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Assessment of element concentrations in surface sediment samples from Sığacık Bay (eastern Aegean)

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Abstract: Concentrations of Al, Fe, As, Co, Cr, Cu, Mn, Ni, Pb, Zn, Hg, and organic carbon, and grain size distribution were investigated in the surface sediments of 7 sampling stations in the Sığacık Bay (western Anatolia) in December 2016. At all of the sampling stations, the concentrations of Pb, Ni, Cr, and As were higher than the average shale values. The highest concentrations of Pb, Cu, Zn, As, and Hg were found at stations near Doğanbey Cape. The possible sources of pollution were evaluated using several parameters: the enrichment factor (Ef), contamination factor (Cf), and contamination degree (Cd). The Ef values ranged between 0.12 and 7.61 in the bay. The high Ef (>1.5) values of Pb, Cu, Ni, Co, and As were assessed to explain the influence of anthropogenic sources. Additionally, the Cf values ranged from 0.46 to 5.61, while the Cd values ranged from 11.69 to 20.45 in the study area. The Cd of the Cr and As ranged between moderate and considerable, and the highest Cd was measured at stations near Doğanbey Cape. Additionally, the pollution degrees were assessed using sediment quality guidelines (SQGs), the threshold effect level (TEL), the probable effect level (PEL), the effects range low (ERL), and the effects range median (ERM). It was demonstrated that the sediments were generally heavily polluted with Cr and Ni, and moderately with Pb and Cu, according to the numerical SQGs. The concentrations of Pb, Cr, Cu, Zn, and Ni were above the TEL, while Cr and Ni were also higher than the PEL levels for all of the samples.

Keywords: Western Anatolia, Sığacık Bay, pollution, sediment quality, enrichment factor, contamination factor

1. Introduction

Pollution in the aquatic environment is a worldwide problem and studies have been performed extensively for many years. Pollution levels by heavy metals in the aquatic environment can be estimated by analyzing water, sediments, and marine organisms (Bazzi, 2014). Changes in the sedimentary environment can release accumulated heavy metals that cause heavy metal pollution and deterioration of the marine environment. In such a case, sediment can be both the sink and source of heavy metals (Anderson Abel et al., 2016; Nethaji et al., 2017; Sun et al., 2017; Baysal and Akman, 2018; Ding et al., 2019).

The metal deposition in marine sediments is associated with various parameters, such as particle size, sediment characteristics, and organic carbon content (Akçalı and Kucuksezgin, 2011). The majority of metal emissions from land sources accumulate in marine and river sediments, where they are absorbed onto fine-gained sediments, like clay and silt and other fine-gained materials (Hieu Ho et al., 2010). Therefore, marine sediment samples are used as a sensitive indicator to determine the spatial trends of heavy contaminations in marine environments (Larsen and Jensen, 1989). The spatial distribution of heavy metals in sediments can be affected by natural (river inputs, geological impacts, etc.) and anthropogenic factors (parent rock weathering, agriculture, wastewater, transportation, and industrial wastewater) (Morillo et al., 2002; El Nemr et al., 2006; Luo et al., 2007).

To evaluate the level of contamination and possible anthropogenic impact on the sediments, 2 different techniques, the enrichment factor (Ef) and contamination factor (Cf), are calculated for sediment samples (Zhang and Liu, 2002). These factors are popular indices that have been used by researchers (e.g., Bonnail et al., 2016; Costa et al., 2015; Zalewska et al., 2015; Remeikaitė-Nikienė et al., 2018; Desena et al., 2018; Ding et al., 2019).

Element concentrations were evaluated in surficial sediments of Sığacık Bay with respect to the sediment quality guidelines (SQGs) of the United States Environmental Protection Agency (USEPA) (1997). These guidelines are widely used to evaluate the ecotoxicity of sediments (Duman et al., 2012; Saleem et al., 2013; Atalar et al., 2013; Kara et al., 2015). The SQGs are helpful in indicating sediment contamination compared to such

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concentrations according to the corresponding quality guidelines. This method is based on the relation between the measured concentrations of elements and observed biological effects, such as the mortality, growth, or reproduction of living organisms (Kara et al., 2015). In order to make an assessment of the ecotoxicological sense of trace element concentrations in sediments, 2 types of levels were developed: the threshold effect level (TEL; below which, adverse effects are not expected to occur) and a probable effect level (PEL; above which, adverse effects are expected to occur) (MacDonald et al., 2000).

The effects range low (ERL) and the effects range median (ERM), developed in the SQGs by Long and Morgan (1990), were adopted as an informal tool to assess sediment chemical data in relation to possible adverse effects on aquatic biota. ERL and ERM values are employed as useful techniques for toxicity prediction (Long and McDonald, 1998). If metal concentrations are lower than the ERL values, this indicates that adverse effects are likely to rarely occur on fauna in the sediments. On the other hand, if the metal concentrations are above the ERM values, this indicates that adverse effects are likely to frequently occur on the fauna. The possible toxicity effects in current study were evaluated using the ERL and ERM values determined by the Canadian Council of the Ministers of the Environment (CCME) (1995)[1].

Metal contamination of Fe, Pb, Cr, Cu, Zn, Mn, Ni, and Co in sediments and soil is one of the largest threats to environmental and human health (Salmons and Forstner, 1984). Due to their high degree of toxicity, these elements rank among the priority metals that are of public health significance (Tchounwou et al., 2012). Unfortunately, over the past few decades, heavy metal concentrations (e.g., Zn, Pb, Cd, Cu, and Hg) have increased in marine sediments 5 or 10 times higher than those recorded 50 or 100 years ago (Cardoso et al., 2001; Mashiatullah et al., 2013; Sharifuzzaman et al., 2015). A number of studies in the current literature have been carried out regarding heavy metal contamination in surficial sediments from the coastal region of Turkey. These surveys were conducted in the Marmara Sea (Algan et al., 2004), Black Sea (Baltas et al., 2017), Izmit Bay (Pekey, 2006), Aegean Sea (Aloupi and Angelidis, 2001), Aliağa-Turkey (Kara et al., 2015), Izmir Bay (Kucuksezgin et al., 2006; 2011; Atalar et al., 2013), NW Aegean Sea (Karageorgis et al., 2005), Nemrut Bay (Esen et al., 2010), Eastern Aegean Sea (Pazı, 2011), and Cyprus (NE Mediterranean) (Abbasi and Mirekhtiary, 2020; Duman et al., 2012). However, no data is available from the published literature discussing contamination in the sediments of Sığacık Bay.

Pollution in surficial sediment samples of Sığacık Bay was evaluated based on: 1) the grain size, element concentrations, total organic carbon (TOC) levels in the sediments; 2) metal contamination using the Ef, Cf, and Cd; 3) element concentrations in compliance with the numerical TEL, PEL, ERM, ERL, and SQGs of the USEPA; 4) statistical analysis applied to determine the relationship between the content, grain size and organic carbon; and 5) a comparison of the metal concentrations with those performed in previous studies in different regions.

2. Study area

Sığacık Bay is bordered by Doğanbey Cape in the east and Teke Cape in the west, south of the Karaburun Peninsula (western Anatolia) (Figure 1). The study area was approximately 118 km^2 (12.2 km in a N-S direction and 9.67 km in a E-W direction). The topographic data were obtained from the map of the Çeşme and Dilek straits (1/100.000) prepared by the Department of Navigation, Hydrography, and Oceanography of the Turkish Navy. The bathymetry map of the study area was produced by digitizing 20-m contours using the Surfer software program (Golden Software, Golden, CO, USA) (Figure 1). The depth values of the bay ranged from 20 m to 300 m. The contour intervals were intensified around Teke and Doğanbey capes as a result of the topographical uplift.

Along the coastline from Sığacık Bay to Doğanbey Cape, the sand, silty sand, sandy silt, and silt units continued to approximate depths of 7 m, 7–20 m, 20–50 m, and 50–200 m, respectively (Eryılmaz and Eryılmaz-Yücesoy, 2014). All of these sediment types in Sığacık Bay were observed as parallel bands in accordance with the shape of the coastline. The bottom structure of the coastline was also locally covered with Posidonia Oceanica on the seafloor (Orçun and Sunlu, 2007). Poulos (2009) demonstrated the origin and spatial distribution of the terrigenous material of the surficial unconsolidated seabed sediments of the whole floor of the Aegean Sea. In their investigation, it was indicated that the particulate matter deposition took place around the river mouth area and at a short distance offshore (prodelta area), but was always within the limits of the continental shelf. According to Poulos (2009), the sediment types of Sığacık Bay were classified as terrigenous-low calcareous and biogenic-terrigenous calcareous, which demonstrated the same sedimentary types as the Edremit, Dikili, İzmir, and Kuşadası gulfs.

Located at the southeastern part of Sığacık Bay, in the region between Doğanbey Cape and Bölme Island, are shallow submarine hot springs (maximum temperature of 62 °C) (Eşder, 1988; Toygar, 2012). It has been indicated that these hot sources were formed by the effect of the submarine active fault that was referred to as the Tuzla

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[1] Canadian Council of Ministers of the Environment-CCME (1995). Protocol for the derivation of Canadian sediment quality guidelines for the protection of aquatic life [online]. Website http://ceqg-rcqe.ccme.ca/download/en/226 [accessed 02 August 2018].

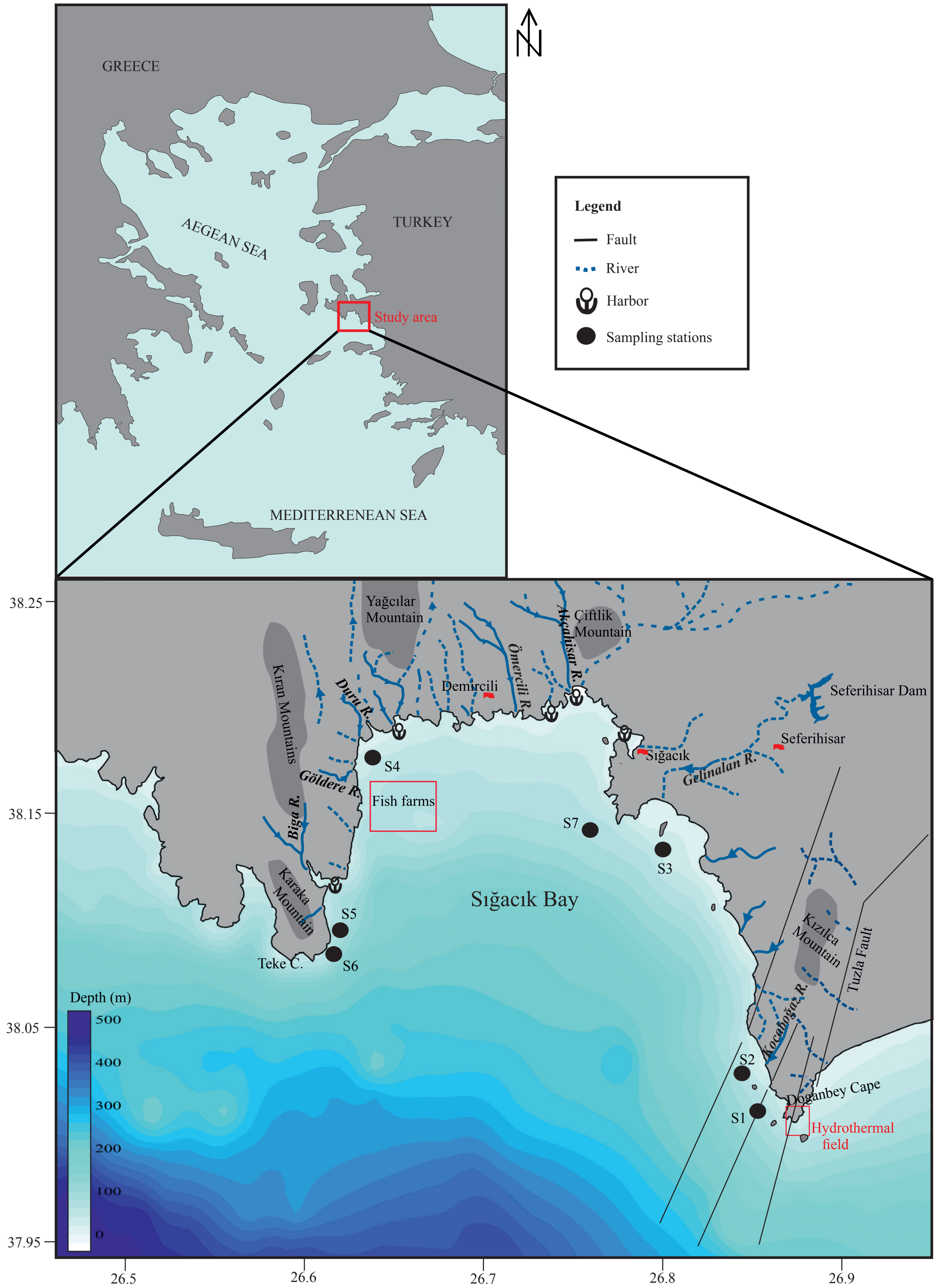

Figure 1. Location map of sampling stations and fish farms; bathymetry map of the study area (derived from the depth map of the Çeşme and Dilek straits (1:100.000) prepared by the Department of Navigation, Hydrography and Oceanography of the Turkish Navy); and black lines showing the simplified active faults (Ocakoğlu et al., 2005).

Fault in previously studies (Eşder, 1988; Toygar, 2012; Meriç et al., 2018a). The offshore continuity of the Tuzla Fault was also clearly demonstrated in the results of marine geophysical surveys applied by Ocakoğlu et al. (2004, 2005) (Figure 1). In addition, Sığacık Bay experienced significant serious earthquakes on 17 to 20 October, 2005; therefore, the region has been a center of interest by many researchers (Gürçay et al., 2007; Ocakoğlu et al., 2004; 2005; Benetatos et al., 2006; Aktar et al., 2007; Sözbilir et al., 2009; Gürçay, 2014; Bakak et al., 2015; Yolsal-Çevikbilen et al., 2014; Bakak, 2017).

The chemical (Ca^+, Mg^{+2}, Na^{+2}, K^+, Li^+, As, B^+, Cl^-, SO_4^{-3}, SiO_2, and HCO^{-3}) and physical (temperature, salinity, conductivity, and density) effects to seawater of the submarine thermal springs in Sığacık Bay and Doğanbey Cape were evaluated by Bakak and Özel (2019). In their study, the deep water samples were analyzed and the concentrations of Ca^+, Mg^{+2}, Na^{+2}, K^+, Li^+, As, B^+, Cl^-, SO_4^{-3}, SO_2, and HCO^{-3}, and the temperature, salinity, conductivity, and density values were measured. Bakak and Özel (2019) reported that there were no chemical effects on the seawater of the submarine thermal springs; on the other hand, the temperature values of the deep water samples were higher in the stations near Doğanbey Cape.

Investigations related to the surface currents in the Aegean Sea are available in the literature (e.g., Lykousis et al., 2002; Sayın et al., 2011; Poulos, 2009; Sylaios, 2011). The upper 50–100-m layer of the Aegean Sea consists of mixed water comprising Black Sea water, Levantine surface water and Levantine intermediate waters (Poulos, 2009). The Levantine currents were formed in the Levantine Basin in the northern part of the Aegean Sea, where it enters the Aegean Sea. These currents travel through the southern part of Aegean Sea and are divided into branches by various effects, such as the locations of the islands, the intensity and direction of the wind, etc. The seasonal current maps demonstrated that the offshore region of Sığacık Bay is generally under the effects of the secondary surface currents that enter the Kuşadası Gulf, in approximately E-W and S-N directions (Meriç et al., 2018b). Sayın et al. (2011) published the general circulation pattern of the Aegean Sea (including the current study area), and according to this model, the study area was approximately under a counterclockwise seawater current. The temperature values in Sığacık Bay were also observed as lower than those in the Ikaria Basin and Kuşadası Gulf, for the summer of 1991 (22.5–23 °C) and spring of 1992 (16–17 °C) (Sayın et al., 2011).

Fish farms were located in the northwestern part of the bay, which were owned by a private company, and investigated with regards to their effects on the water quality by Orçun and Sunlu (2007). In their study, they did not observe any negative effects of the fish farms on the water quality of Sığacık Bay. In that region, the livelihood of the local people is tourism, fishing, agriculture, and animal husbandry (Orçun and Sunlu, 2007). As a result of the fisheries, there are a number of harbors along the coastline of Sığacık Bay. The bay is boundaried by the Kıran, Yağcılar, and Kızılca mountains, and is under the influence of rivers flows from those mountains into it. There are no settlements along the coastline of the bay; however, the region is used extensively as a beach during the summer months (Orçun and Sunlu, 2007). The abovementioned possible pollution factors (fish farms, harbors, active fault structures, and drainage channels) that could affect the project area are mapped in Figure 1.

3. Methodology

3.1. Sediment sampling and geochemical analysis

The surface sediment samples were collected from 7 sampling stations (numbered as S1–S7) using a boxcorer during cruises by the Dokuz Eylül-1 research vessel of the Marine Science and Technology Institute (Dokuz Eylül University) between 4 and 6 November, 2016 (Figures 1 and 2). The coordinates of the sampling stations and their locations in the study area are presented in Figure 1 and Table 1. Stations were located along the coastal zone of Sığacık Bay, and the sampling depths ranged from 43 to 110 m. In each station, triplicate samples were collected and analyzed separately. The boxcorer sampler was opened carefully and first, the uppermost 1–2 cm of the sediment was taken, and then the remaining sediment was put into a polyethylene bag. Surficial sediment samples were stored in a deep freezer until geochemical analysis. The concentrations of elements (Fe, Al, Pb, Cr, Cu, Zn, Mn, Ni, Co, As, and Hg) in the surface sediment samples were analyzed by ACME Analytical Labs (Vancouver, BC Canada) using ICP-ES/MS. A reference sediment (OREAS25A-4A) sample (from ACME) was used as a control for accuracy of the analytical methods. The values obtained (in mg/kg^{-1} dry wt) for the analysis of the sediment samples were as follows: Cu (standard: 41.5, observed : 33.9), Pb (standard: 27.8, observed: 26.6), Zn (standard: 50, observed: 44.4), Ni (standard: 51.4, expected: 45.6), Co (standard: 9.8, expected: 8.2), Mn (standard: 518, observed: 500), Fe (standard: 7.17, observed: 6.7), As (standard: 11, observed: 10.7), Cr (standard: 128, observed: 120), and Hg (standard: 0.30, observed: 0.3).

3.2. Sediment grain size

The sediment grain size analysis applied to assess the sediment distribution was performed using the dry sieving and hydrometer analysis reported by Folk (1980). The grain size distribution of the sediments was determined based on classifications at certain ratios of clay (<0.002 mm), silt (0.002–0.063 mm), sand (>0.063 mm), and gravel (>2 mm).

Figure 2. Boxcorer equipment used for the surficial sediment samples (photo taken during sediment sampling for this project).

Table 1. Locations of the sampling stations, total organic carbon (% dry weight), grain size, and sediment type.

Station	Longitude	Latitude	TOC (%)	Sand (%)	Silt (%)	Clay (%)	Sediment type
S1	38.0337	26.8507	0.87	36.88	39.58	23.54	Sandy mud
S2	38.0588	26.8493	0.78	48.22	33.67	18.11	Sandy mud
S3	38.1413	26.8037	1.03	55.4	32.79	11.81	Silty sand
S4	38.1718	26.6307	0.70	40.68	39.61	19.71	Sandy mud
S5	38.1299	26.6206	1.20	31.4	40.41	28.19	Sandy mud
S6	38.1072	26.6149	1.21	72.35	15.09	12.56	Muddy sand
S7	38.1477	26.7591	1.28	31.45	47.62	20.93	Sandy mud

TOC: Total organic carbon

3.3. Total organic carbon distributions

The TOC concentration was detected using the sulfochromic oxidation method, after the sediment samples were dried. This method has a percentage of accuracy of ±0.017% organic matter. In this study, the total organic carbon levels were evaluated with regards to the concentration of elements and grain size distribution of the sediments.

3.4. Enrichment factor

The Ef and Cf were defined as the accumulation of a given toxin substance in a reservoir by Hakanson (1980). Shale values of some metals were given by Krauskopf (1985), and used to calculate the Ef values. The Ef is used as an index to evaluate anthropogenic and natural sources (Özkan and Buyukisik, 2012). The Ef values of the elements in the sediments at all of the stations were calculated for each metal using the equation by Salati and Moore (2010), as follows:

$$\mathrm{Ef} = (C_x / C_{Al})\ \textit{sample}\ (C_x / C_{Al})\ \textit{backround} \qquad (1)$$

where (Cx) sample is the measured metal concentration, (C_{Al}) sample is the measured concentration of the Al metal, (Cx) background is the unpolluted reference value, and (C_{Al}) background is the concentration of Al in the unpolluted reference value. Ef values of the trace metal were evaluated in 2 categories: 1) 0.5 ≤ Ef ≤ 1.5 (from crustal materials or natural weathering processes) and 2) Ef >1.5 (from other sources) (Hakanson, 1980).

3.5. Contamination factor and contamination degree

The CF method evaluates the enrichment in metals in relation to the background concentrations of each metal in the sediments. The CF is the ratio obtained by dividing the concentration of each metal in the sediments by the background value (Bonnail et al., 2016), as follows:

$$C_f = C_e / C_b \qquad (2)$$

where Ce and Cb are concentrations of the element in the sediment sample and the background value of the element, respectively. In this study, the Cf ratio was obtained by dividing the concentration of each metal/metalloid in the sediments by the Earth's shale values reported by Krauskopf (1985), which were used as the background values of the metals. In order to evaluate the degree of contamination in sediments, Cfs were interpreted according to the 4 groups suggested by Hakanson (1980) and Bonnail et al. (2016), as low: Cf < 1, moderate: 1 < Cf < 3, considerable: 3 < Cf < 6, and high: Cf > 6s.

The Cd is defined as the sum of all Cfs of the metals for a given basis.

$$C_d = \Sigma_{i=1}^{n} Cfi \tag{3}$$

The following terminologies were adopted to describe the Cd: low degree: Cd < 8, moderate degree: 8 ≤ Cd < 16, considerable degree: 16 ≤ Cd < 32, and very high degree: Cd ≥ 32, indicating seriously anthropogenic inputs (Hakanson, 1980).

3.6. Statistical analysis

Statistical analysis was performed using STATISTICA 8.0 software (StatSoft, Inc., Tulsa, OK, USA). This analysis is a multivariate analytical tool used to explore the relationship of the measured parameters and facilitate the assessment of potential input sources. Spearman rank order correlation coefficient ($P < 0.05$) was computed between the variables, including element levels, grain size, and organic carbon in the sediment samples.

4. Results and discussions

The grain size distribution of Sığacık Bay varied from sandy mud, silty sand, to muddy sand, according to Folk (1980) (Figure 3 and Table 1). The percentages of sand, silt, and clay ranged between 31.4% and 72.3%, 15.1% and 47.6%, and 11.81% and 28.2%, respectively. The highest fine-grained (clay + silt) sediments were measured at sampling stations S1 (63.1%), S5 (68.6%), and S7 (68.5%).

TOC values of the surface sediments of Sığacık Bay ranged between 0.7% and 1.28% (Table 1). The highest TOC values were observed as 1.20% (station S5) and 1.28% (station S6) in surface sediments near Teke Cape, in the western part of the study area. TOC concentrations along the north coastline of Izmit Bay ranged between 2.13% and 7.55%, which indicated a high organic matter flux into the sediments (Pekey, 2006). In addition, Atalar et al. (2013) and Yılgör et al. (2012) reported that high concentrations of TOC originated from the anthropogenic and aquaculture activities at some stations in Izmir Bay and Bafa Lake, respectively. On the other hand, the TOC concentrations in the sediments from study area were similar to those of the Fethiye Harbor sediments (Yılgör and Avcı, 2004). The high organic carbon content in the surface sediments of Sığacık Bay was evaluated as under the influence of anthropogenic inputs due to the fish farms. Accumulation in the sediments can be associated with organic carbon deposits, grain size, and the characterization of the sediment (Akçalı and Kucuksezgin, 2011). However, the organic carbon levels were also evaluated in accordance with the metal levels and grain size distribution (Yılgör et al., 2012; Atalar et al., 2013). Carvalho et al. (2005) indicated that fine-grained sediments tended to bind to high quantity organic matter. No correlation was observed between the elements and organic carbon levels in the study area.

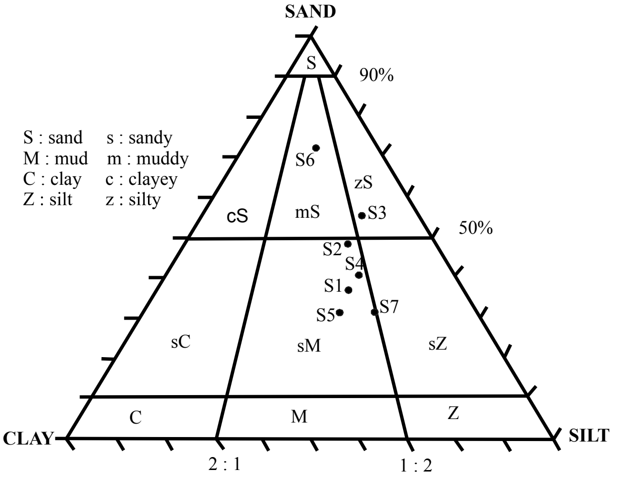

Figure 3. Triangular diagram of the sediment type (Folk, 1980).

The element concentrations were normalized using the fine-grain contents (clay + silt) and are given in Table 2. The grain size distribution in the eastern part of Sığacık Bay was found to be compatible with the results of Meriç et al. (2018a). However, in previous studies, the grain size distribution was parallel along the coast band of the bay. At the same time, this distribution shape was also almost similar to the surface sediment distribution map of Poulos (2009).

The background concentrations of Fe, Al, Mn, Cu, Zn, Ni, Pb, Hg, Cr, Cd, Co, and As in the average shale obtained by Krauskopf (1985) were used in this study (Table 2). The levels of Pb, Cr, Ni (except for S6), and As were higher than the shale values given by Krauskopf (1985) at all of the sampling stations. The highest levels of Pb, Cr, Zn, Ni, Fe, Co, and As were detected at stations near Doğanbey Cape in the eastern part of the bay. The concentrations of Pb, Cr, Co, Ni, Zn, Co, and Mn were investigated in Doğanbey Cape to detect the chemical effects of the submarine hot springs (Meriç et al., 2018a). In their study, the element concentrations were measured as: Cr (231–1283 mg/kg), Mn (235–1056 mg/kg), Co (21.14–57.74 mg/kg), Ni (153–1009 mg/kg), Cu (2.49–22.24 mg/kg), Zn (16.02–61.43 mg/kg), and Pb (4.48–26.06 mg/kg), and this dataset was used to compare with the element levels of the present study. In this paper, the concentrations of Pb, Zn, and Mn were greater than the numerical values reported by Meriç et al. (2018a) at all of

Table 2. Mean ± SE concentrations of the metals (mg kg^{-1} dry weight) in the surficial sediments collected from Sığacık Bay.

Station	Pb	Cr	Cu	Zn	Ni	Al	Fe	Mn	Co	As	Hg
S1	42 ± 0.58	269 ± 17	44 ± 2.7	112 ± 2.1	191 ± 2.3	68.916 ± 204	51.806 ± 219	794 ± 19	35 ± 1.6	73 ± 1.4	0.21 ± 0.02
S2	33 ± 1.2	294 ± 3.2	35 ± 1.7	116 ± 2.1	210 ± 3.8	73.001 ± 57	57.937 ± 194	859 ± 10	41 ± 1.0	44 ± 0.80	0.10 ± 0.01
S3	31 ± 0.58	188 ± 1.5	30 ± 2.6	94 ± 1.7	156 ± 1.7	44.170 ± 70	37.220 ± 119	760 ± 13	28 ± 1.0	43 ± 0.70	0.04 ± 0.01
S4	20 ± 0.58	180 ± 2.3	22 ± 1.5	57 ± 2.1	94 ± 2.1	40.121 ± 213	22.084 ± 101	480 ± 10	12 ± 0.95	2 7 ± 0.58	0.07 ± 0.01
S5	31 ± 0.88	224 ± 2.3	28 ± 1.2	76 ± 2.1	106 ± 2.0	53.790 ± 113	34.985 ± 95	685 ± 7.1	19 ± 0.87	26 ± 0.64	0.09 ± 0.01
S6	37 ± 1.2	163 ± 2.1	34 ± 2.3	80 ± 2.3	73 ± 1.5	32.188 ± 136	21.700 ± 153	882 ± 11	17 ± 1.0	40 ± 0.58	0.10 ± 0.01
S7	37 ± 0.58	233 ± 2.6	28 ± 2.1	86 ± 1.5	138 ± 2.1	57.768 ± 168	21.700 ± 123	783 ± 5.5	24 ± 0.96	42 ± 0.58	0.10 ± 0.01
Average Shale*	20	100	50	90	80	80000	47000	850	20	13	0.30
TEL**	30.2	52.3	18.7	30.2	15.9						
PEL**	112	160	108	112	42.8						
ERL***	46.7	81	34	150	20.9						
ERM***	218	370	270	410	51.6						
SQG**** Nonpolluted	<40	<25	<25	<90	<20						
Moderately	40–60	25–75	25 –50	90–200	20–50						
Heavily	>60	>75	> 50	>200	>50						

*Krauskopf, 1985; **MacDonald, 1994; ***CCME, 1995; ****Long et al., 1995

the sampling stations. On the other hand, when compared to the other stations, the concentrations of Pb, Cr, Cu, Zn, Ni, Al, Fe, Co, and As were higher at stations (S1 and S2) near Doğanbey Cape in southeastern part of the bay. The high levels were interpreted as geological impact/natural inputs of the submarine active fault (Ocakoğlu et al., 2004; 2005) and the possible submarine thermal springs, because there was no available an anthropogenic input. The highest concentrations of Ni were observed in the eastern part of Sığacık Bay and this was evaluated as originating from the geochemical structure of western Anatolia (Ergin et al., 1993).

The concentrations of elements were evaluated in the surficial sediments of Sığacık Bay in terms of the numerical SQGs of the USEPA (1997). In the SQGs, sediments are classified as nonpolluted, moderately polluted, and heavily polluted. The concentrations of important heavy metals (Pb, Cr, Cu, Zn, and Ni) were compared with the numerical SQG concentrations (Table 2). The results showed that the surficial sediments were heavily polluted with Ni and Cr at all of the stations, and moderately polluted with Cu (except for station S4). Pollution by Ni and Cr was associated with those concentrations having exceeded the background average shale values. The contamination levels of Zn were classified as moderately at stations S1 and S2, while it was nonpolluted at the other stations. On other hand, the Pb levels were defined as moderately polluted at station S1 in Sığacık Bay.

Sediment quality criteria were proposed for 5 elements (Pb, Cr, Cu, Zn, and Ni). The element concentrations in the surface sediments from the study area were also evaluated using the TEL and PEL values of MacDonald (1994) (Table 2). The TEL and PEL values of the SQGs established contamination for Pb, Cr, Cu, Zn, and Ni. The concentrations of Pb (except for station S4), Cr, Cu, Zn, and Ni at all of the stations exceeded the numerical TEL values stated in the SQGs. Moreover, the Cr, Zn (for stations S1 and S2), and Ni values were higher than the PEL values. Accordingly, the high concentrations of Cr, Zn, and Ni were evaluated as reflecting the influence of the anthropogenic activities of the harbor and fish farms. It was thought that these pollution factors were located in the south of the bay and could affect the entire bay as a result of the currents. Additionally, the concentrations of Pb, Cu, Zn (except for stations S1 and S2) were lower than PEL.

The ERL and ERM values of surficial sediments were assessed using the CCME guidelines (1995)[2] (Table 2). The Cr and Ni concentrations were higher than the ERL values, which indicated that adverse effects might occur at all of

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[2] Canadian Council of Ministers of the Environment-CCME (1995). Protocol for the derivation of Canadian sediment quality guidelines for the protection of aquatic life [online]. Website http://ceqg-rcqe.ccme.ca/download/en/226 [accessed 02 August 2018].

Table 3. Efs and Cfs of the Sığacık Bay sediments.

	Station	S1	S2	S3	S4	S5	S6	S7
Ef	Fe	1.28	1.35	1.43	0.94	1.11	1.15	0.64
	Pb	2.44	1.81	2.81	1.99	2.31	4.60	2.56
	Cr	3.12	3.22	3.41	3.59	3.33	4.05	3.23
	Cu	1.02	0.77	1.09	0.88	0.83	1.69	0.78
	Zn	1.44	1.41	1.89	1.26	1.26	2.21	1.32
	Ni	2.77	2.88	3.53	2.34	1.97	2.27	2.39
	Mn	1.08	1.11	1.62	1.13	1.20	2.58	1.28
	Hg	0.08	0.04	0.02	0.05	0.04	0.08	0.05
	Co	2.03	2.25	2.54	1.20	1.41	2.11	1.66
	As	6.52	3.71	5.99	4.14	2.97	7.67	4.47
	Station	S1	S2	S3	S4	S5	S6	S7
Cf	Al	0.86	0.91	0.55	0.50	0.67	0.40	0.72
	Fe	1.10	1.23	0.79	0.47	0.74	0.46	0.46
	Pb	2.10	1.65	1.55	1.00	1.55	1.85	1.85
	Cr	2.69	2.94	1.88	1.80	2.24	1.63	2.33
	Cu	0.88	0.70	0.60	0.44	0.56	0.68	0.56
	Zn	1.24	1.29	1.04	0.63	0.84	0.89	0.96
	Ni	2.39	2.63	1.95	1.18	1.33	0.91	1.71
	Mn	0.93	1.01	0.89	0.56	0.81	1.04	0.92
	Hg	0.70	0.33	0.13	0.23	0.30	0.33	0.33
	Co	1.75	2.05	1.40	0.60	0.95	0.85	1.20
	As	5.62	3.38	3.31	2.08	2.00	3.08	3.23

the stations. On the other hand, the Ni concentrations were above the ERM values at all of the sampling stations, which also indicated that toxicity was expected to occur.

The Ef values of Fe, Pb, Zn, Cr, Cu, Ni, Mn, Co, As, and Hg were calculated using the observed metal to Al or Fe ratio (Table 3) of those concentrations that were unaffected by contaminant inputs. Therefore, the numerical values of the measured metal concentrations were divided by the background metal/Al or metal/Fe ratio (Kucuksezgin et al., 2011). A number of researchers have used the concentrations of Al as a normalizing element to obtain the Ef values of target metals and successful results were attained (Kucuksezgin et al., 2011; El Nemr et al., 2006; Zhou et al., 2007; Talas et al., 2015; Atalar et al., 2013). In this paper, to obtain the Ef values of the elements, Al concentrations were also used to calculate the Ef values of Fe, Pb, Zn, Cr, Cu, Ni, Mn, Co, As, and Hg. It was determined that the levels of Pb, Cr, Ni, and As were increased, while Fe, Cu, and Hg were lower than 1.5 at all of the sampling stations. In addition, the high Ef values of Co and Mn indicated a random spatial distribution in the sampling area. The highest levels of Pb, Cr, Ni, and As indicated anthropogenic input/noncrustal inputs for these elements according to Zhang et al. (2002) and Hakanson (1980). The Cf values were evaluated as low, moderate, considerable, and high degree of contamination according to the classification of Hakanson (1980). The Cf values of Pb, Cr, and Ni were found to be moderately contaminated in all of the sediment samples, and the Cf values of Fe and Zn were found at the same contamination classifications at stations S1 and S2. Additionally, the Cf values of As were found to be considerably contaminated, except for stations S4 and S5. The Cd values for Fe, Pb, Cr, Cu, Ni, Co, Mn, Zn, As, and Hg were classified as low, moderate, considerable, and very high degree of contamination. The Cd values were calculated as S1 (20.27), S2 (18.13), S3 (14.10), S4 (9.49), S5 (11.99), S6 (2.12), and S7 (14.29) in the study area (Table 3). The maximum Cd values were found at stations S1 and S2, and their Cd values were categorized as considerable ($16 \leq Cd < 32$), whereas other stations were moderate ($8 \leq Cd < 16$), according to the classification of Hakanson (1980).

Statistical analysis was used to find a correlation between the concentration of elements (Al, Fe, Pb, Cr, Cu, Co, As, Ni, Zn, Mn, and Hg), grain size (clay, silt, and sand), and organic carbon in the surface sediment samples. Nonparametric Spearman rank order correlation was performed and the analysis results are given in Table 4. The highest coefficients were those for Co-Ni ($r = 0.9643$), Co-Mn ($r = 0.9643$), As-Zn ($r = 0.9286$), Pb-Hg ($r = 0.9058$), Ni-Cr ($r = 0.8929$), Co-Al ($r = 0.8571$), Co-Cr ($r = 0.8571$), As-Co ($r = 0.8571$), and Ni-Fe ($r = 0.8469$). The lowest correlation ($r = 0.0901$) was observed between Mn and Fe. In addition, a significant and positive correlation was found between Mn and sand, while there was an insignificant and negative correlation between Mn and fine-sized matter. On the other hand, a correlation between the concentrations of elements, sediment texture (clay and silt), and organic carbon levels was not observed.

Several studies concerning metal contaminations have been carried out in different coastal regions of Turkey (Algan et al., 2004; Kucuksezgin et al., 2006; Pekey, 2006; Esen et al., 2010; Pazı, 2011; Atalar et al., 2013). The concentrations in surficial sediments from Sığacık Bay were compared to the previous studies (Table 5). The concentrations of Pb, Cr, Cu, Zn, Ni, and Mn in the present study were similar to those in the Marmara Sea (Algan et al., 2004) and Izmir Bay (Kucuksezgin et al., 2006). On the other hand, the levels of Cr, Ni, and Mn were slightly higher than those in Izmir Bay, Nemrut Bay, Aegean Sea, Izmit Bay, Eastern Aegean Sea (Pekey, 2006; Esen et al., 2010; Pazı, 2011; Atalar et al., 2013), whereas the levels of Cu and Zn were higher than those in Izmir Bay (Atalar et al., 2013).

Table 4. Spearman rank-order correlation matrix for all of the geochemical parameters in the surface sediment samples from Sığacık Bay.

	Sand (%)	Clay (%)	Silt (%)	Organic carbon (%)	Al ppm	Fe ppm	Pb ppm	Cr ppm	Cu ppm	Zn ppm	Ni ppm	Mn ppm	Co ppm	As ppm	Hg ppm
Sand	1.000														
Clay	–0.9286	1.000													
Silt	–0.9286	0.7857	1.000												
Organic carbon	–0.1429	0.0714	0.1429	1.000											
Al	–0.4286	0.3929	0.3214	–0.1786	1.000										
Fe	0.0180	0.0180	–0.2162	–0.6307	0.6847	1.000									
Pb	0.0000	0.1637	–0.1091	0.4364	0.3819	0.0000	1.000								
Cr	–0.4286	0.3929	0.3214	–0.1786	10.000	0.6847	0.3819	1.000							
Cu	0.3214	–0.1071	–0.5714	–0.1071	0.4643	0.6307	0.6547	0.4643	1.000						
Zn	0.2143	–0.2143	–0.3214	–0.1071	0.7500	0.7027	0.5455	0.7500	0.7857	1.000					
Ni	–0.1071	0.0357	0.0000	–0.3214	0.8929	0.8469	0.2728	0.8929	0.5714	0.8929	1.000				
Mn	0.5000	–0.3214	–0.5714	0.2857	0.2143	0.0901	0.7638	0.2143	0.7500	0.6071	0.2143	1.000			
Co	0.0000	–0.0357	–0.1429	–0.1429	0.8571	0.7928	0.4364	0.8571	0.7143	0.9643	0.9643	0.4286	1.000		
As	0.2500	–0.2143	–0.3214	–0.2143	0.6429	0.6307	0.6001	0.6429	0.7500	0.9286	0.8214	0.5357	0.8571	1.000	
Hg	–0.1482	0.3706	0.0371	0.1853	0.5189	0.1122	0.9058	0.5189	0.6301	0.4818	0.2965	0.7042	0.4077	0.5189	1.000

Table 5. Metal concentrations (mg kg^{-1} dry weight) in the surface sediments of Sığacık Bay and various coastal regions in the current literature.

Area	Pb	Cr	Cu	Zn	Ni	Mn	Fe	Reference
Marmara Sea	10–85	11–654	3–107	33–410	8–1731	100–2610	0.6–7.7 (%)	Algan et al. (2004)
Izmit Bay	23.8–178	57.9–116.1	60.6–139	510–1190	3.4–70.7	-	-	Perkey (2006)
Aegean Sea	20.7–93.0	40.0–154	5.34–86.2	12.9–230	-	171–360	0.80–2.75 (%)	Aloupi and Angelidis (2001)
Izmir Bay	14–113	29–316	-	-	-	-	-	Kucuksezgin et al. (2006)
NW Aegean	52.00	222.00	34	120	146	1378	-	Karageorgis et al. (2005)
Erdek Bay	19–61	11–238	3–52	23.1	8–149	168–746	0.8–4.6 (%)	Balkıs and Çagatay (2001)
Nemrut Bay	22.3–89.4	35.7–98.8	9.6–43.7	75–271	18.1–63.4	222–343	10.507–45.828	Esen et al. (2010)
Izmir Bay	3.1–119	19–316	2.2–109	14–412	11–174	128–942	-	Kucuksezgin et al. (2011)
Izmir Bay	29–82	77–112	33–66	116–196	66–82	491–532	25.800–29.500	Atalar et al. (2013)
Aegean Sea	15–138	16–71	2.7–35	55–358	7.6–100	173–1423	-	Pazi (2011)
Sığacık Bay	10.1–26.2	45–170	9.3–28	22–71	20.2–120.4	244–501	21.700–57.937	Present study

5. Conclusions

Surficial sediment samples were taken from 7 stations in the coastal zone of Sığacık Bay. The study area was generally determined as fine-grained material based on the surficial sediment samples. Statistical analysis demonstrated that there was no available positive correlation between the concentrations of elements, organic carbon, and fine-size (clay and silt). The highest metal concentrations were measured in surficial sediment samples collected near Doğanbey Cape. High Ef values of Pb, Cr, Ni, Co, and As originated from anthropogenic inputs, such as domestic waste, fish farms, which were located in the southwestern part of the bay, rivers, and harbors. The Cf values of Pb, Cr, and Ni were classified as moderately contaminated in the sediments, while the Cf values of Fe, and Zn were also evaluated as moderately contaminated near Doğanbey

Cape, where high Cd values were observed and classified as a considerable degree. Moreover, the concentrations of the element were interpreted by comparing them with the ERL and PEL in order to obtain the origin of contamination in the surface sediments taken from Sığacık Bay. Therefore, the levels of Pb (except for station S4), Cr, Cu, Zn, and Ni were higher than the TEL, while the levels of Cr, Zn (only at stations S1 and S2), and Ni were above the PEL. Additionally, the levels of Cr and Ni were higher than the ERL and ERM in the study area. The Cr and Ni levels were interpreted as being the effects of negative and toxicity inputs. The results of this study indicated that the element concentrations, especially in the surface sediments, were high near the thermal springs and tectonic structures in Doğanbey Cape.

The sediment distribution of the Sığacık Bay coastal region was revealed as a result of this paper. Moreover, the concentration of elements in the surface sediments was assessed in terms of contamination. Accordingly, the levels of elements were found to be high, especially in the western part of Doğanbey Cape. There are similar studies available in the literature on the eastern part of Doğanbey Cape; however, there are no detailed studies about the study area (the western part) in the current literature. This research was of great importance in terms of providing general information about the sediment properties and element concentrations of Sığacık Bay. Information about regional surface currents was needed to interpret deposits in the surface sediments of the bay; however, research concerning regional currents could not be found in the literature. It was concluded and suggested that long-term or annual periodic current measurements should be conducted in Sığacık Bay. This paper provides a baseline of the concentrations of elements in the surface sediments of the bay for future works. In addition, geochemical analysis and oceanographic surveys should be carried out from both sides of Bölge Island (offshore of Doğanbey Cape) and Sığacık Bay, and the possible effects of submarine thermal springs should be investigated in more detail.

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