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Metals/metalloid in Marine Sediments, Bioaccumulating in Macroalgae and a Mussel

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ABSTRACT

The aim of the present work is to broaden our knowledge on the variability of metals and metalloid concentration levels in surface sediments, macroalgae and mollusc. Accordingly, As, Co, Cr, Cu, Mn, Mo, Ni, Pb, and Zn levels in surface sediments, marine macroalgae species (*Ulva intestinalis* and *Ceramium rubrum*) and mollusk (mussel *Mytilus galloprovincialis*) collected from nine stations along the Sürmene Bay, Black Sea, Turkey, have been investigated using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Hence, higher concentration levels of As, Cu, Mn, Pb and Zn have been recorded in the sediments and macroalgae collected from the harbor area, largely exceeding those recorded in previous studies carried out in the Turkish Black Sea. Consequently, sampled sediments from such area have revealed the highest Contamination Factor (Cf) values as well as the highest Contamination Degree (CD) levels, signaling higher ecological risks. Furthermore, U. intestinalis has shown higher accumulation capacity than *C. rubrum* and *M. galloprovincialis*. The Target Hazard Quotient (THQ) and the Hazard Index (HI) have been carried out in order to evaluate the non-carcinogenic health risks posed by metals/metalloid via *M. galloprovincialis* consumption, revealing values below 1 for all sampling sites, indicating thus no adverse effects on human health.

KEYWORDS

Black Sea; *Ceramium rubrum*; mining; *Mytilus galloprovincialis*; *Ulva intestinalis*; Sürmene Bay

1. Introduction

The causes of metal pollution in the marine environment are natural such as weathering, erosion and volcanic eruptions, and anthropogenic activities as the leading causes contaminating the environment through domestic sewage and industrial effluents, agriculture, aquaculture, mining processes discharging metal-containing waste, landfill leachates, as well as secondary precipitation of polluted airborne matter (Nriagu 1989; Vodopivez et al. 2015). Several factors such as mineralogical composition, reduction & oxidation state, sediment texture, adsorption & desorption processes have been known to strongly regulate the distribution and accumulation of metals in marine sediments (Buccolieri et al. 2006). The accumulation of heavy metals in marine sediments can pose threats to human health if transported through the food web (Hapke 1996; Manahan 2000). The intake of heavy metals through consumption of aquatic products can cause serious health disorders if ingested beyond the permitted level (Babel and Kurniawan 2004). Generally, heavy metals accumulate in vital body organs such as kidney, liver, heart, and brain; altered their normal biological functioning (Rehman et al. 2018; Singh et al. 2011).

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According to Phillips (1990), to be considered as appropriate for used as a bioindicator, it is highly recommended that a species should display some properties such as (i) Sessile or sedentary; (ii) Tolerant to high levels of contaminants and wide ranges of salinity, yielding laboratory studies of the kinetics of contaminants; (iii) Abundant in the study area, permitting an easy collect and should provide sufficient amounts of tissue for analysis; and (iiii) A simple correlation between the concentration of the contaminant in the tissues of the organism and the average concentration bioavailable in the environment should be revealed. Accordingly, marine macroalgae and bivalve mollusks fulfill the general prerequisites for a bioindicator. Hence, they have been widely used for the biomonitoring of metal contamination in a given milieu (Phillips 1977; Rainbow 2002; Shulkin, Presley, and Kavun 2003; Villares, Puente, and Carballeira 2001).

The Black Sea receives yearly about 354 km^3 of river water that also transport metals toward the sea (Galatchi and Tudor 2006; Topcuoglu, Kirbasoglu, and Gungor 2002). The metals are also delivered to the Black Sea through direct discharge of municipal, industrial, agricultural, mining wastes, oil, and pollutants of atmospheric origin (Alkan et al. 2015; Topcuoglu, Kirbasoglu, and Gungor 2002). According to Alkan et al. (2015), the sediments collected from the south-eastern region of the Turkish Black Sea have exhibited metal concentrations higher than those of Interim Sediment quality guidelines (ISQG). However, little information is available about the level of different metals in the sediments of the Sürmene bay (Alkan et al. 2015). Moreover, the determination of accumulation process of metals in organisms (i.e. macroalgae) of this area has been more scarcely evaluated compared to other parts of the Black Sea.

In this study, *Ulva intestinalis* (syn. *Enteromorpha intestinalis*), *Ceramium rubrum* (macroalgae), and mussel (*Mytilus galloprovincialis*) were chosen as bioindicators. Accordingly, the aim of this study is: (1) to analyze the level of As, Co, Cr, Cu, Mn, Mo, Ni, Pb, and Zn in sediment and aforementioned biota collected from nine different sites along the Sürmene Bay of the Black Sea, (2) to calculate the biota-sediment accumulation factor (BSAF) and (3) to identify the level of above-mentioned metals/metalloid in mussel *M. galloprovincialis* to investigate public health risks.

2. Material and Methods

2.1. *Sample collection*

Surface sediments (0–5 cm), with biota (macroalgae, *U. intestinalis* and *C. rubrum*; mollusks *M. galloprovincialis*), have been collected during November 2016 from nine stations along the Sürmene Bay, close to Trabzon-Rize highway from Turkey (Figure 1, Table 1), using the Van-Veen grab samplers. It has been revealed that Van-Veen grab samplers, the most commonly used grab samplers, have been used to collect information related to the horizontal surface distribution of sediments. The sampled mussels *M. galloprovincialis* and macroalgae were washed thoroughly with pure water to remove sand and other fouling substances and placed in acid-rinsed polypropylene bags using plastic spatula. All samples were kept in a cooler until they reached the laboratory. After then, they were stored at −20 C until analysis.

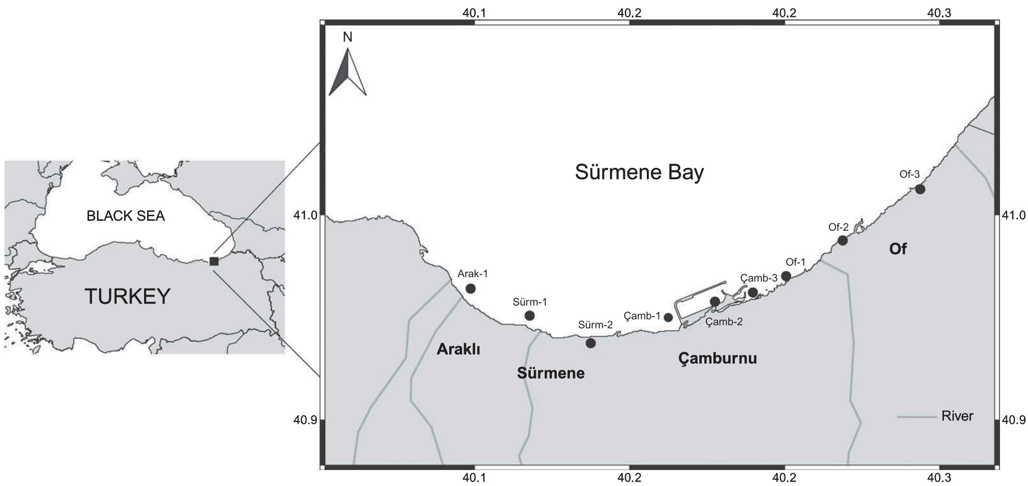

Figure 1. Map of the study area.

2.2. Laboratory work

2.2.1. Sediment Characterization

The sediment samples were wet sieved (2 mm–63 µm) with a vibratory shaker (Retch, Germany) for grain-size analysis and classified according to Udden–Wentworth grain-size classification scheme (Wentworth 1922). The sediment samples were passed through a sieve of 63 µm mesh size for metal/metalloid analysis and 500 µm for total organic carbon (TOC) analysis. After then they dried at 45° C until a constant weight. The modified Walkley-Black titration method was used for TOC determination of sediment (Gaudette et al. 1974). The pH and oxidation reduction potential (ORP) measurements were realized in samples sieved through 2 mm pore size and dried at 105° C with a portable multi-meter (Hach Lange HQ40D) followed by water dilution (1:5) (Jackson 1958).

2.2.2. Mussels and macroalgae

Mytilus galloprovincialis mussels, 30 from each site, of weight ranging 1.2 to 8.1 g, total shell length 25 to 41 mm and height 8 to 13 mm, were collected for the metal analysis. The length range (25–41 mm) is an indication that the mussels *M. galloprovincialis* are smaller than the adult size group (Rosioru 2014). The edible tissues were carefully separated from the hard part to prevent contamination. Pooled samples were used for metal analysis in mussel *M. galloprovincialis* samples. Algal samples were collected by hand at low tide from each site (Figure 1). The tissues and the algal samples were individually dried in a freeze dryer to a constant weight.

2.3. Metal/metalloid analysis

Metal/metalloid analysis of sediment, macroalgae, and mussel *M. galloprovincialis* (soft tissue) were measured with ICP-MS at ACME (Vancouver, BC, Canada) laboratory. AQ251 digestion method was used (with aqua regia, 1:1:1 HNO_3:HCl:H_2O) for sediment samples. Mussel *M. galloprovincialis* and macroalgae samples were digested in HNO_3 then

Table 1. Characterization of selected sampling sites from the Sürmene Bay of the Black Sea in November 2016 and physical-chemical characteristics of sampled sediment.

						General description			
Location	Coordinate	Sample depth (m)	Dry matter content (%)	pH	Organic matter (%)	Carbonate	TOC (%)	ORP (mV)	
Western part									
Arak-1	40°55′35.84″N 40°04′48.47″E	34	99.17 ± 0.17	7.99 ± 0.03	4.89 ± 0.88	10.49 ± 0.31	1.29 ± 0.08	175.67 ± 0.06	Located near the discharge of Küçükdere and Karadere streams. Population: 47.191
Sürm-1	40°54′55.98″N 40°06′50.71″E	11	99.45 ± 0.09	7.65 ± 0.06	2.64 ± 0.24	15.72 ± 0.30	0.37 ± 0.08	172.47 ± 0.12	Located near the discharge of Sürmene stream. Also. partly influenced by abandoned mining area. Population: 25.669
Sürm-2	40°54′50.00″N 40°08′11.12″E	16	99.94 ± 0.01	7.88 ± 0.02	1.29 ± 0.12	17.29 ± 0.14	0.34 ± 0.01	197.27 ± 1.10	
Harbor area									
Çamb-1	40°54′55.64″N 40°10′46.93″E	11	99.68 ± 0.01	8.10 ± 0.03	1.89 ± 0.08	17.61 ± 0.03	0.35 ± 0.14	176.57 ± 0.06	The area has a harbor and is surrounded by an abandoned mining area and a shipyard. The mine named Kutlularmine which was one of the most important volcanogenic massive sulfide (VMS) deposits in Turkey. Population: 1.210
Çamb-2	40°55′17.88″N 40°11′49.65″E	10	99.04 ± 0.23	7.51 ± 0.03	4.24 ± 0.06	17.45 ± 0.15	1.04 ± 0.03	201.20 ± 1.82	
Çamb-3	40°55′28.81″N 40°12′32.12″E	14	99.70 ± 0.00	6.91 ± 0.08	8.27 ± 3.49	17.34 ± 0.37	0.38 ± 0.04	269.50 ± 0.26	
Eastern part									
Of-1	40°55′51.28″N 40°13′53.84″E	12	99.70 ± 0.04	6.91 ± 0.09	8.27 ± 0.29	17.34 ± 0.00	0.38 ± 0.02	269.50 ± 0.31	Located near the discharge of the Solaklı and Iyidere streams. Population: 41.248
Of-2	40°57′03.88″N 40°16′03.32″E	15	99.04 ± 0.07	8.07 ± 0.07	2.89 ± 0.09	18.70 ± 0.08	0.28 ± 0.04	200.00 ± 8.22	
Of-3	40°58′24.66″N 40°18′20.82″E	20	99.24 ± 0.04	8.01 ± 0.03	1.95 ± 0.26	13.17 ± 0.71	0.26 ± 0.02	159.87 ± 0.12	

TOC. Total organic carbon (%). ORP. Oxidation-reduction potential. Arak. Araklı; Sürm. Sürmene; Çamb. Çamburnu aqua regia (VG104). All digested samples were analyzed by ICP-MS for ultralow detection limits. STD ASH-1 and STD DS11 reference materials were used for accuracy test of mussel *M. galloprovincialis* and macroalgae samples and STD OXC129 for the sediment. The accuracy of the sediment, mussel *M. galloprovincialis* and algae metal/metalloid analysis ranged from 92 to 107%, 92 to 102% and 92 to 102%, respectively.

2.4. Sediment quality assessment

The levels of metal contamination in the surface sediments were assessed by calculating contamination factor (C_f), contamination degree (CD), potential ecological risk (PER), and pollution load index (PLI) (Hakanson 1980; Pekey et al. 2004; Savvides et al. 1995; Tomlinson et al. 1980)

2.4.1. Contamination factor (C_f)

The contamination factor (C_f) has been carried out in order to evaluate sediment contamination by each analyzed metal concentration. It has been calculated based on the following equation:

$$C_f = C_m / C_B \tag{1}$$

Whereby, C_m is the level of metal in the sediment, C_B is background levels (Table 2). The computed Cf values have been classified into four categories:

- Low contamination: Cf < 1;
- Moderate contamination: 1 ≤ Cf < 3;
- Considerable contamination: 3 ≤ Cf < 6;
- Very high contamination: Cf ≥ 6

2.4.2. Contamination Degree (CD)

The Contamination Degree (CD) has been estimated based on the summation of the average contamination factors for each analyzed metal. Accordingly, it has been calculated as follows:

$$BAFS = \frac{C_t}{C_s} \tag{2}$$

The computed CD values have been classified into four categories:

- Low degree of contamination: CD < 8;
- Moderate degree of contamination: 8 ≤ CD < 16;
- Considerable degree of contamination: 16 ≤ CD < 32

Table 2. Background levels of analyzed metals referring to various studies carried out in southeastern Black Sea areas.

	As	Co	Cr	Cu	Mn	Ni	Pb	Zn
Concentrations (mg/Kg) (Ergin et al. 1991; Yücesoy and Ergin 1992; Ergül et al. 2008)	5.2	7.1	22.5	22.2	322	11.8	20.2	64.8

- Very high degree of contamination: CD ≥ 32

Contamination factor, considered as a simple and effective tool, has been widely used in monitoring each analyzed metal contamination. Moreover, contamination degree, based on summation of average Cf, has been used to investigate contamination of all analyzed metals at the same time for a given sampling site.

2.4.3. *Potential Ecological Risk (PER)*

The potential ecological risk index (PER) was calculated by:

$$E_f^i = Tr^i \times C_f^i \tag{3}$$

$$C_f^i = \left(\frac{C_s^i}{C_n^i}\right) \tag{4}$$

$$PER = \sum\nolimits_f^i E_f^i \tag{5}$$

where $E^i{}_f$ s the PER for a chemical element i, Tr^i is the biological toxic factor of a chemical element i, with As = 10, Co = Cr = Ni = Pb = 5, Cr = 2 and Zn = 1 (Bahloul et al. 2018; Javed, Ahmad, and Mashiatullah 2018;), C_f^i, C_s^i and C_n^i are the contamination factor, the level of element i in the sediment and the background reference value.

2.4.4. *Pollution Load Index (PLI)*

The pollution Load Index (PLI) was calculated by the following equation (Tomlinson et al. 1980;):

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

where (n) is the number of metals taken into consideration and CF is the contamination factor.

The computed PLI values were classified into six categories (Tomlinson et al. 1980): Six classes of PLI were proposed by Tomlinson et al. (1980):

- Unpolluted: 0 < PLI ≤ 1;
- Unpolluted to moderately polluted: 1 < PLI ≤ 2;
- Moderately polluted: 2 < PLI ≤ 3;
- Moderately to highly polluted: 3 < PLI ≤ 4;
- Highly polluted: 4 < PLI ≤ 5;
- Very highly polluted: PLI > 5

2.5. *Health risk assessment*

The dry weight of metal/metalloid concentration (mg kg^{-1}) was converted to wet weight using the method proposed by Cresson et al. (2017) prior to calculate the target hazard quotient (THQ) and hazard index (HI). The conversion factor was 9.4.

THQ was calculated as described by Dalipi et al. (2015):

$$\mathrm{THQ} = \frac{\mathrm{Efr} \times \mathrm{EDtot} \times \mathrm{Cw} \times \mathrm{FIR}}{\mathrm{RfDo} \times \mathrm{BWa} \times \mathrm{ATn}} \times 0.001 \quad (7)$$

where Efr is the exposure frequency (365 days/year), EDtot is the exposure duration (70 years), C is the metal/metalloid concentration (mg kg^{-1} wet weight) in a sample, FIR is the average daily consumption of mussel *M. galloprovincialis*, which was kept as 1.01 g/per person/d (daily mollusk consumption in Turkey), referring to Bat et al. (2018). On the other side, RfDo is the oral reference doses (mg/kg/day) of metals/metalloid (As, 3.0×10^{-4}; Co, 3.0×10^{-4}; Cr, 3.0×10^{-3}; Cu, 5.0×10^{-3}; Mn, 1.4×10^{-1}; Mo, 5.0×10^{-3}; Ni, 2.0×10^{-2}; Pb, 2.0×10^{-3}, and Zn 3.0×10^{-1}) were taken from USEPA (2018), BWa is the average body weight (kg) which was taken as 72.5 kg for a Turkish person (Gedik 2018), and ATn is the average exposure for non-carcinogens in a year (365 days/year × 70 years). THQ value greater than 1 evince a potential health risk, and indicate that the local inhabitants are in a level of concern interval (USEPA 2018).

Hazard index was calculated as described by Jia et al. (2016):

$$\mathrm{HI} = \mathrm{THQ_{As}} + \mathrm{THQ_{Co}} + \mathrm{THQ_{Cr}} + \mathrm{THQ_{Cu}} + \mathrm{THQ_{Mn}} + \mathrm{THQ_{Mo}} + \mathrm{THQ_{Ni}} + \mathrm{THQ_{Pb}} + \mathrm{THQ_{Zn}} \quad (8)$$

2.6. *Bioaccumulation of metals/metalloid in macroalgae and mussel*

Biota-sediment accumulation factors (BSAF) were used to evaluate the efficiency of metal/metalloid bioaccumulation in macroalgae and mussel *M. galloprovincialis* Burkhard (2009). BASFS was calculated by following formula:

$$CD = \sum_{i=1}^{n} CF_i \quad (9)$$

C_t is the metal/metalloid concentration in biota (mg kg^{-1}) and C_s is metal/metalloid concentration in sediment (mg kg^{-1}).

2.7. *Statistical analyses*

Each reported result is the average of three analyses and provided as mean ± SD. The transformation of data (log + 0.1) was done prior to data analyses. The Pearson correlation was used to evaluate a direct (a positive correlation) or an inverse relationship (a negative correlation) between environmental parameters (e.g. depth, organic matter, ORP, TOC) and metal/metalloid concentrations in sediments and biota. Accumulation affinity behaviors (similarities and dissimilarities) of analyzed metals in each sample category (sediments, mussels, and macroalgae) have been investigated through obtained dendrograms from cluster analysis applied to all data.

Also, the calculated BSAF values of studied metals/metalloids for *Ceramium rubrum, Ulva intestinalis* (macroalgae), and mussel *M. galloprovincialis* were compared using One-way ANOSIM and SIMPER tests to determine their similarities. The R v3.4.4 was used for Pearson correlation and cluster analyses while PAST 3.14 was used to run ANOSIM and SIMPER tests.

3. Results and Discussion

3.1. Physical and chemical characterization of sediments and grain size

The mean values (±SD) of dry matter content (%), water content (%), pH, organic matter, carbonate, TOC, and ORP (mV) in sediments are presented in Table 1. The highest values of pH (>8.0) were recorded at Çamb-1 (harbor area), Of-2, and Of-3 (Eastern area) while the lowest pH was found at Çamb-3 and Of-1. Generally, metals are more mobile when present in acidic environment resulting in increased metal concentrations in soil/sediments and water column (Akan et al. 2013). The lowest organic matter (<2.0%) was recorded at Sürm-2 and Of-3 while the mean maximum values were recorded at Çamb-3 (harbor area) and Of-1. The organic matter tends to absorb metals and plays an important role in the accumulation of metals in the sediment (Saher and Siddiqui 2016; Yona, Fuad, and Hidayati 2018). The greater values of ORP were recorded at Çamb-3 and Of-1 (Table 1). Generally, the solubility of metals in sediments increase with rise an ORP value leading to metal release from the sediment (Kelderman and Osman 2007; Popenda 2014).

The metal/metalloid concentrations can vary according to grain size and their highest concentrations (both natural and contaminant metals/metalloid) are generally found in the very fine-grained muddy sediments (De Groot, Zschuppel, and Salomons 1982). In the present study, silt and clay (mud, <63 μm), very fine sand (63–125 μm), and fine sand (125–250 μm) were the dominant fractions in the sediments sampled from the Sürmene Bay of the Black Sea (Table 3). Mud was the dominant fraction (>43%) in sediments collected from the Araklı (Arak-1), Sürmene (Sürm-1) and Çamburunu (Çamb-2). The western part of the study area had relatively a higher fraction of very fine sand. Consequently, due to the favorable grain size, pH, level of ORP and organic matter of the harbor and eastern part (i.e. Çamb-3 and Of-1) of the study area for metal/metalloid accumulation, these areas relatively had metals/metalloid with a higher concentration than other sites (Table 3).

3.2. Metal/metalloid concentration in sediment and biota

The mean (±SD) metal/metalloid concentration of sediments, marine macroalgae (*U. intestinalis* and *C. rubrum*), and mussel *M. galloprovincialis* are presented in Table 4. Manganese, Zn, and Cu were the first three metals present thoroughly with the highest concentration in sediments as well as in biota. In the present study, the mean maximum metal/metalloid concentration was decreased in the following order:

(i) Sediment: Zn > Cu > As > Mn > Pb > Cr > Co > Ni > Mo with 4259.5, 3107.3, 557.7, 446.9, 208.2, 40.2, 32.8, 23.4, and 4.9 mg kg-1 concentration, respectively.
(ii) *Ceramium rubrum*: Mn > Zn > Cu > As > Cr > Ni > Pb > Co > Mo with 223.1, 52.6, 43.6, 25.4, 14.4, 7.3, 3.5, 1.5, and 0.4 mg kg^{-1} (dry weight) concentration, respectively.
(iii) *Ulva intestinalis*: Mn > Cu > Zn > Cr > As > Pb > Ni > Co > Mo with 856.9, 493.0, 351.5, 39.4, 36.2, 18.9, 15.8, 9.1, and 1.5 mg kg^{-1} (dry weight) concentration, respectively.
(iv) Mussel (*M. galloprovincialis*): Zn > Cu > Mn > Cr > As > Ni > Pb > Co > Mo with 478.4, 267.0, 152.0, 16.1, 7.5, 7.1, 5.9, 2.7, and 0.7 mg kg^{-1} (dry weight) concentration, respectively.

Table 3. Grain size distribution (%) of the surface sediments collected from the Sürmene Bay of the Black Sea in November 2016.

	SEDIMENTS GRAIN SIZE						
	Granule	Very Coarse sand	Coarse sand	Medium sand	Fine sand	Very fine sand	Silt + Clay
STATION	<2 mm	1-2 mm	500 µm–1 mm	250 µm–500 µm	125 µm–250 µm	63 µm–125 µm	<63 µm
Western part							
Arak-1	0.02	0.02	0.03	0.11	1.16	10.66	88.00
Sürm-1	0.12	0.01	0.14	0.16	7.93	48.64	43.01
Sürm-2	0.41	0.04	0.04	0.20	32.81	46.60	19.91
Harbor area							
Çamb-1	0.68	0.08	0.07	0.50	42.40	47.51	8.76
Çamb-2	0.17	0.09	0.05	0.22	5.10	8.64	85.73
Çamb-3	0.15	0.01	0.05	2.25	33.49	40.69	23.36
Eastern part							
Of-1	12.68	0.27	0.18	1.82	39.83	40.53	4.69
Of-2	10.40	0.02	0.04	0.57	21.62	52.87	14.48
Of-3	0.63	0.01	0.10	3.11	54.14	31.48	10.53

Arak. Araklı; Sürm. Sürmene; Çamb. Çamburnu

3.3. *Sediment*

In this study, the overall highest concentrations of the studied metals/metalloid (except Mn) were recorded in the sediment than biota. Moreover, the highest concentration of metals/metalloid in sediment was recorded in samples acquired from the harbor area except Mn and Ni. Manganese and Ni were present in higher concentrations in the eastern part of the studied area (Of-2 and Of-3). Such areas were demonstrated to be under the impact of streams that flow in these areas. According to Alkan et al. (2015) the concentrations of metals considerably differ across the evaluated regions indicating the influence of several environmental factors such as local geological and hydrological conditions as well as industrial activities. The highest concentration of metals/metalloids in the harbor area compared to western and eastern parts of the studied area suggests a higher delivery of metals/metalloids to this area.

Comparison with literature values, the present study revealed that the harbor area (Çamburnu) had much higher concentrations of As, Cu, Mn, Pb, and Zn than other parts of the Turkish Black Sea (Çagatay, Saltoglu, and Gedik 1987; Gedik and Boran 2013; Topcuoglu, Kirbasoglu, and Gungor 2002; Topcuoğlu, Kirbaşoğlu, and Yilmaz 2004). These high concentrations likely correspond to the impact of copper mines in the region and an increase in anthropogenic pollutant inputs (Alkan et al. 2015; Al-Mur, Quicksall, and Al-Ansari 2017). Whereas, lower concentrations of Co, Cr, and Ni were observed in the present study than other parts of Turkish Black Sea (Ergül et al. 2008; Topcuoglu, Kirbasoglu, and Gungor 2002; Topcuoğlu, Kirbaşoğlu, and Yilmaz 2004).

3.3.1. *Contamination factor*

Calculated contamination factors as well as contamination degrees of all analyzed metals in sediments collected from selected sites have been summarized in Table 5, showing significant fluctuations reflecting different contamination levels.

In general, CF values were ranged between 0.63 and 139.97 indicating thus a low to very high contamination factor. In fact, the highest CF level was obtained for Cu and the

Table 4. Summary of mean (± SD.) of metals/metalloid concentration (mg kg^{-1} dry weight) in surface sediment (0–5 cm). *Ulva intestinalis. Ceramium rubrum* (macroalgae) and mussel (*Mytilus galloprovincialis*) from the Sürmene Bay of the Black Sea in November 2016.

	Western part			Harbor area			Eastern part		
	ARAKLI	SÜRMENE		ÇAMBURNU			OF		
Metals/metalloid	Arak-1	Sürm-1	Sürm –2	Çamb-1	Çamb-2	Çamb-3	Of-1	Of-2	Of-3
As									
Sediment	6.62 ± 0.01	6.65 ± 0.02	6.57 ± 0.03	9.14 ± 0.01	93.8 ± 0.01	557.7 ± 0.07	69.20 ± 0.02	31.92 ± 0.04	16.27 ± 1.14
U. intestinalis	5.50 ± 0.02	3.58 ± 0.02	3.43 ± 0.03	4.11 ± 0.01	7.32 ± 0.02	36.22 ± 0.02	7.32 ± 0.03	*	4.44 ± 0.03
C. rubrum	2.63 ± 0.04	2.50 ± 0.02	2.42 ± 0.02	2.72 ± 0.02	3.81 ± 0.01	*	25.36 ± 0.04	25.05 ± 2.82	3.33 ± 0.03
Med. mussel	7.12 ± 0.02	6.52 ± 0.02	6.90 ± 0.02	5.14 ± 0.07	5.06 ± 0.05	7.48 ± 0.03	6.67 ± 0.15	6.52 ± 0.02	4.77 ± 0.15
Co									
Sediment	10.13 ± 0.01	12.08 ± 0.13	8.89 ± 0.08	10.12 ± 0.08	12.26 ± 0.02	32.80 ± 0.03	16.24 ± 0.01	13.59 ± 0.11	13.62 ± 0.02
U. intestinalis	3.44 ± 0.10	2.99 ± 0.01	0.41 ± 0.01	2.11 ± 0.01	6.12 ± 0.02	9.11 ± 0.01	3.82 ± 0.02	*	0.62 ± 0.02
C. rubrum	1.32 ± 0.02	0.77 ± 0.09	0.80 ± 0.02	1.50 ± 0.02	1.01 ± 0.01	*	0.31 ± 0.01	0.32 ± 0.02	1.53 ± 0.03
Med. mussel	1.61 ± 0.02	1.43 ± 0.03	2.23 ± 0.29	0.51 ± 0.02	1.01 ± 0.03	1.42 ± 0.02	2.17 ± 0.32	2.65 ± 0.14	1.83 ± 0.06
Cr									
Sediment	20.14 ± 0.15	16.28 ± 0.27	19.97 ± 0.09	17.85 ± 0.08	40.22 ± 0.10	26.69 ± 0.17	35.33 ± 0.18	37.55 ± 0.57	34.48 ± 0.04
U. intestinalis	16.2 ± 0.40	29.36 ± 0.92	1.80 ± 0.22	13.43 ± 0.12	39.41 ± 0.45	5.67 ± 0.12	18.22 ± 0.09	*	2.84 ± 0.09
C. rubrum	3.66 ± 0.17	3.24 ± 0.40	5.98 ± 0.02	14.43 ± 0.45	5.15 ± 0.15	*	1.45 ± 0.06	2.91 ± 0.06	5.39 ± 0.19
Med. mussel	3.97 ± 0.09	3.00 ± 0.18	3.58 ± 0.60	1.01 ± 0.06	4.44 ± 0.41	2.29 ± 0.04	4.57 ± 0.25	16.12 ± 0.14	14.47 ± 0.15
Cu									
Sediment	29.48 ± 0.07	31.23 ± 0.02	29.39 ± 0.04	39.69 ± 1.14	820.86 ± 0.03	3107.26 ± 0.06	389.02 ± 0.01	214.97 ± 0.07	112.93 ± 1.97
U. intestinalis	14.37 ± 0.01	8.94 ± 0.04	7.20 ± 0.06	8.05 ± 0.02	15.89 ± 0.08	492.95 ± 0.09	27.06 ± 0.01	*	10.02 ± 0.01
C. rubrum	10.27 ± 0.21	8.74 ± 0.02	13.08 ± 0.06	10.38 ± 0.17	10.01 ± 0.02	*	43.6 ± 0.02	36.80 ± 0.08	19.37 ± 0.11
Med. mussel	11.78 ± 0.01	11.26 ± 0.02	10.59 ± 0.06	24.67 ± 0.02	14.30 ± 0.02	267.01 ± 0.06	197.27 ± 1.56	29.41 ± 0.13	17.13 ± 0.21
Mn									
Sediment	311.55 ± 0.09	402.64 ± 0.45	343.19 ± 0.02	383.91 ± 0.11	336.24 ± 0.10	204.41 ± 0.08	382.40 ± 0.08	431.95 ± 0.03	446.87 ± 0.03
U. intestinalis	231.07 ± 0.12	150.92 ± 0.07	49.04 ± 0.17	166.18 ± 0.16	395.10 ± 0.09	856.92 ± 0.12	304.00 ± 0.12	*	62.92 ± 0.12
C. rubrum	129.18 ± 0.16	86.12 ± 0.12	130.10 ± 0.11	108.12 ± 0.12	138.13 ± 0.12	*	41.14 ± 0.12	79.04 ± 0.07	223.11 ± 0.18
Med. mussel	31.11 ± 0.11	56.96 ± 0.06	52.04 ± 0.07	26.39 ± 0.07	31.12 ± 0.95	36.82 ± 0.22	55.13 ± 0.21	151.96 ± 0.06	103.63 ± 0.21
Mo									
Sediment	0.35 ± 0.03	0.46 ± 0.01	0.54 ± 0.02	0.54 ± 0.01	4.86 ± 0.01	20.18 ± 0.16	1.79 ± 0.02	0.74 ± 0.02	0.85 ± 0.01
U. intestinalis	0.54 ± 0.26	0.39 ± 0.02	0.13 ± 0.01	0.26 ± 0.01	0.92 ± 0.02	1.47 ± 0.02	0.37 ± 0.01	*	0.17 ± 0.02
C. rubrum	0.19 ± 0.01	0.18 ± 0.01	0.23 ± 0.02	0.35 ± 0.02	0.28 ± 0.02	*	0.16 ± 0.01	0.18 ± 0.01	0.28 ± 0.02
Med. mussel	0.72 ± 0.02	0.73 ± 0.03	0.68 ± 0.03	0.53 ± 0.05	0.63 ± 0.04	0.52 ± 0.02	0.52 ± 0.02	0.72 ± 0.02	0.59 ± 0.03
Ni									
Sediment	13.51 ± 0.04	12.15 ± 0.01	12.75 ± 0.05	10.82 ± 0.03	12.51 ± 0.06	11.72 ± 0.05	15.01 ± 0.03	23.43 ± 0.02	19.21 ± 0.03
U. intestinalis	7.72 ± 0.02	11.73 ± 0.10	3.33 ± 0.06	6.25 ± 0.06	15.75 ± 0.12	7.39 ± 0.07	7.92 ± 0.05	*	2.31 ± 0.02
C. rubrum	3.52 ± 0.03	4.79 ± 0.1	4.21 ± 0.02	7.26 ± 0.04	4.74 ± 0.04	*	2.21 ± 0.02	4.53 ± 0.04	7.28 ± 0.05
Med. mussel	3.49 ± 0.02	4.39 ± 0.14	3.83 ± 0.03	1.17 ± 0.01	2.01 ± 0.02	2.53 ± 0.04	4.40 ± 0.20	7.12 ± 0.02	6.8 ± 0.1

Pb									
Sediment	22.91 ± 0.03	21.05 ± 0.03	17.26 ± 0.02	17.86 ± 0.01	132.65 ± 0.04	208.19 ± 0.01	48.35 ± 0.34	26.82 ± 0.08	26.42 ± 0.04
U. intestinalis	5.87 ± 0.06	3.37 ± 0.06	0.90 ± 0.03	2.65 ± 0.02	7.65 ± 0.01	18.85 ± 0.06	4.64 ± 0.02	*	1.23 ± 0.08
C. rubrum	2.08 ± 0.01	2.03 ± 0.02	3.52 ± 0.01	2.67 ± 0.02	1.50 ± 0.02	*	0.73 ± 0.04	0.51 ± 0.02	3.35 ± 0.01
Med. mussel	1.55 ± 0.01	2.06 ± 0.01	2.04 ± 0.01	2.06 ± 0.10	1.49 ± 0.01	3.05 ± 0.02	4.53 ± 0.31	4.38 ± 0.01	5.93 ± 0.15
Zn									
Sediment	106.34 ± 0.02	109.39 ± 0.15	123.58 ± 0.01	138.67 ± 0.04	1409.64 ± 0.07	4259.46 ± 0.01	830.57 ± 0.03	461.14 ± 0.03	265.62 ± 0.08
U. intestinalis	32.43 ± 0.03	23.40 ± 0.18	13.48 ± 0.10	21.12 ± 0.03	49.70 ± 0.02	351.52 ± 0.03	43.92 ± 0.03	*	28.20 ± 0.16
C. rubrum	17.90 ± 0.01	23.72 ± 0.17	32.23 ± 0.09	15.79 ± 0.01	14.24 ± 0.10	*	52.62 ± 0.02	31.34 ± 0.03	42.72 ± 0.02
Med. mussel	271.94 ± 0.03	243.34 ± 0.20	353.57 ± 0.58	155.99 ± 28.84	387.09 ± 0.12	478.42 ± 0.11	409.70 ± 0.70	406.33 ± 0.04	379.60 ± 0.98

***"Not determined"**

Table 5. Calculated Contamination Factor (Cf), Contamination Degree (CD) and Pollution Load Index (PLI).

	Contamination factor (CF)								Contamination Degree (CD)		Pollution Load Index (PLI)	
Stations	As	Co	Cr	Cu	Mn	Ni	Pb	Zn	Values	Classification	Values	Classification
Arak 1	1.27	1.43	0.90	1.33	0.97	1.14	1.13	1.64	**10**	**Moderate**	**5**	**Very highly polluted**
Sürm 1	1.28	1.70	0.72	1.41	1.25	1.03	1.04	1.69	**10**	**Moderate**	**6**	**Very highly polluted**
Sürm 2	1.26	1.25	0.89	1.32	1.07	1.08	0.85	1.91	**10**	**Moderate**	**4**	**Highly polluted**
Camb 1	1.76	1.42	0.79	1.79	1.19	0.92	0.88	2.14	**11**	**Moderate**	**8**	**Very highly polluted**
Camb 2	18.04	1.73	1.79	36.98	1.04	1.06	6.57	21.75	**89**	**Very high**	**368,978**	**Very highly polluted**
Camb 3	107.25	4.62	1.19	139.97	0.63	0.99	10.31	65.73	**331**	**Very high**	**39,838,398**	**Very highly polluted**
Of 1	13.31	2.29	1.57	17.52	1.19	1.27	2.39	12.82	**52**	**Very high**	**43,973**	**Very highly polluted**
Of 2	6.14	1.91	1.67	9.68	1.34	1.99	1.33	7.12	**31**	**Considerable**	**5415**	**Very highly polluted**
Of 3	3.13	1.92	1.53	5.09	1.39	1.63	1.31	4.10	**20**	**Considerable**	**642**	**Very highly polluted**

lowest one was obtained for Mn. Both of them have been obtained in the case study of sediments sampled from Camb 3. All analyzed metals have shown distinct CF values, indicating diverse levels of contamination of the sampled sediments. Based on average CF values, the sampled sediments may be considered to be contaminated by the selected metals in the following order: Cu > As > Zn > Pb > Co > Ni > Cr > Mn. For all sampled sediments, CF levels in the case of Mn, Ni, and Cr have never exceeded 3, indicating thus low to moderate contamination. Contrary, the sediments sampled from Camb 2, Camb 3 have exhibited very high CF levels in the case of Pb, on the one hand, and in the case of As, Cu, and Zn, sediments sampled from Camb 2, Camb 3, Of 1, and Of 2 have shown very high CF levels, on the other hand, suggesting high pollution level due to anthropogenic activities (sewage effluents, fishing activities, damaged ships and boats, human refuse, shipping, transportation, fuel smuggling, and the industrial facilities).

The spatial distribution of contamination level (Table 6) for the selected metals has shown that:

- Sediments sampled from Arak 1, Sürm 1, Sürm 2, and Camb 1 showed low to moderate contamination level for all analyzed metals;
- Sediments sampled from Camb 2, Camb 3, Of 1, Of 2, and Of 3 showed moderate through considerable to very high contamination level for all analyzed metals;

3.3.2. *Contamination degree*

Computed contamination degree for all analyzed elements in the case study of different sampled sediments (Table 5) has revealed that:

- In the case study of Arak 1, Sürm 1, Sürm 2, and Camb 1 sampled sediments have revealed a moderate degree of contamination;
- Sampled sediments form Of 2 and Of 3 have shown a considerable degree of contamination;
- For Camb 2, Camb 3, and Of 1, collected sediments have exhibited a very high degree of contamination indicating alarming anthropogenic contamination.

Table 6. Spatial distribution of contamination level for all selected metals.

Analyzed Metal/ Contamination	Low (CF < 1)	Moderate (1 ≤ CF < 3)	Considerable (3 ≤ CF < 6)	Very high (CF ≥ 6)
As	x	**Arak1/Sürm 1/Sürm 2/Camb 1**	**Of3**	**Camb 2/Camb 3**
Co	x	**Arak 1/Sürm 1/Sürm 2/Camb 1/ Camb 2/Of 2/Of 3**	**Camb 3**	x
Cr	**Arak1/Sürm 1/ Sürm2/Camb 1**	**Camb 2/Camb 3/Of 1/Of 2/Of 3**	**x**	x
Cu	x	**Arak 1/Sürm 1/Sürm 2/Camb 1**	**Of 3**	**Camb 3/Of 1/Of 2**
Mn	**Arak 1/Camb 3**	**Sürm 1/Sürm 2/Camb 1/Camb 2/ Of 1/Of 2/Of 3**	**x**	x
Ni	**Camb 1/Camb 3**	**Arak 1/Sürm 1/Sürm 2/Camb 2/ Of 1/Of 2/Of 3**	**x**	x
Pb	**Sürm 2/Camb 1**	**Arak 1/Sürm 1/Of 1/Of 2/Of 3**	**x**	**Camb 2/Camb 3**
Zn	x	**Arak 1/Sürm 1/Sürm 2/Camb 1**	**Of 3**	**Camb 2/Camb 3/ Of 1/Of 2**

3.3.3. *Potential ecological risk*

The results of evaluation on potential ecological risk factor (Er) and the potential ecological risk index (PER) are summarized in Table 7.

The potential ecological risk coefficient (Er) of As, Co, Cr, Cu, Mn, Ni, Pb, and Zn ranged between 0.63 and 1072, indicating low to very high ecological risk, respectively. In fact, the individually potential ecological risk factors for Mn, Ni and Cr were lower than 40, belonging to low ecological risk in all sampled sediments. In the case study of Pb and Zn, calculated potential ecological risk showed moderate risk in surface sediments collected from "Camb 3" and low ecological risk in all remaining sites. However, the potential ecological risk factors of As and Cu were higher than 600 in surface sediments sampled from "Camb 3" signaling the highest ecological risk. These metals were showed also, high, considerable, and moderate ecological risks in the case study of sampled sediments from "Camb 2," "Of 1," and "Of 2", respectively. For the other remaining sites, As and Cu showed low ecological risk.

The total ecological risk index (RI) of seven heavy metals in the study sites ranged between 10.07 (in the case of Mn) and 1534.38 (in the case of As) thus falling within the class of low (Mn, Cr, Ni, Pb, and Zn) to very high ecological risk (Cu and As). The order of total potential ecological risk coefficient (RI) of heavy metals in sampled surface sediments was: As > Cu > Pb > Zn > Ni > Cr > Mn.

3.3.4. *Pollution load index*

The computed values of Pollution Load Index (PLI) (Table 5) for all analyzed metals revealed that surface sediments in Sürmene bay, Black Sea, Turkey were highly to very highly polluted suggesting thus the impact of anthropogenic activities in the study area.

The order of PLI of heavy metals in sampled surface sediments was: Camb 3 > Camb 2 > Of 1 > Of 2 > Of 3 > Camb 1 > Sürm 2 > Arak 1 > Sürm 2.

3.4. *Marine macroalgae*

3.4.1. *Metal concentrations*

Ulva intestinalis had higher concentrations of metals/metalloid than *C. rubrum* which is in line with the findings of Villares, Puente, and Carballeira (2001) and Akcali and Kucuksezgin (2011) about the high susceptible of *U. intestinalis* to contamination. Similar to sediment, the

Table 7. Calculated values of Potential Ecological Risk factor (ER) and Potential Ecological Risk Index (PER).

		Potential ecological risk factor (ER)							
Stations	Indices	As	Co	Cr	Cu	Mn	Ni	Pb	Zn
Arak 1	**ER**	12.72	50.65	1.79	6.64	0.97	5.72	5.67	1.64
Sürm 1	**ER**	12.79	60.38	1.45	7.03	1.25	5.15	5.21	1.69
Sürm 2	**ER**	12.64	44.43	1.78	6.62	1.07	5.40	4.27	1.91
Camb 1	**ER**	17.58	50.58	1.59	8.94	1.19	4.58	4.42	2.14
Camb 2	**ER**	180.38	61.28	3.58	184.88	1.04	5.30	32.83	21.75
Camb 3	**ER**	1072.51	164.02	2.37	699.83	0.63	4.97	51.53	65.73
Of 1	**ER**	133.07	81.20	3.14	87.62	1.19	6.36	11.97	12.82
Of 2	**ER**	61.39	67.95	3.34	48.42	1.34	9.93	6.64	7.12
Of 3	**ER**	31.29	68.12	3.06	25.43	1.39	8.14	6.54	4.10
PER	**ΣER**	**1534.38**	**648.62**	**22.09**	**1075.41**	**10.07**	**55.55**	**129.09**	**118.90**

highest concentrations of metals/metalloids were found in *U. intestinalis* sampled from the harbor area. The present study reported a higher concentration of Ni, Pb and Zn in *U. intestinalis* than Çulha et al. (2013) for Ordu, Samsun, and Trabzon. Excluding the harbor area, a higher concentration of Zn from El – Mex Bay (Egypt) and Romanian Black Sea coast was recorded for *U. intestinalis* (Mohamed and Khaled 2005; Trifan et al. 2015). Also, a much higher concentration of As and Cr in *U. intestinalis* was reported from Delmarva Peninsula by Chaudhuri et al. (2007).

For *C. rubrum*, the highest mean concentration of Mn, Zn, Cu, As, Ni, and Co were recorded from the eastern zone (Of-9 and Of-7) while Cr and Mo in the harbor area (Çamb-1). The highest mean concentration of Pb in *C. rubrum* was found in the samples collected from the western zone of the study area (Sürm-2). The concentrations of Co, Cr, Cu, Mn, Ni, Pb, and Zn in *C. rubrum* from Araklı, Sürmene, Çamburnu and Of (present study) were relatively lower than Sinop (Topcuoğlu et al. 2003). Also, Tuzen et al. (2009) and Çulha et al. (2013) reported a higher concentration of Co and Cr in *C. rubrum* from Turkish Black Sea coast than the present study. However, *C. rubrum* collected from Aegean Sea (Sawidis et al. 2001) and Romanian Black Sea (Cadar et al. 2018; Lupsor et al. 2009) had lower concentrations of Cu, Mn, Pb, and Zn than the present study.

3.5. *Mussel*

3.5.1. *Metal concentrations*

In contrast to macroalgae, mussel *M. galloprovincialis* collected from the harbor area had lower concentrations of studied elements except Zn, Cu, and As. Accordingly, the highest concentrations of Zn, Cu, and As were recorded in *M. galloprovincialis* sampled from the harbor area (Çamb-3). Manganese, Cr, Ni, Pb, and Co in *M. galloprovincialis* with highest concentration levels were found in sampled collected in the eastern part of the study area (Of-8 and Of-9). The Mo with its highest mean concentration was recorded in the western zone from Sürmene (Sürm-2). It is noteworthy that apart from metal concentration in sediments, their bioavailability and uptake were a complex function of many factors including water pH, redox potential, temperature, hardness, nutrients concentration, total organic content (both particulate and dissolved fractions). Moreover, both the aqueous chemistry and the physiology of the living organisms could be important in affecting metal bioavailability. Furthermore, such difference in registered concentration levels of analyzed elements in mussels *M. galloprovincialis* and macroalgae may indicate that the specimens in our study were still at an intensive development stage and had high metabolic demand on essential elements that resulted in a high capacity to accumulate Mn, Zn, and Cu in their tissues (Rzymski et al. 2014). Consequently, bioaccumulation of heavy metals in aquatic organisms such as mussels *M. galloprovincialis* depends not only on environmental concentrations but also on a variety of biological and environmental factors (Mubiana and Blust 2007).

In this study, the presence of Zn, Cu, and Mn as the first three metals with a higher concentration is in line with the findings of Gedik (2018) for Artvin, Giresun, Rize, and Trabzon. Except Ni, the concentration of As, Co, Cr, Cu, Mn, and Zn in mussel *M. galloprovincialis* were relatively higher than the Çulha et al. (2017), Belivermiş, Kılıç, and Çotuk (2016) and Topcuoglu, Kirbasoglu, and Gungor (2002) values reported from different regions of the Turkish Black Sea. In the present study, the concentration of Ni was found relatively higher (except the harbor area) than Gedik (2018)'s values (converted to dry weight) for Artvin, Giresun, Rize, and Trabzon.

3.5.2. *Health risks assessments*

THQ and HI methods were used to assess the non-carcinogenic health risks posed by metals/metalloid via mussel *M. galloprovincialis* consumption. These methods are convenient for the evaluation of the non-carcinogenic health risks from the ingestion of chemical elements via seafood consumption (Zhelyazkov et al. 2018). The estimated values of THQ and HI for studied metals/metalloid are provided in Table 8. The THQ and HI values recorded for all the stations were below 1 indicating no adverse effects on human health for continuous consumption of mussel *M. galloprovincialis* for 70 years. This result is in line with the findings of Belivermiş, Kılıç, and Çotuk (2016) and Gedik (2018) for mussel *M. galloprovincialis* caught in Turkish Black Sea. Belivermiş, Kılıç, and Çotuk (2016) assessed the non-carcinogenic health risks of chemical elements (Ag, Al, As, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Sn, V, and Zn) by estimated daily intakes (EDI), while Gedik (2018) used bioaccessibility of Cd, Cu, Zn, Mn, Cr, Pb, and Ni. The results of the present study were also in line with those of Zhelyazkov et al. (2018) with respect to low THQ for Pb (0.0014), Cd (0.0032), and Hg (0.0006) in mussel *M. galloprovincialis* caught in the Varna Bay, Bulgarian Black Sea.

3.6. *Pearson correlation*

The correlation sampling depth and metals/metalloid concentration in sediments and marine macroalgae was mostly negative, while it is positively correlated to metals/metalloid concentration (except Cu) in mussel *M. galloprovincialis* but their correlations were statistically not significant (Table 9). The metals/metalloid concentration (As, Co, Cr, Cu, Mo, Pb, and Zn) in sediments increased with increasing its organic matter content and correlation between As, Co, Cu, Pb, and Zn and organic matter were significantly positive. A similar trend of correlations was observed between metals/metalloid concentration and ORP in sediments (Table 9). The strong correlation between the organic matter and metals/metalloid (particularly in sediment) indicated that they share common sources of

Table 8. Target hazard quotient (THQ) and corresponding Hazard index (HI) for analyzed metals and metalloid from consumption of mussel collected during November 2016 from the Sürmene Bay of the Black Sea.

	Target hazard quotient (THQ)									
Stations	As	Co	Cr	Cu	Mn	Mo	Ni	Pb	Zn	Hazard index (HI)
Western part										
Arak-1	0.035	0.008	0.002	0.003	0.000	0.000	0.000	0.001	0.001	0.052
Sürm-1	0.032	0.007	0.001	0.003	0.001	0.000	0.000	0.002	0.001	0.048
Sürm −2	0.034	0.011	0.002	0.003	0.001	0.000	0.000	0.002	0.002	0.054
Harbor area										
Çamb-1	0.025	0.003	0.000	0.007	0.000	0.000	0.000	0.002	0.001	0.038
Çamb-2	0.025	0.005	0.002	0.004	0.000	0.000	0.000	0.001	0.002	0.040
Çamb-3	0.037	0.007	0.001	0.079	0.000	0.000	0.000	0.002	0.002	0.129
Eastern part										
Of-1	0.033	0.011	0.002	0.058	0.001	0.000	0.000	0.003	0.002	0.110
Of-2	0.032	0.013	0.008	0.009	0.002	0.000	0.001	0.003	0.002	0.069
Of-3	0.023	0.009	0.007	0.005	0.001	0.000	0.001	0.004	0.002	0.053

Table 9. Pearson correlation between environmental parameters and metals/metalloid levels in sediments and biota sampled from the Sürmene Bay of the Black Sea in November 2016. The symbol (*) indicates significant correlations at the level of 0.05.

					`Marine macroalgae								Mollusks			
	Sediment				*Ulva intestinalis*				*Ceramium rubrum*				*Mytilus galloprovincialis*			
Metals/metalloid	Depth	OM	ORP	TOC	Depth	OM	ORP	TOC	Depth	OM	ORP	TOC	Depth	OM	ORP	TOC
As	−0.33	0.73*	0.80**	0.01	−0.11	0.61	0.69	−0.07	−0.19	0.55	0.74*	−0.29	0.28	0.42	0.53	0.077
Co	−0.17	0.70*	0.71*	−0.21	−0.19	0.80*	0.67	0.34	0.30	−0.43	−0.78*	0.30	0.37	0.10	0.23	−0.24
Cr	−0.12	0.37	0.36	−0.02	−0.31	0.27	−0.07	0.57	−0.09	−0.71*	−0.62	−0.04	0.26	−0.21	−0.25	−0.39
Cu	−0.34	0.70*	0.75*	0.02	−0.10	0.54	0.65	−0.13	−0.02	0.37	0.64	−0.47	−0.24	0.74*	0.89**	−0.26
Mn	−0.09	−0.56	−0.58	−0.33	−0.17	0.77*	0.74*	0.17	0.39	−0.59	−0.80*	0.14	0.10	−0.24	−0.12	−0.63
Mo	−0.35	0.65	0.73*	0.07	−0.11	0.70	0.58	0.33	−0.21	−0.53	−0.48	−0.028	0.35	−0.38	−0.54	0.25
Ni	0.29	−0.08	−0.12	−0.36	−0.34	0.41	0.12	0.60	−0.09	−0.74*	−0.82*	−0.29	0.37	−0.07	−0.095	−0.37
Pb	−0.30	0.72*	0.68*	0.26	−0.07	0.73*	0.66	0.20	0.23	−0.65	−0.67	0.02	0.03	0.082	0.21	−0.72
Zn	−0.35	0.70*	0.78*	0.02	−0.11	0.59	0.66	−0.08	0.09	0.08	0.41	−0.64	0.07	0.45	0.59	−0.08
Env. para																
Depth		0.05	−0.32	0.46												
OM			0.76*	0.37												
ORP				−0.09												

Envi. para.: environmental parameters; OM: organic matter. ORP: oxidation-reduction potential. TOC: total organic carbon.

enrichment (Skordas et al. 2015; Yona, Fuad, and Hidayati 2018). Furthermore, a strong positive correlation between ORP and metals/metalloid concentration is consistent with the results of Kelderman and Osman (2007) and Popenda (2014). The correlations between organic matter and ORP in sediments and metals/metalloid concentrations in mussel *M. galloprovincialis* were not significant except Cu which was significantly positively correlated to organic matter and ORP. The correlation between TOC and metals/metalloid concentration in sediments and biota was thoroughly not significant. This indicates that metals/metalloid concentrations in sediments and biota are not controlled by TOC which was in line with the findings of Skordas et al. (2015) and Javed, Ahmad, and Mashiatullah (2018). In the case study of macroalgae, selected heavy metals have revealed significant correlations with organic matter and ORP. In fact, positive correlations have been exhibited between CO, Mn, Mo, and Pb concentrations in *Ulva intestinalis* and OM, on the one hand, and between Mn concentrations in *Ulva intestinalis* and ORP, on the other hand. Nevertheless, negative significant correlations have been revealed between Cr and Ni concentrations in *Ceramium rubrum* and OM, on the one hand, and between As, Co, Mn and Ni concentrations in *Ceramium rubrum* and ORP, on the other one. It is worth to mention that, no significant correlations between selected metals in the two selected marine macroalgae species (*Ulva intestinalis, Ceramium rubrum)* and TOC have been revealed. Such correlations could be attributed to the biological, biochemical, physical-chemical and phylogenic characteristics of selected macroalgae species (*Ulva intestinalis* and *Ceramium rubrum*).

3.7. *Cluster analysis*

Dendrogram based on Ward's method, with Euclidian distances has been carried-out as the criterion for forming clusters of elements were used to depict similarities between the concentration of elements. Manganese, Zn, and Cu made cluster in the dendrogram constructed with data from sediments, *U. intestinalis, C. rubrum* and mussel *M. galloprovincialis* (Figure 2). In fact, in the case study of *C. rubrum* and *U. intestinalis*, obtained dendrograms have revealed two classes. The first class has been composed of two subclasses, where the first subclass has been presented by Mn and the second one has been represented by Cu and Zn. The second class has been defined by As, Co, Cr, Mo, Ni, and Pb. In the case study of *C. rubrum*, the first subclass has been covered by As, Cr, and Ni and the second one by Mo, Co, and Pb. In the case study of *U. intestinalis*, such affinities have been modified. Accordingly, the first subclass articulated around Mo and the second one covers Cr, Ni, As, Co, and Pb.

Cluster analysis applied to studied metal concentrations in mussel *M. galloprovincialis* has shown a dendrogram combined from two classes. The first class contains Mo (representing the first subclass), Co, and Pb (representing the second subclass) and As, Cr, and Ni (representing the third subclass). The second class covers Zn, considered as the first subclass, and Mn and Cu, representing the second subclass.

The cluster analysis carried out for metal concentrations in the sediments has revealed a dendrogram containing two classes. The first class has been composed of two subclasses: the first one revolves around Mn and the second subclass containing Cu and Zn. The second class has been defined Mo, representing the first subclass, and Co, Ni, As, Cr, and Pb, representing the second subclass.

For macroalgae species, mussels *M. galloprovincialis* and sediments statistical affinities between analyzed metals have been revealed, generating diverse subclasses in classes in focus .

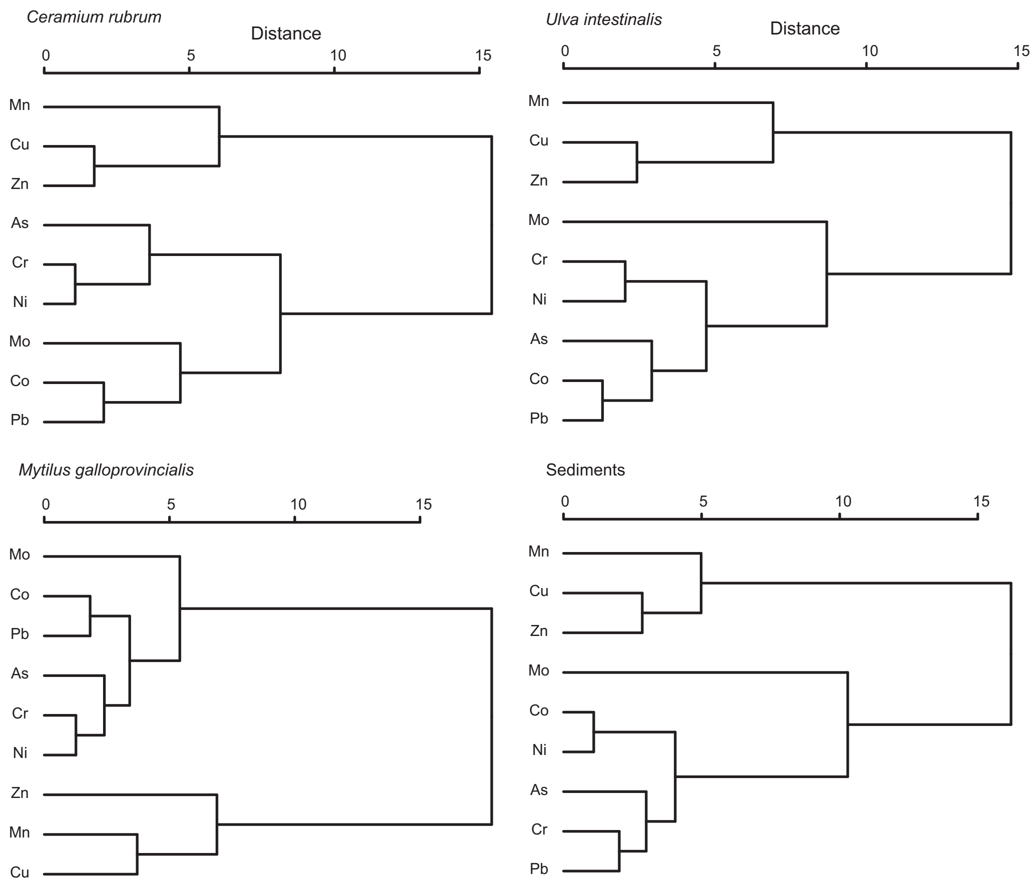

Figure 2. Dendogram based on Ward's method, with Euclidian distances depicting similarities between the concentration of 9 metals in the sediment sampled along the Eastern Black Sea coast of Turkey in 2016.

3.8. *Biota Sediment Accumulation Factor* (BSAF)

The calculated values of BSAF for sediment and biota are given in Table 10. The BSAF has been widely used to describe bioaccumulation of sediment-associated metals into tissues of ecological receptors such as fish, bivalves, crustaceans, and polychaetes (Burkhard 2009; Wong, Capel, and Nowell 2001). According to (Dallinger 1993), based on BSAF estimated values, organism can be classified as macro-concentrator (BSAF > 2), micro-concentrator (1 < BSAF and < 2), and de-concentrator (BSAF < 1). The de-concentrators are deduced to release the metal in sediment. The BSAF values >2 depict the high ability of an organism to absorb metal from sediment and hence can be used as a bioindicator for biomonitoring of metals/metalloid contamination in the environment (Bohac 1999; Ndimele et al. 2014). In the present study, the BSAF values of As in *C. rubrum* were >2 for stations Arak-1, Sürm-2, and Of-3 while >1 for Çamb-1. The highest mean BSAF value (>1) of Cr was estimated for *U. intestinalis* at Sürm-1. The highest mean BSAF value of Mn was (>2) estimated for *U. intestinalis* at Çamb-3. The BSAF values of Zn in mussel *M. galloprovincialis* were found to be >2 in samples caught from Arak-1, Sürm-1, and Sürm –2. The highest mean BSAF values (>1) of Mo were estimated for *M. galloprovincialis* at stations from Araklı and Sürmene and

Table 10. Biota–sediment accumulation factors (Mean ± SD) for *Ceramium rubrum*. *Ulva intestinalis*. and mussels (*Mytilus galloprovincialis*) collected from the Sürmene Bay of the Black Sea in November 2016.

	Western part			Harbor area			Eastern part		
	ARAKLI	SÜRMENE		ÇAMBURNU			OF		
Metals/metalloid	Arak-1	Sürm-1	Sürm −2	Çamb-1	Çamb-2	Çamb-3	Of-1	Of-2	Of-3
As									
U. intestinalis	0.83 ± 0.00	0.54 ± 0.01	0.52 ± 0.01	0.45 ± 0.00	0.08 ± 0.00	0.06 ± 0.00	0.11 ± 0.00	*	0.27 ± 0.02
C. rubrum	**2.70 ± 0.01**	**3.57 ± 0.02**	**4.90 ± 0.01**	**1.73 ± 0.00**	0.15 ± 0.00	*	0.76 ± 0.00	0.98 ± 0.00	**2.63 ± 0.18**
Med. mussel	**1.08 ± 0.00**	0.98 ± 0.00	**1.05 ± 0.00**	0.56 ± 0.01	0.05 ± 0.00	0.01 ± 0.00	0.1 ± 0.00	0.20 ± 0.00	0.29 ± 0.03
Co									
U. intestinalis	0.34 ± 0.01	0.25 ± 0.00	0.05 ± 0.00	0.21 ± 0.00	0.50 ± 0.00	0.28 ± 0.00	0.24 ± 0.00	*	0.05 ± 0.00
C. rubrum	0.13 ± 0.00	0.06 ± 0.01	0.09 ± 0.00	0.15 ± 0.00	0.08 ± 0.00	*	0.02 ± 0.00	0.02 ± 0.00	0.11 ± 0.00
Med. mussel	0.16 ± 0.00	0.12 ± 0.00	0.25 ± 0.03	0.05 ± 0.00	0.08 ± 0.00	0.04 ± 0.00	0.13 ± 0.02	0.2 ± 0.01	0.13 ± 0.00
Cr									
U. intestinalis	0.80 ± 0.02	**1.80 ± 0.08**	0.09 ± 0.01	0.75 ± 0.01	0.98 ± 0.01	0.21 ± 0.00	0.52 ± 0.00	*	0.08 ± 0.00
C. rubrum	0.18 ± 0.01	0.20 ± 0.03	0.30 ± 0.00	0.81 ± 0.03	0.13 ± 0.00	*	0.04 ± 0.00	0.08 ± 0.00	0.16 ± 0.01
Med. mussel	0.20 ± 0.01	0.18 ± 0.01	0.18 ± 0.03	0.06 ± 0.00	0.11 ± 0.01	0.09 ± 0.00	0.13 ± 0.01	0.43 ± 0.00	0.42 ± 0.00
Cu									
U. intestinalis	0.49 ± 0.00	0.29 ± 0.00	0.25 ± 0.00	0.20 ± 0.01	0.02 ± 0.00	0.16 ± 0.00	0.07 ± 0.00	*	0.09 ± 0.00
C. rubrum	0.35 ± 0.01	0.28 ± 0.00	0.45 ± 0.00	0.26 ± 0.01	0.01 ± 0.00	*	0.11 ± 0.00	0.17 ± 0.00	0.17 ± 0.00
Med. mussel	0.40 ± 0.00	0.36 ± 0.00	0.36 ± 0.00	0.62 ± 0.02	0.02 ± 0.00	0.09 ± 0.00	0.51 ± 0.00	0.14 ± 0.00	0.15 ± 0.00
Mn									
U. intestinalis	0.74 ± 0.00	0.37 ± 0.00	0.14 ± 0.00	0.43 ± 0.00	**1.18 ± 0.00**	**4.19 ± 0.00**	0.79 ± 0.00	*	0.14 ± 0.00
C. rubrum	0.41 ± 0.00	0.21 ± 0.00	0.38 ± 0.00	0.28 ± 0.00	0.41 ± 0.00	*	0.11 ± 0.00	0.18 ± 0.00	0.5 ± 0.00
Med. mussel	0.10 ± 0.00	0.14 ± 0.00	0.15 ± 0.00	0.07 ± 0.00	0.09 ± 0.00	0.18 ± 0.00	0.14 ± 0.00	0.35 ± 0.00	0.23 ± 0.00
Mo									
U. intestinalis	**1.49 ± 0.66**	0.86 ± 0.03	0.24 ± 0.01	0.48 ± 0.02	0.19 ± 0.00	0.07 ± 0.00	0.2 ± 0.00	*	0.20 ± 0.02
C. rubrum	0.53 ± 0.03	0.39 ± 0.02	0.43 ± 0.05	0.65 ± 0.02	0.06 ± 0.00	*	0.09 ± 0.00	0.24 ± 0.01	0.33 ± 0.02
Med. mussel	**2.04 ± 0.23**	**1.59 ± 0.08**	**1.25 ± 0.09**	0.99 ± 0.09	0.13 ± 0.01	0.03 ± 0.00	0.29 ± 0.01	0.96 ± 0.01	0.70 ± 0.03
Ni									
U. intestinalis	0.57 ± 0.00	0.97 ± 0.01	0.26 ± 0.01	0.58 ± 0.01	**1.26 ± 0.02**	0.63 ± 0.01	0.53 ± 0.00	*	0.12 ± 0.00
C. rubrum	0.26 ± 0.00	0.39 ± 0.01	0.33 ± 0.00	0.67 ± 0.00	0.38 ± 0.01	*	0.15 ± 0.00	0.19 ± 0.00	0.38 ± 0.00
Med. mussel	0.26 ± 0.00	0.36 ± 0.01	0.30 ± 0.00	0.11 ± 0.00	0.16 ± 0.00	0.22 ± 0.00	0.29 ± 0.01	0.3 ± 0.00	0.35 ± 0.01
Pb									
U. intestinalis	0.26 ± 0.00	0.16 ± 0.00	0.05 ± 0.00	0.15 ± 0.00	0.06 ± 0.00	0.09 ± 0.00	0.10 ± 0.00	*	0.05 ± 0.00
C. rubrum	0.09 ± 0.00	0.10 ± 0.00	0.20 ± 0.00	0.15 ± 0.00	0.01 ± 0.00	*	0.02 ± 0.00	0.02 ± 0.00	0.13 ± 0.00
Med. mussel	0.07 ± 0.00	0.10 ± 0.00	0.12 ± 0.00	0.12 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	0.09 ± 0.01	0.16 ± 0.00	0.22 ± 0.01
Zn									
U. intestinalis	0.30 ± 0.00	0.21 ± 0.00	0.11 ± 0.00	0.15 ± 0.00	0.04 ± 0.00	0.08 ± 0.00	0.05 ± 0.00	*	0.11 ± 0.00
C. rubrum	0.17 ± 0.00	0.22 ± 0.00	0.26 ± 0.00	0.11 ± 0.00	0.01 ± 0.00	*	0.06 ± 0.00	0.07 ± 0.00	0.16 ± 0.00
Med. mussel	**2.56 ± 0.00**	**2.22 ± 0.00**	**2.86 ± 0.00**	**1.12 ± 0.21**	0.27 ± 0.00	0.11 ± 0.00	0.49 ± 0.00	0.88 ± 0.00	**1.43 ± 0.00**

for *U. intestinalis* at Arak-1. Furthermore, the BSAF value of Ni in *U. intestinalis* was higher (>1) at Çamb-2 from other areas as well as *C. rubrum* and *M. galloprovincialis* (Table 10).

The ANOSIM and SIMPER based on BSAF values for *U. intestinalis, C. rubrum*, and mussel *M. galloprovincialis* revealed relatively smaller similarity among them compared to the element concentrations. Mussel *M. galloprovincialis* shared low similarity than the *U. intestinalis* and *C. rubrum* which had slightly greater similarity when compared together (Table 11).

4. Conclusion

Concentration levels, contamination hazard, and human health risk of arsenic, chromium, cobalt, copper, manganese, molybdenum, nickel, lead, and zinc in sediments, two marine macroalgae (*U. intestinalis and C. rubrum*) and a mollusk (mussel *M. galloprovincialis*) collected from the Sürmene bay, Black Sea, Turkey have been carried out, revealing a noteworthy finding. Accordingly, concentrations of analyzed metals in the sediments have been higher than those recorded in biota. Moreover, the highest metal concentrations have been recorded in the sediments sampled from the harbor (especially Of-1) area and sites located in the eastern zone of the studied area (particularly Camb-2 and Camb-3). Consequently, the sampled sediments from such areas have revealed the highest Cf values, yielding to the highest contamination degree levels indicating thus such sediments have been highly contaminated with analyzed metals, signaling a high ecological risk.

In the case study of marine macroalgae, *U. intestinalis* has revealed higher concentration levels of metals/metalloid than *C. rubrum*. Compared to other studies carried out nearby the present study area, recorded concentrations of metals in selected macroalgae species have been comparable.

For mussels *M. galloprovincialis*, highest levels of As, Cu, and Zn concentrations have been recorded in the harbor area (Camb-3). For the remaining analyzed metals, highest concentration levels have been recorded in mussels *M. galloprovincialis* sampled from the eastern and western zones of the study area.

On the basis of the above finding, the THQ and the HI have been carried out in order to evaluate the non-carcinogenic health risks posed by metals/metalloid via mussel *M. galloprovincialis* consumption. The calculated THQ and HI have revealed values below 1 for all sampling sites, indicating thus no adverse effects on human health.

Pearson correlation and Hierarchical Cluster Analysis have been carried out in order to investigate association and similarities/dissimilarities, respectively, between analyzed metals in sediments, macroalgae species (*U. intestinalis and C. rubrum*) and a mollusk (mussel *M. galloprovincialis*). Accordingly, diverse positive and/or negative significant correlations as well as statistical affinities explained by a grouping in subclasses have been revealed between some analyzed metals and sediments, on the one hand, and between the former and biota, on the other hand, indicating a probably common source of enrichment and/or signaling the impact of biological, biochemical, physical-chemical, and phylogenic characteristics of selected biota.

The BSAF has been carried out based on ANOSIM and SIMPER analysis, showing a slight similarity between *U. intestinalis* and *C. rubrum*, on the one hand, and insignificant similarity between intestinalis, C. *rubrum*, and mussel *M. galloprovincialis*.

Table 11. Summary of ANOSIM and SIMPER analyses depicting dissimilarity in biota–sediment accumulation factors (BSAF) of *Ceramium rubrum. Ulva intestinalis* (macroalgae) and Mussels (*Mytilus galloprovincialis*) collected from the Sürmene Bay of the Black Sea in November 2016.

	One-way ANOSIM		SIMPER									
Groups	*R* value	*p* value	Average Dissimilarity %	Discriminating element 1	Contribution (%)	Discriminating element 2	Contribution (%)	Discriminating element 3	Contribution (%)	Discriminating element 4	Contribution (%)
*U. intestinalis***C. rubrum*	0.3646	0.0001	56.01	As	40.14	Mn	17.3	Cr	12.51	Ni	9.079
*U. intestinalis**Med. mussel	0.3869	0.0001	58.67	Zn	24.24	Mn	17.97	Mo	15.64	Cr	11.94
*C. rubrum**Med. mussel	0.4436	0.0001	58.99	As	39.46	Zn	24.43	Mo	14.71	Cu	5.219

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