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Trace Metal Levels in Seawater, Suspended Particulate Matter and Sediment in Mersin Bay, Turkey

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ABSTRACT

The concentrations and distributions of trace metals in surface sediment, water and suspended particulate matter (SPM) in coastal area of Mersin Bay were studied to determined the anthropogenic inputs from surrounding activities. Elevated zinc levels (275 ppm) represent the trace metal with the highest concentration, as measured in suspended particulate matter samples collected from the Kazanlı and Karaduvar areas. The high concentrations are associated with terrestrial inputs from the anthropogenic (domestic +industrial) sources. An important observation is that increasing concentrations are found in dissolved phase, sediment and particulate phase, respectively. But this is not the case for Cr which is higher in sediment. This is related to intense activity of chromium processing plant working for many years. Moreover, Cd and Cr concentrations in surface sediments are above the shale average. Heavy metal concentrations in surface sediments are Cr>Zn>Cu>Pb>Cd, respectively. The elevated copper level relative to cadmium in surface sediments is likely attributable to the higher stability of surface complexes with clay minerals, which constitute the primary components of the sediments. Adsorption of zinc to iron and manganese oxide compounds in the sediment is a possible explanation for the high amounts of zinc that were found in the sediments. The estimated index values (enrichment factor, geoacumulation index and pollution load index) indicated widespread contamination of Cr and Cd in Mersin Bay. The origins of these trace metals in the sediments were caused by human activity, and the region was categorized as a moderately severely polluted area.

KEYWORDS: Heavy metal, Aegean Sea, pollution, green algae

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1. Introduction

Mersin Bay is surrounded by coastal urbanization where over one million people live. Maritime transport, intense urbanization, agricultural activities, industrial plants and rivers (Berdan, Delicay, Muftu, Mezitli) in the area were taken into consideration in determining the sampling locations. This coastal area is characterized by increased population related to industrialization and economic development (chromium processing plant, fertilizer and cement production factories, textile and plastic production plants and various food production factories).

Effluents from untreated domestic wastewater and river waters loaded with chemical fertilizers and pesticides discharge to Mersin Bay. Moreover, port transport and petroleum storage facilities threaten the coastal area. River waters in the region transfer these pollutants to marine environment. Kumbur and Vural, 1989 determined the pollution originated from trace metals and detergents in Berdan river. Higher concentrations of Cd, Pb, and As in fertilizers containing phosphorus used commonly in the area show that the agricultural activities play a role in trace metal pollution (Köleli and Kantar, 2005). Also, increased concentrations of Cr, Cu, and Mn in rivers and irrigation canals in Kazanli region indicate the agricultural runoff (Kumbur et al., 2008). Low levels of trace metal concentrations were determined in some seagrasses consumed by Chelonia mydas in Kazanli region, which is one of the most important reproduction areas. This zone is under the pressure of industrial and agricultural activities. Çelik et al., 2006 stated that the population can be affected if contamination continues increasingly.

Trace metals may enter the aquatic environments and be distributed among dissolved and particulate phase. The suspended particulate matter acts as a carrier of contaminants. However, sediment has a role in providing a source for contaminants in aquatic systems and biota transition of trace metals among these phases depends on the physical, chemical and biological properties of the aquatic environment. For this reason, heavy metal distribution in an aquatic system can be monitored by the measuring them in water, sediment and biota. Taking into consideration Mersin Bay, various investigations were carried out in determining the bioaccumulation of trace metals in biota. Kalay et al., 1999 and 2004 observed the high levels of Cd and Pb in samples of *Mugil cephalus* and *Mullus barbatus* taken from Mersin Bay and increased concentration of Cd was determined in *Patella caerulea* and *P. rustica* (Ayas et al., 2009).

Research carried out in the Taşucu area of Mersin revealed elevated levels of chromium in the sediment of local beaches as a consequence of anthropogenic activities (Yalçın et al., 2020). A study conducted in the Tarsus region revealed that the Berdan Stream transports heavy metal pollution from the agricultural basins of the area into the coastal environment, as indicated by the increased trace metal levels in the sediment (Ozbay et al., 2013). In their study on the beaches of the Mersin region, Ozbay and Akçay, (2023) found that the beach sediments were contaminated with Cd, Cr, and Ni. This pollution was attributed to both natural and human activities, as indicated by the high ecological risk score estimated by the researchers.

Dissolved trace metal levels are generally lower than those of particulate phase and sediment (Malea and Haritonidis, 2000; Küçüksezgin et al., 2008; Boubonani et al., 2009). Different investigations were supported these findings. Concentrations of Cd and Pb measured in Dardanels were as low as critical level (Süren et al., 2000). Also, lower concentrations of Zn, Cd, Pb, and Cu were obtained in Red Sea and Bay of Aqaba (Shriadah et al., 2004).

Seawater concentrations of Cd and Pb in Basra Bay were lower than in sediment (Pourang et al., 2005). Elevated levels of Cd, Cu and Zn in sediment were measured in Bay of Heraklion (Crete) with respect to seawater (Stamatis et al., 2002).

In this study the seasonal and spatial occurrence and distribution of the trace elements in dissolved and particulate phase and sediment in the coastal area of Mersin Bay, located at northeastern Mediterranean Sea, were investigated.

2. Material and Methods

Samples were collected seasonally in four stations in Mersin Bay located in north-eastern Mediterranean (Figure 1). ST1 is situated close to discharge points of rivers around the agricultural activities in region. ST2 is situated in proximity of chromium processing plant in Kazanlı. ST3 is located close to industrial harbor which is under intense ship traffic. ST4 is situated close to various discharge points of domestic wastes.

The surface sediments were collected using an Ekman bottom sampler (Hydrobios). When adequate sediment samples were collected (6-8 sampling from each station) these samples were homogenized and stored in polyethylene bags at 4 °C. The sediment samples were dried in an oven at 105 °C and sieved through 63 µm mesh. Sieved sediment samples were stored in 100 ml polyethylene containers.

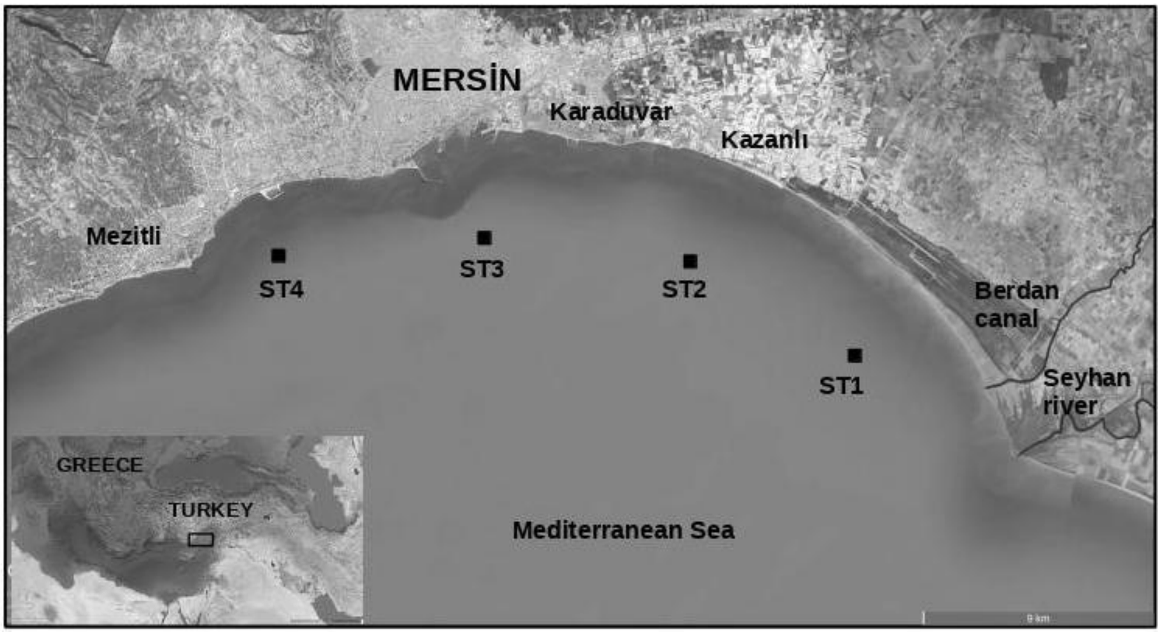

Figure 1. Locations of sampling stations in Mersin Bay.

Three replicate water samples were taken from surface by using standard water sampler (acc. to Ruttner, Hydrobios). Water samples in low density polyethylene (LDPE) bottles were filtered through 0.45 µm membrane filters. Then filtered seawater were acidified (pH 2.5) using 6M HCl and stored in pre-cleaned (1N HCl) LDPE bottles. Suspended particulate matter (SPM) loaded filters were dried at 105°C and weight of SPM was determined gravimetrically. 1.5 ml concentrated nitric acid was added to 1L of seawater and measured without further process (Malea and Haritonidis, 2000). Extraction of sediment and SPM samples were carried out according to EPA Method 200.7 (1994). 4 ml nitric acid (1+1) and 10 ml HCl were added to sediment and SPM samples and heated at 90 °C. Clear part of the extract was then diluted to 25 ml and was analyzed by using ICP-AES (Varian Model-Liberty Series II). The accuracy of the measurements was checked by using certified reference material (NIST, 2711) and recoveries was given as follows;

	Reference value (µg g^{-1})	Analytical value (µg g^{-1})	Recovery (%)
Cd	41	43.87	93
Pb	1162	1107.82	95
Cu	114	109.26	95
Cr	47	51.83	92
Zn	350	347	98
Fe	%2.89	%2.75	95

The enrichment factor (EF), geoaccumulation index (I_{geo}) and pollution load index (PLI) were computed using methods from previous studies (Wedepohl 1995, Müller 1979 and Tomilson 1980, respectively). Comprehensive computations of the methodologies can be located in the text. Mean concentrations of trace metals were analyzed using one-way ANOVA with Tukey HSD as the post-hoc test, utilizing the R statistical program.

3. Results and Discussion

SPM levels ranged between 8.5–14.7 mgL^{-1}. Low levels of SPM were measured at ST4 in fall. However, concentrations of SPM increased in spring, reaching maximum values at ST1 (Figure 2).

SPM concentrations changed according to their geographic locations, riverine input and sampling stations. Seasonal and spatial variations were also recorded in other studies, showing the higher SPM values in winter (Stagnone Di Marsala Bay, Pusceddu et al., 1997; Sara et al., 1999). Taking into account annual mean values, lower values were observed compared to our values. In comparison to other reported values (MEDPOL, 2007), referring to the same bay, a similar seasonal trend was observed, increasing in spring. Higher SPM values in ST1 are associated with the increasing Seyhan and Berdan river water flow (167 and 12 m^3 sn^{-1}, respectively), transporting particulate matter into the sea (47.6 and 38.3 mg L^{-1}, respectively) (MEDPOL, 2007).

One-way ANOVA revealed a statistically significant difference ($p<0.05$) in the fluctuation of trace metal concentrations across different matrices among stations (Table 1). Nonetheless, no significant difference was observed across ST1, ST2, and ST3 for all matrices. This situation may indicate that the Seyhan and Berdan currents, which convey the pollution burden to the area, are transported across the gulf.

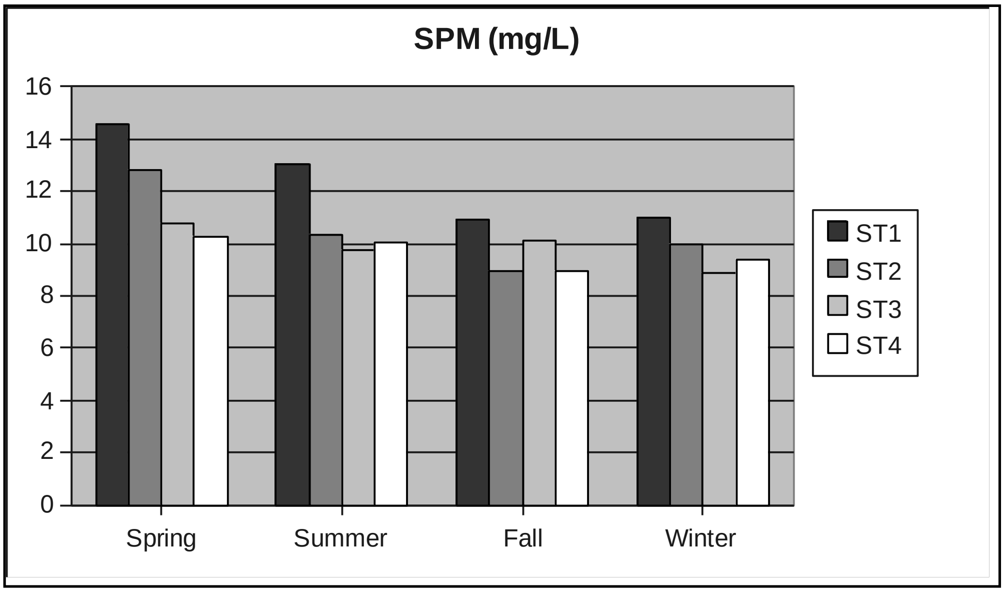

Figure 2. Mean seasonal concentrations of suspended particulate matter from different sampling sites.

Table 1. Analysis of variance (ANOVA) for comparing matrix metal concentrations across various stations.

	Seawater			SPM			Sediment		
	Df	*F*	*p*	*Df*	*F*	*p*	*Df*	*F*	*p*
Model parameters	3	5.29	0.002	3	4.21	0.009	3	5.23	0.002
ST1		a			a			a	
ST2		b			b			b	
ST3		b			b			b	
ST4		b			b			b	

Stations with the same letter are not significantly different at alpha level of 0.05. Post-hoc comparison of subset was performed using Tukey-HSD. *Df;* degree of freedom, *F*; Fisher's F value.

Most trace metals have high affinity for particulate matter in marine environments. Particulate metals eventually sink to bottom and they are absorbed by organisms or may be released to water column via resuspension processes (Balls, 1989). The levels observed for the metals in the SPM showed seasonal and spatial variations (Table 2 and 3). Seasonal analysis revealed an increase in Cd and Pb levels throughout winter. This elevation parallels prior research investigations. A study conducted in İskenderun Bay reported that Cd levels were measured higher in the winter season compared to other seasons (Türkmen and Türkmen, 2004). In addition, Fernandez-Severini (2019) reported that during periods when phytoplankton increased, Cd concentration increased in SPM by binding to sulfur-containing ligands on the phytoplankton cell surface. Demirak et al. (2012) indicated in their research conducted in Gökova Bay that the copper concentration in suspended particulate matter rose due to the bilge water released by vessels, particularly during the summer months, corresponding with the tourism season. This finding may elucidate the explanation of the increase in Cu during the spring-summer period in our research. Zn was the dominant trace metal in particulate phase in all sampling sites (Figure 3). The percentage of particulate-bound Zn found in the present study was above 50% at ST3 and ST2 with respect to other metals. The average percentages of other metals associated with SPM were as follows: Cu > Cr > Pb > Cd. Higher percentages for Cu, Cr, and Pb were observed at ST1. This can be explained with the riverine input, which transports the large amount of SPM to the area. Particulate Cd had the smallest value among the metals studied. Similar results for Cd in SPM have been previously reported in other studies (Türkmen and Türkmen, 2004). In addition, in the Karataş (Adana, Akdeniz) region, where intensive agricultural activities are carried out, seasonal differences are observed in the Cd levels measured in seston, but an increasing trend was detected in terms of average values (Dural and Göksu, 2006).

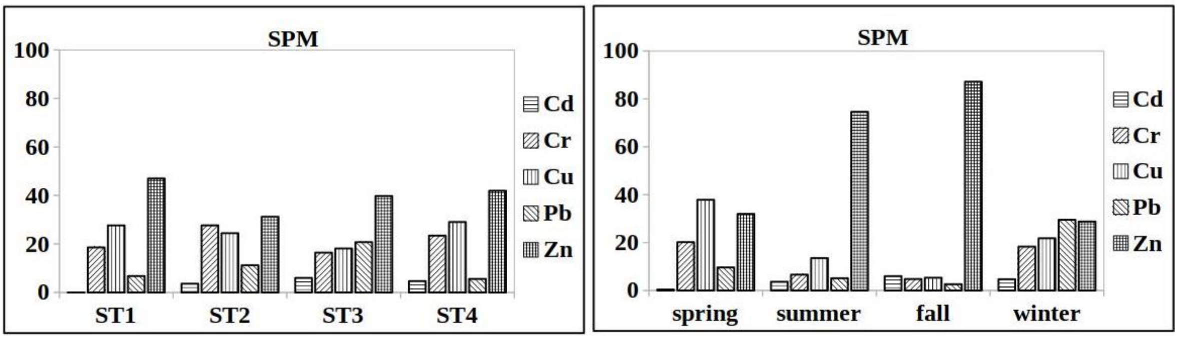

Figure 3. Proportions of particulate trace metal concentrations in relation to the total concentrations.

Table 2. Mean spatial concentrations of Cd, Cr, Cu, Pb and Zn in seawater, SPM and sediment.

		Cd		**Cr**		**Cu**		**Pb**		**Zn**	
		Mean	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**
seawater^{a}	**ST1**	N.D	N.D.	16.51	0.96 - 45.69	24.58	4.34 - 75.08	6.02	4.03 - 8.02	41.77	21.77 - 57.89
	ST2	2.24	0.15 - 4.34	11.32	0.19 - 32.31	10.00	4.17 - 23.63	4.58	3.59 - 6.52	12.77	2.89 - 20.41
	ST3	1.97	0.86 - 3.08	6.57	1.56 - 14.77	7.25	5 - 10.14	8.30	3.23 - 21.36	15.91	10.76 - 23.47
	ST4	N.D	N.D.	18.53	0.11 - 59.18	22.97	0.4 - 60.8	4.41	0.84 - 9.62	33.16	5.84 - 84.5
SPM (ppm)	**ST1**	3.00	0.5 - 6.85	56.87	21.13-141.24	86.41	24.84 - 200.17	63.11	13.1 - 173.16	145.01	123.66 - 177.3
	ST2	3.62	0.41 - 7.66	60.62	8.73 - 134.98	101.53	22 - 242.06	53.55	3.64 - 122.19	274.96	91.78 - 706.24
	ST3	5.98	2.56 - 9.41	64.23	5.85 - 115.94	99.20	19.19 - 276.16	56.64	6.35 - 144.9	259.13	145.2 - 516.21
	ST4	4.68	2.69 - 6.67	74.70	24.07-141.33	122.79	21.25 - 282.84	53.33	5.97 - 116.53	219.32	73.65 - 365.24
Sdiment (ppm)	**ST1**	0.20	N.D. - 0.62	82.93	28.58-178.35	19.29	7.19 - 31.68	4.63	0.59 - 10.28	55.63	26.14 - 94.77
	ST2	0.22	0.04 - 0.59	98.20	40.26-182.4	17.40	6.15 - 36.43	2.90	0.06 – 5.07	60.64	24.73 - 111.32
	ST3	0.24	0.02 - 0.52	94.45	31.06-225.93	15.31	7.61 - 24.06	3.53	0.42 – 7.18	61.14	27.93 - 124.17
	ST4	0.09	N.D. - 0.21	113.30	39.2 - 243.23	13.47	8.24 - 21.54	2.26	0.11 – 3.84	44.32	27.16 - 59.73

(^{a} : Seawater concentrations of all elements are in ppb), N.D. : Not detected.

Table 3. Mean seasonal concentrations of Cd, Cr, Cu, Pb and Zn in seawater, SPM and sediment.

		Cd		Cr		Cu		Pb		Zn	
		Mean	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**
seawater^a	**spr**	0.51	0.15 - 0.86	14.35	11.94-17.17	14.33	8.08 - 23.63	8.61	0.84 - 21.36	10.38	2.89 - 17.5
	sum	N.D.	N.D.	0.70	0.11 - 1.56	3.48	0.4 - 5	4.83	2.76 - 6.52	18.77	13.5 - 24.79
	fall	N.D.	N.D.	1.62	0.84 - 2.21	6.87	5.76 - 7.72	3.72	3.4 - 4.03	26.55	5.84 - 57.89
	win	4.88	3.08 - 6.85	36.26	7.86 - 59.18	37.96	5.81 - 75.08	6.11	3.23 - 9.62	43.50	20.41 - 84.5
SPM (ppm)	**spr**	2.42	1.65 - 2.78	133.37	115.94-141.33	250.31	200.17-282.84	63.44	46.4 - 74.51	211.43	144.32-309.99
	sum	0.41	0.41 - 0.41	17.14	5.85 - 24.07	35.06	27.87 - 43.49	13.29	6.35 - 19.86	193.61	116.3 - 365.24
	fall	0.50	0.5 - 0.5	19.57	8.73 - 24.66	21.82	19.19 - 24.84	10.70	3.64 - 19.78	357.71	73.65 - 706.24
	win	7.65	6.67 - 9.41	86.35	42.07 - 113.32	102.75	73.59 - 148.26	139.20	116.53 - 173.16	135.67	91.78 - 177.3
Seiment (ppm)	**spr**	0.16	0.11 - 0.2	207.48	178.35-243.23	21.03	15.64 - 30.22	6.26	2.52 - 10.28	97.50	59.73 - 124.17
	sum	0.04	0.03 - 0.06	34.77	28.58 - 40.26	7.30	6.15 - 8.24	2.85	2.58 - 3.55	26.49	24.73 - 27.93
	fall	0.02	N.D. - 0.04	43.27	34.36 - 48.82	8.72	8.06 - 10.02	3.91	3.79 - 4.08	32.57	30.59 - 35.02
	win	0.49	0.21 - 0.62	103.34	77.45 - 123.55	28.43	21.54 - 36.43	0.30	0.06 - 0.59	65.18	57.46 - 73.02

(^{a} : Seawater concentrations of all elements are in ppb), N.D. : Not detected.

Zn was the dominant trace metal measured in SPM during summer and fall (Figure 3). High level of Pb was observed in winter and it showed a decreasing trend from winter to fall. The increase in SPM in winter due to the winter-mixing process in the region may elucidate the elevation of Pb levels, since SPM has the capacity to absorb higher levels of Pb during this season (Zhang et al., 2018). Cu and Cr levels increased in winter and spring. Taking into account reports from other Mediterranean regions (Bloundi et al., 2009; Puig et al., 1999; Rossi and Jamet, 2008; Violintzis et al., 2009; Küçüksezgin et al., 2008, Abdallah and Muhammed, 2015), lower trace metal levels were measured in present study.

Trace metal content of the sediment could be affected not only by anthropogenic and lithogenic sources but also by a textural structure, organic content, rate of precipitation and mineralogy. Trace metals interact with fine particles with large surface area. Adsorption, co-precipitation and binding to surface are the main mechanisms of this interaction.

The most abundant elements in marine sediment were Cr and Zn. The spatial and seasonal distribution were given in Table 2 and 3. The other elements did not show distinct spatial and seasonal patterns. The high levels of Cr in whole area could be explained with the environmental impact of the chromium processing plantation, which has been working for about 25 years.

In comparison to previously reported values, values of the present study were lower. Increased concentrations of Cd, Cu and Pb measured in coastal sediment and biota indicated that the coast of Alexandria was defined as polluted (El Nemr et al., 2007, Abdallah, 2007; Abdallah and Abdallah, 2008). Also, this area showed higher level of Cd concentration. Compared to Mersin Bay.

In Marmara Sea, the highest mean concentrations of Pb were approximately two to three times higher than those found in Mersin Bay (Algan et al., 2004). Pb and Cd concentrations in the sediments of coast of Algeria was found to be much higher, while lower levels of Cu, Cr and Zn were obtained. Similar results were obtained for Cd, Cr, Cu, Zn in previous investigations (MEDPOL, 2007). The study on Berdan River sediment showed (Özbay et al., 2013) that the river is the primary pathway for the transportation of metal load to Mersin Bay. It has been reported that specifically Cd, Cr, Pb and Zn (4-60 µg g^{-1}) originating from human activities are carried into the marine environment.

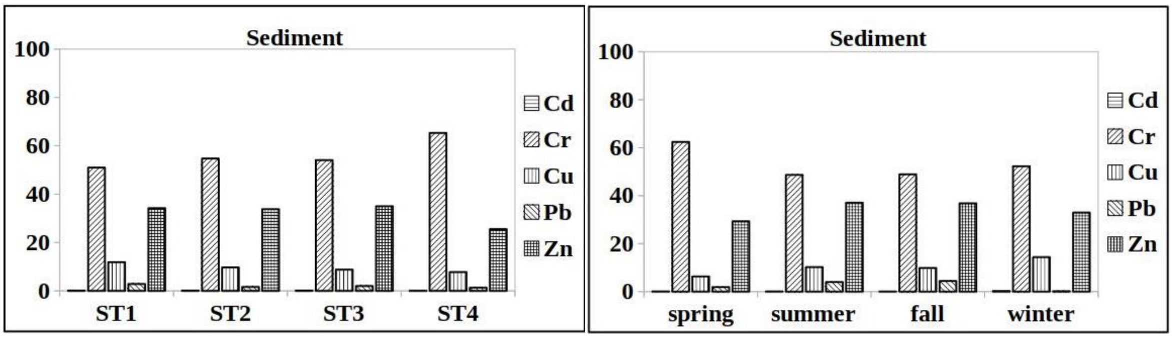

Figure 4. Proportions of sediment trace metal concentrations in relation to the total concentrations.

In contrast to particulate and sediment, levels of trace metal in dissolved phase were lower (Tables 2 and 3). For all elements in dissolved phase, decreased concentrations were observed compared to other Mediterranean areas (Puig et al., 1999; Scoullos et al., 2007; Abdallah, 2008). The temporal and spatial variations of dissolved trace metals were observed due to different chemical and physical characteristics of water masses (Tables 1 and 2). As for Zn, important variations within seasons occurred, notably in summer and fall. However, Cu and Cr were important metals in winter and spring.

When assessing differences between regions, it is evident that pollution diminishes from the Berdan area to the Mezitli region. The Seyhan River and the Berdan Canal cross the area and discharge their pollution burdens into the bay. The existence of a chrome processing facility in the Karaduvar region, along with significant maritime activity in the port area, accounts for the elevated pollution levels along the Karaduvar-Berdan line. This scenario is elucidated when the existing current systems in the Gulf (Ozsoy et al., 1993) are considered. The prevailing currents in the area dilute the contaminants, resulting in a reduction of their concentration in the Mezitli region.

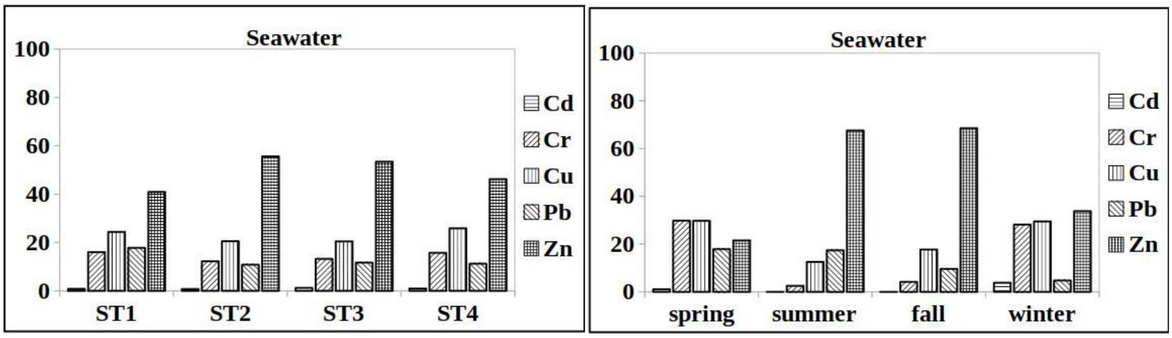

Figure 5. Proportions of dissolved trace metal concentrations in relation to the total concentrations.

Marine sediments serve as significant reservoirs for heavy metals, as these metals adsorb onto suspended particles and subsequently descend to the seafloor, facilitating the transfer of pollutants. Marine sediments significantly influence the diagenesis of heavy metals and can make contaminants accessible to marine species, dependent upon environmental conditions (Xie et al., 2015). Heavy metals bonded to sediment particles can be assimilated by organisms that consume seabed material or can penetrate cells directly (bacteria, microalgae). Subsequent to this phase, they experience biomagnification and increase via several trophic levels in the marine food web. (Gao et al., 2021). Studies show that some metals are more biomagnified than others, while others are subject to biodilution. For example, Cu decreases with biodilution in the herbivores-suspension feeders > detritivores > autotrophs > carnivores food chain (Schneider et al., 2018), while Cd and Cr increase in the cephalopod-fish food chain (Gu et al. 2018). Pb and Zn do not biomagnify in some marine ecosystems and their concentrations remain constant along the trophic chain (Cardwell et al., 2013).

Over a certain threshold, heavy metals are hazardous to aquatic organisms, which display various pathological reactions to this pollution. Some individuals have genetic derangement, while others encounter inflammation, degeneration, alterations in physiology, and developmental abnormalities. The literature contains references to the effects of heavy metals on organisms. For instance, Cr exhibits bioaccumulation and biomagnification features, along with unique toxicological characteristics, since the hexavalent form, rather than the trivalent form, is required for efficient transmembrane passage (Popa, 2006). Chromate ions are also structural mimics of sulfates and can readily permeate the cell through enhanced transport (Viti et al., 2014). Viti et al. (2014) indicated in their study on the mussel *Corbicula fluminea* that chromium (Cr) permeates the cells via the gills and digestive glands, influencing mRNA expression. In a separate investigation, chromium was demonstrated to induce oxidative stress in *Oryzias melastigma* and lead to lipid peroxidation (Ni et al., 2020). Research on Cu have shown that concentrations as high as 280 ppm in sediment can induce anemia, liver malfunction, and renal dysfunction in bivalves, potentially resulting in the mortality of marine organisms. Research indicates that even minimal concentrations of Cu can lead to accumulation in marine creatures (Li et al., 2023). Copper, utilized as an antifungal and pesticide, endangers aquatic life by infiltrating ecosystems and sediments from terrestrial sources through many pathways. Kalatehjari et al. (2015) noted that copper, utilized as an antifungal agent, causes DNA damage in their work using Rutilus frisii. The gills and gastrointestinal system (GT) are the primary pathways for metal absorption in fish. Even at minimal quantities, Cd is fatal to several aquatic creatures and is absorbed by organic materials, facilitating its transit to higher trophic levels. Furthermore, it impairs aerobic respiration through oxidative stress, subsequently resulting in cellular damage (Kurochkin et al., 2009). Guo et al. (2019) indicated that goby (*Mugilogobius chulae*) absorbs cadmium from sediments, mostly via the gastrointestinal tract. Pb interferes with ion control and impacts calcium and sodium absorption. In aquatic ecosystems, lead absorption occurs through sediment consumption. The study using *Oncorhynchus mykiss* indicated that sodium intake was impaired when the fish were fed a species of sediment-dwelling worm that consumes organic materials (Alsop et al., 2016). Zn is crucial for the growth and development of all organisms. When the Zn content beyond a specific threshold, aquatic species endure different acute or chronic toxic consequences. Owing to its distinctive physicochemical characteristics, including stability, non-degradability, and environmental persistence, Zn readily experiences bioaccumulation and biomagnification within the food chain, hence posing a risk to human health (Zhang et al., 2021).

Organisms exposed to sea sediments considered contaminated under laboratory conditions may exhibit physiological and biochemical alterations. This material illustrates the impact of a contaminated environment on the biota. A study utilizing cell culture revealed that sediment extract heightened hepatotoxicity and disrupted glycogenesis in the cells (Lin et al., 2023).

The use of bottom sediment as a contamination indicator of the marine environment provides an establishment of several factors that, by means of certain indices, enabled an evaluation. Some of the most often used indicators of contamination in the sediment are:
enrichment factor, geoaccumulation index, and pollution load index.

In this study, the enrichment factor (EF) was used to determine the level of contamination and the possible anthropogenic effect in sediment. The EF uses normalized trace metal content with respect to sample reference metal. At this point, Fe or Al is used as a normalizing element (Din, 1992; Abrahim and Parker, 2008). Deely and Ferguson (1994) purposed to use Fe as a normalizing element due to its relatively high concentration. Therefore, Fe is not expected to be derived from anthropogenic origin in an estuarine area. For comparison, average shale (Turekian and Wedepohl, 1961), crust (Wedepohl, 1995) and control values were used as a background level. The values are shown in Table 4.

Table 4. Trace metal concentrations in average continental shale, continental crust and control region

	Cd	Cr	Cu	Fe	Pb	Zn
shale (a)	0.20	90.00	45.00	47200	20.00	95.00
crust (b)	0.10	126.00	25.00	30890	14.80	65.00
control		5.42	3.88	3279	1.38	14.15

a: Turekian and Wedepohl (1961)
b: Wedepohl (1995)

The area, which is defined as a control region, was lacking industrial and urban activity. EF was calculated according to the following formula;

$$EF = (M_x/Fe_x)/(M_b/Fe_b)$$

Where M_x and Fe_x are the sample concentrations of element M and Fe, respectively. M_b and Fe_b are the background values of metal and Fe, respectively (Simex and Helz, 1981).

Trace elements of anthropogenic sources have EF values of several orders of magnitude (Chen et al., 2007). Classification was as follows;
<1 background concentration, 1-3 minor enrichment, 3-5 moderate enrichment, 5-10 moderately severe enrichment, 10-25 severe enrichment, 25-50 very severe enrichment, and >50 extremely severe enrichments.

Table 5 represents the EF values of all trace metals measured in the sediment samples. EF values of Cd in control region could not be compared to other reference values due to its very low concentration which was below detection limit. However, according to EF values calculated using shale and crust values lower levels of Cd, Cu, Pb, and Zn values were calculated for ST4. Based on the classification system, ST1, ST2 and ST3 classified as moderately severe enriched area while ST4 classified as minor enriched. Using the crust Fe concentration (Wedepohl, 1995), resulted in lower EF values and minor enrichment degree for Cr (1-3) due to higher crustal rate of Cr/Fe. On the otherhand based on the shale (Turekian and Wedepohl, 1961) and control values EF levels for Cr were higher, indicating moderately severe enrichment. These results demonstrated that Cr were enriched in all regions.

Based on the different background values, all the studied areas were polluted by Cd and Cr from anthropogenic sources. This was attributed to discharge effluent of the chromium processing plant in the area.

Sediment enrichment of trace elements in aquatic environment was calculated in terms of geoaccumulation index (Müller, 1979). The following formula was used to express the geoaccumulation index (I_{geo}).

$$I_{geo} = \log_2 (C_n/(1.5*B_n))$$

where C_n is the measured metal concentration in sediment. B_n is the background value of that metal and the factor of 1.5 is used for lithogenic variability effects. The geo-accumulation index classification consists of seven classes (0-6), ranging from background concentration to very heavily polluted: < 0 (class 0) background concentration, 0-1 unpolluted, 1-2 moderately polluted, 2-3 moderate to high pollution, 3-4 heavily polluted, 4-5 highly to very highly polluted, 5-6 very heavily polluted (Kumar and Edward, 2009).

Table 5. Enrichment Factor (EF) values in sediments normalized with respect to the iron content in continental shale, continental crust and control.

	Cd	Cr	Cu	Pb	Zn
shale					
ST1	4.91	4.43	2.06	1.11	2.82
ST2	5.23	5.18	1.84	0.69	3.03
ST3	5.51	4.83	1.57	0.81	2.96
ST4	1.96	5.77	1.37	0.52	2.14
crust					
ST1	6.42	2.07	2.43	0.98	2.70
ST2	6.85	2.42	2.16	0.61	2.90
ST3	7.21	2.26	1.85	0.72	2.84
ST4	2.56	2.70	1.62	0.46	2.04
Control					
ST1		5.12	1.66	1.12	1.31
ST2		5.98	1.48	0.69	1.41
ST3		5.58	1.26	0.82	1.38
ST4		6.65	1.10	0.52	1.00

I_{geo} values for control are not readily comparable with the other values calculated from shale and crust values due to their higher background values. The average results showed that, using control background values, all the studied areas were found to be polluted by anthropogenic Cr (Table 6). I_{geo} results indicated that the accumulation level of Cu, Pb, and Zn is moderate (I_{geo} = 1-2) in all sediments.

Pollution Load Index (PLI) was calculated as indicated by Tomilson et al. (1980).

$$PLI=(CF_1*CF_2*...CF_n)^{1/n}$$

Where n is the number of metals and CF is the contamination factor, which can be calculated from the rate of sediment/background trace element values. If the PLI value is <1 then the area is evaluated as non-polluted; otherwise value >1 indicates the pollution. All studied areas were found to be polluted (PLI>1), indicating inputs from anthropogenic sources (Table 6).

Table 6. Geoaccumulation index and pollution load index (PLI) calculated from continental shale, continental crust and control background values in sediments.

shale	**Cd**	**Cr**	**Cu**	**Fe**	**Pb**	**Zn**	**PLI**
ST1	-0.56	-0.70	-1.81	-2.85	-2.70	-1.36	4.96
ST2	-0.44	-0.46	-1.96	-2.83	-3.37	-1.23	4.67
ST3	-0.33	-0.52	-2.14	-2.79	-3.09	-1.22	4.74
ST4	-1.81	-0.25	-2.32	-2.78	-3.73	-1.69	4.11
crust							
ST1	0.44	-1.19	-0.96	-2.24	-2.26	-0.81	2.11
ST2	0.56	-0.94	-1.11	-2.22	-2.94	-0.69	2.19
ST3	0.67	-1.00	-1.29	-2.18	-2.65	-0.67	2.14
ST4	-0.81	-0.74	-1.48	-2.17	-3.29	-1.14	2.85
control							
ST1		3.35	1.73	1.00	1.16	1.39	0.67
ST2		3.59	1.58	1.02	0.49	1.51	0.64
ST3		3.54	1.39	1.06	0.77	1.53	0.66
ST4		3.80	1.21	1.07	0.13	1.06	0.49

5. Conclusion

Five trace metals (Cd, Cr, Cu, Pb, and Zn) were measured in seawater, suspended particulate matter, and marine sediment of Mersin Bay, situated in the northeastern Mediterranean Sea. SPM exhibited a higher compositional pattern of trace metals. Cd, Cu, Pb, and Zn were found as dominant elements in the particulate phase. However, Cr was the major element in sediment. Our results suggested that suspended particulate matter plays an important transitional role by carrying the trace metals within marine systems that are affected by human activities. Sediments in the stations and its surrounding environment accumulate trace metals, changing the quality of the aquatic environment. EF, PLI, and I_{geo} values indicated widespread Cr and Cd pollution in Mersin Bay. The sources of these trace metals in sediments were anthropogenic and the area was classified as moderately severe polluted area.

The findings and assessments suggest that Mersin Bay is considerably impacted by pollution sources. Analysis of other research on the region reveals that the bay is polluted with both metals and organic contaminants. In this context, observational studies may be conducted to assess the impacts over time while accounting for all potential pollutant factors and environmental variables (temperature, salinity, oxygen, chlorophyll, pH). Furthermore, histopathology analyses may be conducted at the cellular level to ascertain the particular impacts of heavy metals. To mitigate the pollution danger in Mersin Bay in the near future, preventive measures must be implemented, considering the biological richness of this ecosystem.

Compliance with Ethical Standards

Conflict of interest

The authors declared that for this research article, they have no actual, potential or perceived conflict of interest.

Ethical approval

Ethics committee approval is not required.

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Data availability

Not applicable.

Consent for publication

Not applicable.

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