for Pb. Pb concentrations are lower than in our study (Shirneshan and Bakhtiari 2012). As in this study, the contamination factor and pollution load indices were used to assess the sediment metal pollution in the study carried out by Alyazichi and his colleagues in Australia's Koragah Bay. The results—determined to be higher and similar for certain metals compared to this study—found contamination with Pb, Cu, and Zn, moderate contamination with As, and no contamination with Ni and Cr (Alyazichi et al. 2015b). In another study conducted in Oyster Bay in Australia, the results were compared to the *ERL* and *ERM* values of this study. While As, Zn, Cu, and Pb exceeded *ERL* values, Cr

and Ni did not exceed them. In our study, the Ni value in Edremit exceeded the *ERM* value; there was no other metal found that exceeded the *ERM* value in other studies (Alyazichi et al. 2015c). In a further study carried out in Cienfuegos Bay (Cuba), the contamination factor, the enrichment factor, and the geoaccumulation index were used in a similar way to this study and the results were compared with the limit values for *TEL* and *PEL*. According to the evaluations, the studied region was found to be most contaminated by Cd and Cu, while Cu was determined to be the most risky element in terms of boundary values (Peña-Icart et al. 2017).

Conclusion

This investigation was one of the biggest assessments—in terms of the study area of the northern Mediterranean Sea (Aegean Sea, Turkish Coasts)—of the human impact on marine sediment by comparing areas of urbanization and industrialization with areas subject to no or little human effects. In this study, two different references were used: firstly, crustal averages and secondly, the Ildır area, which has undergone minimal anthropogenic impact by being far away from urbanization and industrialization. According to the enrichment factor values, the most problematic location was Ayvalık. Due to the normalizing element used in the calculation of *EF*, the results were almost the same

for both references. This location was followed by Edremit and Yeniköy. The locations with the lowest accumulation and contamination were Ildır and Hekimadası. An evaluation of the adverse biological effects of the element profiles showed a similar picture with the most affected location being Edremit, followed by Ayvalık and Yeniköy. The least affected regions once again were Ildır and Hekimadası. When elemental results were evaluated by location, there was a change region by region; however, a general assessment reveals that the most problematic elements were As and Ni. Moreover, concentrations of these elements, particularly Ni, were higher than the toxic threshold concentrations and by themselves exerted the most toxic effects on the sediment. The results of CA for the locations based on their elemental profiles were highly consistent. The cluster formations of the locations, according to the geographic distribution and similarity of the locations in terms of accumulation profiles, were very important for the study.

An evaluation based on both references could not reach a conclusion on an intensive accumulation, contamination, or toxic effect. However, Ayvalık, Edremit, and Yeniköy are the stations that need careful consideration. They should consider As and Ni in terms of elements.

For further studies, alongside sediment contamination assessment, an estimation of metal accumulations in living organisms and BSAF would be of great importance for Ayvalık, Edremit, and Yeniköy.

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