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Research article

A holistic approach to the assessment of heavy metal levels and associated risks in the coastal sediment of Giresun, southeast Black Sea

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ABSTRACT

A seasonal study was conducted to assess the levels, sources, and potential ecological risks of heavy metals (HM) in coastal sediments along the Giresun Coast, located on the southeast coast of the Black Sea. The mean concentrations of HMs as mg/kg were ranked as Fe (27646.37) > Al (27348.55) > Mn (571.87) > Zn (94.16) > Cr (60.64) > Cu (45.66) > Pb (41.37) > Ni (27.29) > Co (14.47) > As (7.36) > Cd (0.20), respectively. At all stations through the year, Al, Cr, Mn, Fe, Co, and Ni were in "the minimum enrichment" class as evaluated by the enrichment factor (EF). As assessed by the contamination factor (CF), all HM levels except Pb, Fe and Cu were "low" or "moderately polluted" at all stations and seasons. With the exception of Cd levels, all HMs in all seasons and stations pointed out "low ecological risk" according to the ecological risk index (E_r^i). According to the sediment quality guidelines, Ni, Cu and Pb were observed to pose a high ecological risk to habitat. The combined risk assessment indices pointed out low to moderate ecological risk. The study concluded that the region is subject to minimum anthropogenic disturbances in the aquatic environment.

1. Introduction

In recent years, rapid population increase, excessive industrialization, disorganized urbanization, and agriculture have triggered substantial environmental damages [1,2]. Heavy metals (HMs) are a universal concern that have been commonly investigated worldwide due to their existence, long-standing mobility, toxicity in the marine environment and their negative effects on marine creatures and eventually humans [3,4]. Most heavy metals have also properties such as persistence, non-biodegradability, and elevated bioaccumulation [5,6]. In developing cities such as Giresun, Turkey HMs are extensively contaminated by various sources into the surrounding waters. The sediment act as a sink for the HMs as well as a source for them [7]. The release of HMs into the overlying water by oxidation-reduction, resuspension, and desorption can cause major marine pollution and harm the aquatic habitat in the long run. The ecologic risk assessments of HMs accumulations in the sediment are important as they pose a potential hazard to aquatic organisms [8]. Approximately 85% of HMs are known to finally accumulate in sediment of the aquatic environment [9]. For this assessment, sediment quality indicators should be selected and evaluated according to sediment quality guidelines. Contamination factor (CF), geoaccumulation index (I_{geo}), enrichment factor (EF), potential ecological risk index (E_r^i), and toxic risk index (TRI) are commonly applied sediment quality indices [10].

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The Black Sea is actually a closed basin sea and is therefore heavily polluted by the pollution loads carried by numerous rivers [11]. Due to the sharply sloping topography along the Turkish Black Sea Region, Giresun is home to large urbanizations in its very constricted coastal flat area [12]. The study area Giresun city coastline has a coastline of 121 km and a total of eight districts are established on this line. Many large and small streams flow through settlements and load with industrial and agricultural wastewater before reaching the sea. Even the color of the sea changes from time to time with this heavy pollution load discharged into the Black Sea. The Black Sea international highway also runs parallel to the coast along this coastline. As far as we know, this is the first study on seasonal HM contamination assessment and environmental ecological risks in the coastal sediments of eight districts of Giresun. In fact, the launching point of the present study is to make comparison among seasonal contamination levels in eight district centers located on this coastline.

The goals of the present study are (1) to determine the HMs concentrations and their potential sources in the coastal sediment, (2) to compare the contamination levels of eight district centers on the coastline, (3) to evaluate the ecological, and environmental risks of the coastal sediments. Finally, a novel useful report will be generated with the obtained results.

2. Materials and methods

2.1. Study area and sampling

Seasonal surface sediment samples were collected from eight sampling stations along the Giresun coast by using a sediment sampler named Van Veen Grab according to the technical manual of USEPA [13]. Each of the 8 selected stations represents the centers of eight districts, including the central district, located on the 121 km long Giresun coastline (Fig. 1). Each station was also located at the side of the busy Black Sea international highway.

Along the Giresun coast, there are three main rivers that flow into the Black Sea named Harşit (S3), Aksu (S6) and Pazarsuyu (S7).

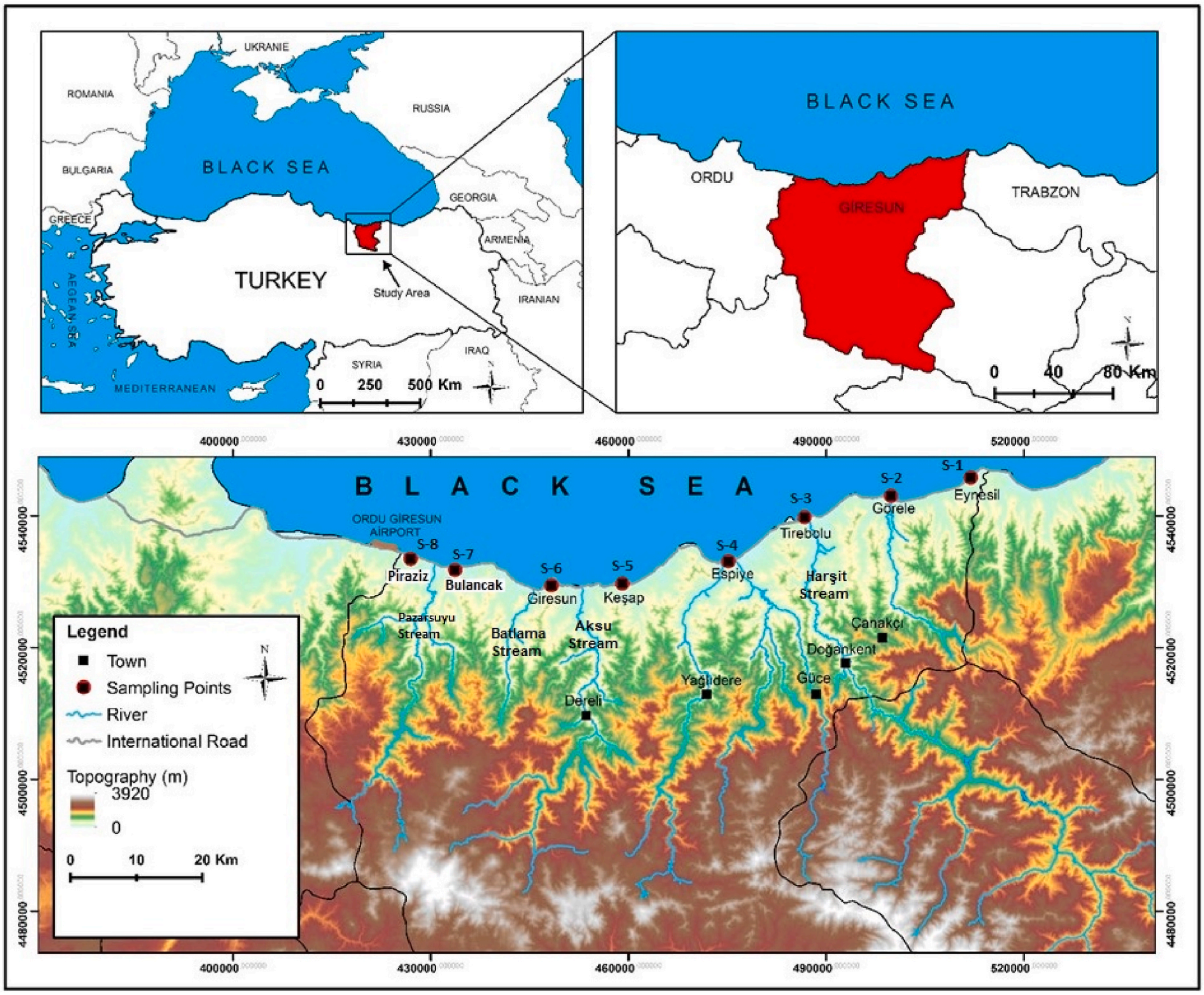

Fig. 1. Sampling sites along the Giresun coasts of Southeast Black Sea.

Table 1

Comparison of mean HMs concentrations in worldwide coastal sediment (mg/kg).

	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb	
Estuaries, Black Sea	27348.55	60.64	571.87	32582.40	14.47	27.29	45.66	94.16	7.36	0.20	41.37	This study
Tekkeköy, Turkey	6246	41.18	241.93	11713		21.57	52.13	97.12		0.61	5.71	[23]
Southern Black Sea					17.4	23.1	76.7	117.8	13.3			[24]
BremenHarbour, Germany		131				60	87	790	15	6	122	[25]
Izmit Bay, Turkey	55125	81.7		37500	20.5	52.1	89.4	754	22.2	6.3	94.9	[26]
Bohai Bay, China		66.4					22.5	70.2	12.8	0.12	12.8	[27]
Gocek Bay, Turkey		235.72	587.91		59.53	1093.53	22.8	61.86	25.2		15.16	[28]
Mid-Black Sea, Turkey		87.31	565.38	46000		34.38	104.06	109.88			32.31	[29]
Mid-Black Sea, Turkey		536.14		14.45		257.8	11.82	22.55	4.48	0.13	12.63	[30]
Gulf of Pozzuoli, Italy	84149	17.3	651	26378	7.90	10.4	18.4	70.3	24.6	0.21	64.2	[31]
Red Sea, Jedda, S.Arabia		9.56	36.52			3.68	9.18	18.02			77.34	[32]
Ivorian coastal zone	11966	4313	249.12	19144		17.37	7.57	28.82	7.93	3.08	8.39	[33]
Sharm El-Sheikh Beach				9711			75.4	36.8		0.15	8.3	[34]

In the old days, this coastal area had a healthy ecosystem with much more marine fauna and flora. The western part of the Giresun coast is affected by various activities like agriculture, harbor and airport, as well as industries such as chemicals, textiles, tanneries, paint, etc [14].

Coastal surface sediment samples were taken from 0 to 10 cm depth, preserved in glass containers kept in cold chain (<4 °C) and immediately brought to the our laboratory. Physical normalization (wet sieving) was not implemented for wet samples as the grain sizes of coastal zone sediments appeared uniform at all stations. The wet sediment samples were first dried at 105 °C for 24 h. Then samples were sieved with a steel sieve (63 μm in size) after grinding.

2.2. *Chemical analyses*

The digestion of dry and sieved samples was performed according to standard USEPA method 3051A [13]. Following digestion, HM levels were measured with the aid of an Agilent 7700× model Inductively Coupled Plasma Mass Spectrophotometer (ICP-MS). We bought all our chemicals from Merck (Darmstadt, Germany).

UME EnvCRM 03A was used as a standard sediment reference material to certify the accuracy and quality control of HMs measurements. Recovery of values of HMs were between 89.6% and 110.8%. Blank samples were run for each seasonal experiments. The coefficients of variance of repeated samples were also all <15%, proving reliable analytical accuracy.

2.3. *Sediment pollution indexes*

Contamination factor (CF), geoaccumulation index (I_{geo}), enrichment factor (EF), potential ecological risk factor (E_r^i), pollution load index (PLI), toxic risk index (TRI), and modified hazard quotient (mHQ) were used to evaluate to the risk of contamination from HMs. The calculations of all these indexes with their explanations are presented in the Supplemental Data Table S1.

As stated by Tepe et al. [15], the coastal sediment in the research area is mostly sourced from pollution loads discharged by rivers along the eastern coasts of Giresun [16]. Therefore, the calculation of EF values plays a key role in monitoring this enrichment in this area. I_{geo} is a broadly used approach to estimate the enrichment of metal concentration above background or baseline concentrations [17]. CF is calculated to display the HMs contamination levels of the surface sediment.

E_r^i is used to assess the ecological risk of HMs in an aquatic ecosystem [18]. Considered as a useful model for evaluating marine contamination, E_r^i can combine common interactions between sedimentation characteristics and marine ecosystems sensitivity.

TRI is an index that gives an opportunity to calculate the toxicological effects of HMs in the marine sediment together with values of PEL and TEL in a mixed way.

mHQ suggested lately to determine the effects of the sediment contamination in agreement with the pollution level triggered by HMs [19]. Actually, mHQ is mainly aim to determine the level and hazard of any HM to aquatic life. mHQ is calculated by evaluating the TEL, and PEL values of HMs in sediments.

PLI refers to the rate of toxic metal pollution for all toxic elements identified in the marine environment studied [20].

The widespread use of derived sediment quality guidelines (SQGs) in order to assess toxicity of HMs accumulated in sediment has encouraged the application of relevant environmental policies and guidelines, also ensuring the control of marine ecosystems and aquatic organisms safety [21,22]. SQGs namely threshold effect level (TEL), probable effect level (PEL), effect range low (ERL), and effects range medium (ERM) were applied to evaluate the probable biotic effect of HMs measured from the coastal sediment.

2.4. *Statistical methods*

Calculation of descriptive and multiple statistical analyzes were accomplished with the SPSS software program (IBM SPSS Statistics 25). One-way ANOVA was used to appraise the variances in the average HMs concentrations, followed by the Tukey post hoc test to reveal the spatial-temporal differences in the HMs levels of the sediment samples. Pearson correlation coefficient (PCC) was employed to test the existence of correlation between HMs. Hierarchical cluster analysis (HCA) was run to classify the relationship and origins of HMs using the Minitap18 program. A p-value less than 0.05 was considered statistically significant. The sampling location map was drawn with ArcGIS 10.2. Heatmaps were created using OriginPro 2021 (Origin Lab Corporation).

3. Results and discussion

According to the measurements made in four seasons, the average levels of heavy metals (mg/kg) were ordered as Fe (27646.37) > Al (27348.55) > Mn (571.87) > Zn (94.16) > Cr (60.64) > Cu (45.66) > Pb (41.37) > Ni (27.29) > Co (14.47) > As (7.36) > Cd (0.20), respectively. Fe and Al levels are typically highest in sediment studies, followed by Mn and Zn. Comparisons with similar studies conducted around the world are presented in Table 1. Tekkeköy coasts had higher average Cu, Zn, Cd levels compared to this study, while all other metal levels were below the current study [23]. Similarly, the mean Co, Zn, Cu, and As concentrations were higher in the southern Black Sea coastal sediment, but all other metal values were below the current study [24]. On the contrary, the levels of Cr, Ni, Cu, Cd, Pb, As, and Zn were higher in the sediment samples collected from Bremen Bay, Germany [25] and the Izmit Bay, Turkey [26]. Likewise, the average levels of Cr, Ni and As are higher in both Bohai Bay in China and Göcek Bay in Turkey [27,28]. Two recent studies conducted in the near region mid Black Sea, Turkey recorded higher levels of Cr, Ni, Cu, and Fe in one, and Fe, Zn, Cu, Cd, Pb, and As in the other, greater than the present study [29,30]. The average concentrations of Al, Mn, As, Cd, and Pb levels were higher in marine sediments in the Pozzuoli Gulf of Southern Italy while the rest of the HMs levels were lower than the present study [31]. Only the mean Pb level was higher in the Red Sea Jeddah sediment, while all other metals were below the current study [32]. Similarly in Ivorian coastal zone, all mean HM levels were recorded at levels below the current study, except for Cr, As, and Cd [33]. While the mean Fe, Zn, Cd, and Pb levels in the Sharm El-Sheikh Beach sediments were lower, the mean Cu level was found to be higher than the present study [34].

One-way ANOVA between seasonal mean values of HMs indicated that Mn and Zn levels were significantly higher in spring than in winter, and Cd concentrations in autumn were considerably higher than in winter ($p < 0.05$). These seasonal variations of HMs concentrations may be due to the variation of the pollution load as well as the effect of precipitation. Statistically insignificant differences were observed in the seasonal levels of all other metals (Table 2). Statistically significant differences were noticed between the annual mean concentrations of HMs along the stations on the Giresun coast ($p < 0.05$). The annual mean Ni and Cr concentrations of both stations S1 and station S2 were higher than those of the other six stations. The Al levels of station S3 and the As levels of S1 remained lower than those of the other six stations on the annual average.

The result of CF pointed out that Pb at station S3 showed “very high contamination” during the winter season. Similarly, Pb in stations S2 and S3, Cu in S3, and Fe in S5 in spring season and Pb in S2 in summer season showed “considerable contamination”. Except for these, all other HMs in all seasons and stations showed “low” to “moderate contamination”.

The average CF levels of HMs are ordered as: Pb > Cu > Zn > Co > Fe > Mn=Cd = Cr > As > Ni > Al (Fig. 2).

EF results for Al, Mn, Cr, Co, Ni, and Fe were <2, indicating “minimum metal enrichment” during all seasons and all stations. The EF value of Pb in S3 exceeded 20 in winter and pointed out “very high enrichment”. Station S3 showed “significantly enrichment” with the EF values calculated for Cd in autumn and Cu in spring. Calculated mean EF levels of HMs are ordered as: Pb > Cu > Zn > Cd > Cr > Co > Mn > As > Ni > Al.

The mean I_{geo} values of sediment shown that Al, Ni, and As were “practically unpolluted” class in all four seasons at the stations on the Giresun coast. In all stations, I_{geo} values for Fe in summer, Mn and Fe in autumn and winter seasons were <0 and found to be “practically unpolluted”. Similarly, it was observed that I_{geo} values of all metals in the summer, autumn, and winter seasons showed negative values at station S5 and were in the “practically unpolluted” class. “Heavily polluted” class was found only in station S3 with Pb in winter with values of 2.03 and “moderately to heavily polluted” class was the case in station S3 with Cu in spring with values of 1.85. The annual average I_{geo} levels of HMs in the sediment are listed as Pb > Zn > Cu > Co > Mn > Fe=Cd > Cr > As > Ni > Al.

Calculated mean E_r^i values (with <40) of all HMs during the year pointed out “low ecological risk” for the coastal sediment with only few exceptions. For Cd, calculated E_r^i values in S2 in spring, and in S3 and S6 in autumn were aforementioned exceptions with E_r^i values between 40 and 80 which posed “moderate ecological risk”. The risks of HMs in the Giresun coastal surface sediments are as follows, in decreasing order: Cd > Pb > As > Cu > Ni > Cr > Zn.

mHQ is applied to estimate the risk levels of each HMs to aquatic habitat (Benson et al., 2018). The mHQ values calculated for all HMs during all seasons were below 0.5, indicating “absence risk”, with the exception of Cd. In autumn season, the mHQ value of Cd with 2.07 in station S3 pointed out “considerable contamination”. Cd showed moderate risk in S6 in autumn and in S2 in spring. With mHQ values of Cd between 1 and 1.5, “low risk” were the cases at stations S2, S7 in the autumn, at stations S1, S3, S6, S7, and S8 in the spring, and at stations S1, S7, and S8 in the summer. The average mHQ values of HMs in all seasons overall are ordered as Cd > As > Pb > Cu > Ni > Cr > Zn.

The PCC among the concentrations of HMs in the sediment are shown in Fig. 3. Ni and Cr ($r = 0.90$) as well as Co and Mn ($r = 0.84$) were correlated with each other strongly. Correlation between Al and Fe ($r = 0.57$), Mn and Zn ($r = 0.62$), Co and Zn ($r = 0.65$) were also relatively strong. It is noteworthy that Al, Fe, Zn, and Pb exhibit positive correlations with all HMs. However, the correlations of Fe with all HMs ($r < 0.5$) are relatively weak. Similarly, Cd, Cu and As were either weakly or negatively correlated with other HMs.

TEL and PEL are frequently utilized tools to estimate the adverse biological effects of HMs in sediment [35–37]. While adverse

Table 2
The mean seasonal HMs concentrations (mg/kg) of the current study and comparison of them with reference values.

Metal	Sediment Average Concentrations				References values[a]			SOGs (EPA)[b]			
	Autumn	Winter	Spring	Summer	WASV[c]	TEC	PEC	ERM	ERL	PEL	TEL
Al	28117 ± 6142	23456.1 ± 5379	29568.3 ± 8682	28252.9 ± 6769	80000						
Cr	45.2 ± 31.7	64.1 ± 30.4	76.8 ± 34.2	56.5 ± 35	90	43.4	111	370	81.00	160	52.3
Mn	522 ± 206^{ab}	408.2 ± 144^{a}	781.2 ± 365^{b}	576.1 ± 205^{ab}	850						
Fe	26549.3 ± 7319	21476.3 ± 6954	55015.6 ± 51865	27288.4 ± 7523	47200						
Co	12.9 ± 4.5	11.1 ± 5.1	19.9 ± 12.6	13.9 ± 5.5	19						
Ni	21.3 ± 12.6	30.1 ± 14.1	30.5 ± 12.2	27.3 ± 16.3	68	22.7	48.6	51.60	20.90	42.80	15.90
Cu	36.6 ± 13.1	36.8 ± 17.6	67.7 ± 72.9	41.5 ± 24.8	45	31.6	149	270.00	34.00	108.00	18.70
Zn	85.8 ± 32.8^{ab}	68.3 ± 28.9^{a}	138.8 ± 61.3^{b}	83.7 ± 34.5^{ab}	95	121	459	410.00	150.00	271.00	124.00
As	7.56 ± 4.10	5.64 ± 2.14	9.09 ± 2.09	7.15 ± 1.66	13	9.79	33	70	8.20	41.6	7.2
Cd	0.28 ± 0.19^{a}	0.12 ± 0.03^{b}	0.24 ± 0.09^{ab}	0.17 ± 0.06^{ab}	0.3	0.99	4.98	10	1.20	2.21	0.68
Pb	39.88 ± 14.49	42.81 ± 33.43	45.02 ± 17.95	37.79 ± 14.64	20	35.8	128	218	46.70	112	30.2

[a,b] The different letters in same row indicate significant differences ($P < 0.05$).

[a] TEC Threshold: Effect Concentration; PEC: Probable Effect Concentration [21].

[b] Sediment SOGs: Numeric Quality Guideline; ERL: Effect Range Low; ERM: Effect Range Median; TEL: Threshold Effect Level; PEL: Probable Effect Level [22].

[c] WASV: World Average Shale Values [37].

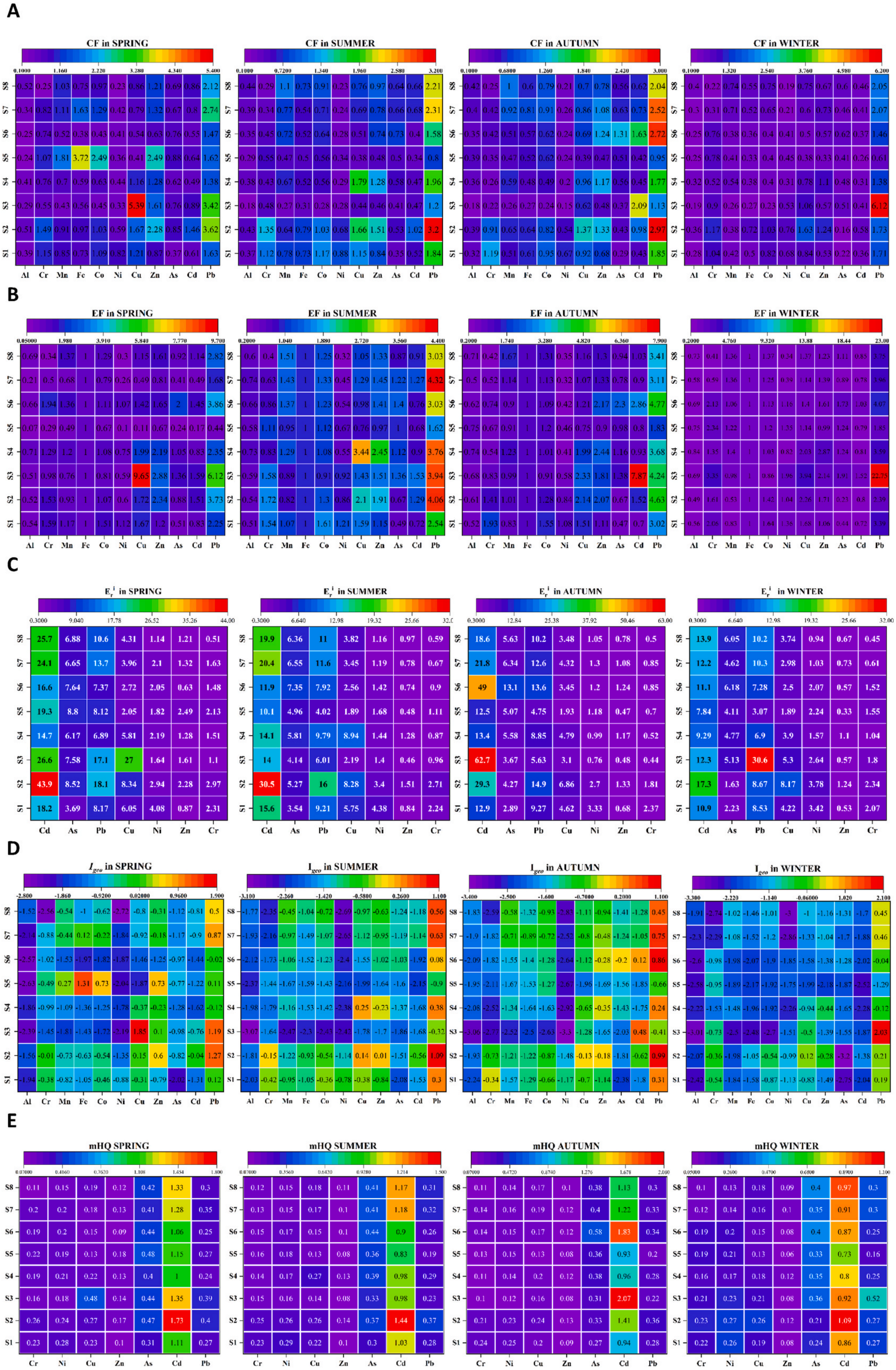

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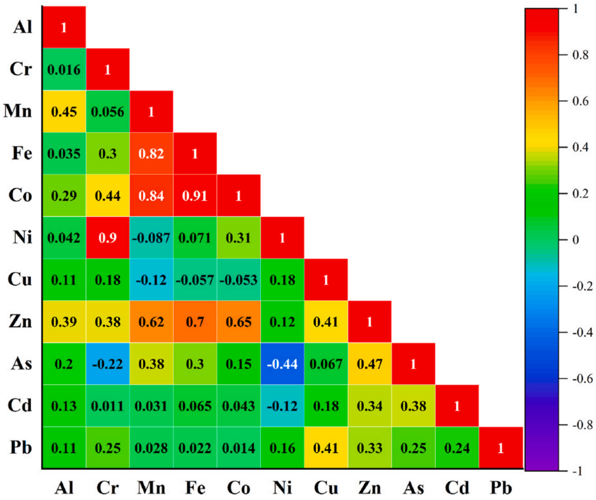
Fig. 2. Heatmaps of indices used for HMs in the Giresun coasts of Southeast Black Sea. CF (A), EF (B), E_r^i (C), I_{geo} (D), mHQ (E).



	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
Al	1										
Cr	0.016	1									
Mn	0.45	0.056	1								
Fe	0.035	0.3	0.82	1							
Co	0.29	0.44	0.84	0.91	1						
Ni	0.042	0.9	-0.087	0.071	0.31	1					
Cu	0.11	0.18	-0.12	-0.057	-0.053	0.18	1				
Zn	0.39	0.38	0.62	0.7	0.65	0.12	0.41	1			
As	0.2	-0.22	0.38	0.3	0.15	-0.44	0.067	0.47	1		
Cd	0.13	0.011	0.031	0.065	0.043	-0.12	0.18	0.34	0.38	1	
Pb	0.11	0.25	0.028	0.022	0.014	0.16	0.41	0.33	0.25	0.24	1

Fig. 3. PCC matrix of HMs in the Giresun coasts of Southeast Black Sea.

biological effects are occasionally observed below TEL values, they are more likely to occur if concentrations exceed PEL values. Seasonal HMs levels of stations were compared with sediment quality guidelines (SQGs) (Table 2). Ni, Cu, and Pb concentrations were found to be 19%, 3% and 3% higher than PEL values, respectively. Ni levels at stations S1 in all four seasons and at station S2 in winter and summer exceeded PEL values. Adverse biological effects sourced from Ni are worrisome. It was noticed that the Cu, Ni, Pb, As, Cr and Zn concentrations of the samples varied between PEL and TEL values at rates of 88%, 78%, 72%, 53%, 47% and 19%, respectively. This means that contamination sourced from metals exhibit significant harmful effects.

Fig. 4 shows the assessment according to the integrated risk evaluation indices of HMs by PERI, PLI, and TRI. It has been proven in studies that integrated risk assessment indices have an effective role in evaluating the pollution status in sediments [38,39]. The annual average values of all stations and all seasons are below the threshold values of 150, and 1 for PERI and PLI, respectively. As a result of these evaluations in terms of PERI and PLI, “low ecologic risk” and “no contamination” can be mentioned, respectively in all seasons and stations. PLI is an easy way to prove that sediment conditions deteriorate with the accumulation of HMs [38], and the average PLI value recorded in our study showed the absence of heavy metal pollution in the sediment. The all seasonal mean TRI values were between 5 and 10 indicating “low toxic risk”. TRI values of stations S5 and S8 were below 5 indicating “no toxic risk” and the rest of the all stations had TRI values between 5 and 10 indicating “low toxic risk”.

Principal component analysis (PCA) with varimax rotation was performed to categorize the possible causes of HMs. Four principal components (PCs) with eigenvalues >1 were found, explaining 77.83% of all variability (Fig. 5A). The PC1 with 32.60%, contribution, Co, Mn, and Zn had loadings of 0.89, 0.88, and 0.73, respectively (Fig. 5B and C). Co made strong positive correlations with Fe, Mn, and Zn ($r = 0.91$, 0.84, and 0.65, respectively) and Mn had strong correlations with Co, Fe, and Zn ($r = 0.84$, 0.82, and 0.62, respectively). Similarly, Zn was correlated strongly with Fe, Co, and Mn ($r = 0.70$, 0.65, and 0.62, respectively). The average EF and I_{geo} levels of Co, Mn, and Zn were <2 and 1, respectively, pointed out “minimum enrichment” which suggests that these HMs are not caused by human activities. On the other hand, they have positive strong correlations with Fe which showed terrigenous sources. Consequently, PC1 characterizes terrigenous sources predominantly attributable to municipal pollution and industrial discharges. The input of PC2 was 20.45%, and Ni, Cr, and As had loadings of 0.96, 0.90, and −0.57. With low contamination degree of all three HMs, PC2 characterizes natural sources that is attributed to parent rocks and sediment accumulation. PC3 contributed 15.66%, and Pb, Cu and Cd clustered together with loadings of 0.74, 0.73, and 0.62, respectively. Positive correlations of all three metals with Fe and their low degree of contamination indicated terrigenous sources. Hence, PC3 refers to terrigenous sources due to fertilizer and pesticide use in intensive hazelnut production in the study area. PC4 contributed 9.11%, and Al and Fe clustered together with loadings of 0.88, and 0.79, respectively. Al and Fe, the most common metals in the earth’s crust, show strong positive correlations with each other which proposes that this factor basically sourced from crustal constituents.

Hierarchical cluster analysis (HCA) among HMs was used to indicate the similarity and origin of HMs (Fig. 6). The cluster analysis results confirmed the factor classes revealed by PCA, with the exception of As. Al and Fe, forming PC4, are in a cluster representing crustal sources. Mn, Co and Zn are in the same cluster, which attributed to urban pollution and industrial emissions and formed PC1. Similarly, Cu, Pb, and Cd were in the same cluster, constituting PC3, which points to terrestrial sources. However, As is also included in this cluster. Finally, Cr and Ni in the last cluster formed PC2 which characterizes natural sources. The four clusters resulting from HCA confirm and agree with the four factor classes resulting from PCA. Therefore, it would be compatible to claim that HMs in the same cluster come from similar sources.

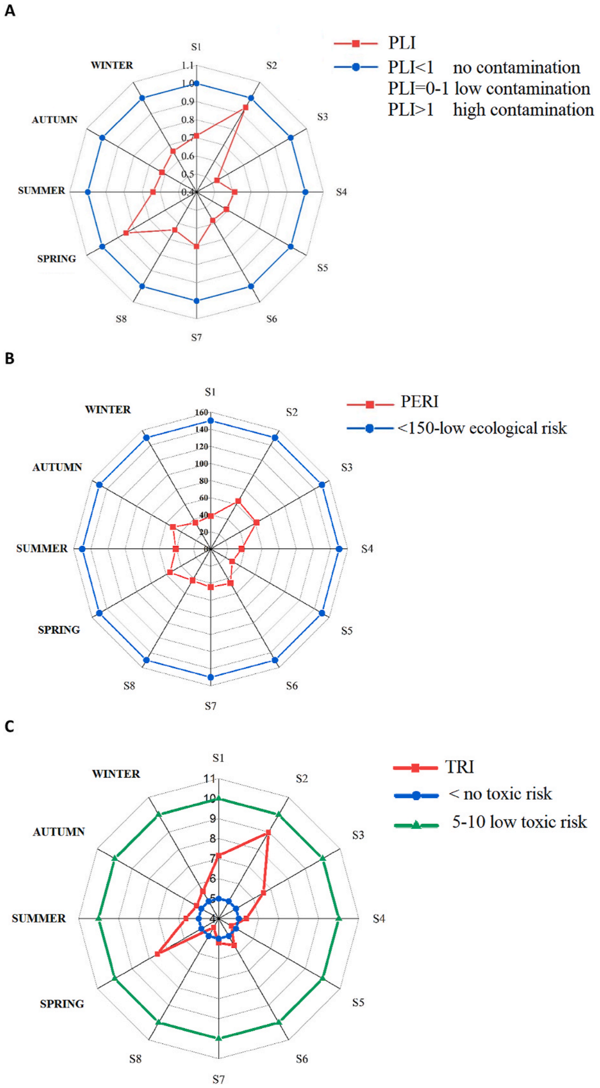


Fig. 4. Radar charts of integrated risk assessment indices of HMs by PLI (A), TRI (B), and PERI (C).

4. Limitations

Sampling was done with difficulty at stations S2 and S3, which have rocky ground. In some seasons, great efforts were made to find enough sediment. In cold weather with heavy rain, there were great difficulties in sampling due to the very large waves of the sea. Sea samples were taken in this type of weather, taking into account the life-threatening dangers. In addition, the Turkish coast of the Black Sea is characterized by immediately rising mountains [40]. For this reason, stream plumes are frequently seen in the region where heavy rainfall is dominant [41]. Deviations can be observed in the results of the analysis in the samples taken after the times when the river plumes were experienced.

5. Conclusions

In the current study conducted in Giresun, Turkey, on the southeast coast of the Black Sea, eight district centers on the coastline were selected as stations. HMs levels of sediment samples taken from these district centers were compared seasonally. The average Zn, and Mn concentrations in winter and Cd in autumn samples were significantly lower than those in spring and generally, lower average HM concentrations were found in winter samples. Statistically significant differences were identified between the annual mean HMs levels of the stations, and the annual mean Ni and Cr levels of station S1 and S2 were higher than the other six stations ($p < 0.05$). On the contrary, the mean Al levels of station S3 and the mean As levels of S1 remained lower than the other six stations on annual average. The results of the present study were compatible with the results of studies conducted around the world. PCA test suggested that four factors were effective in the distributions and origins of HMs. The four factors resulting from PCA were also confirmed by the

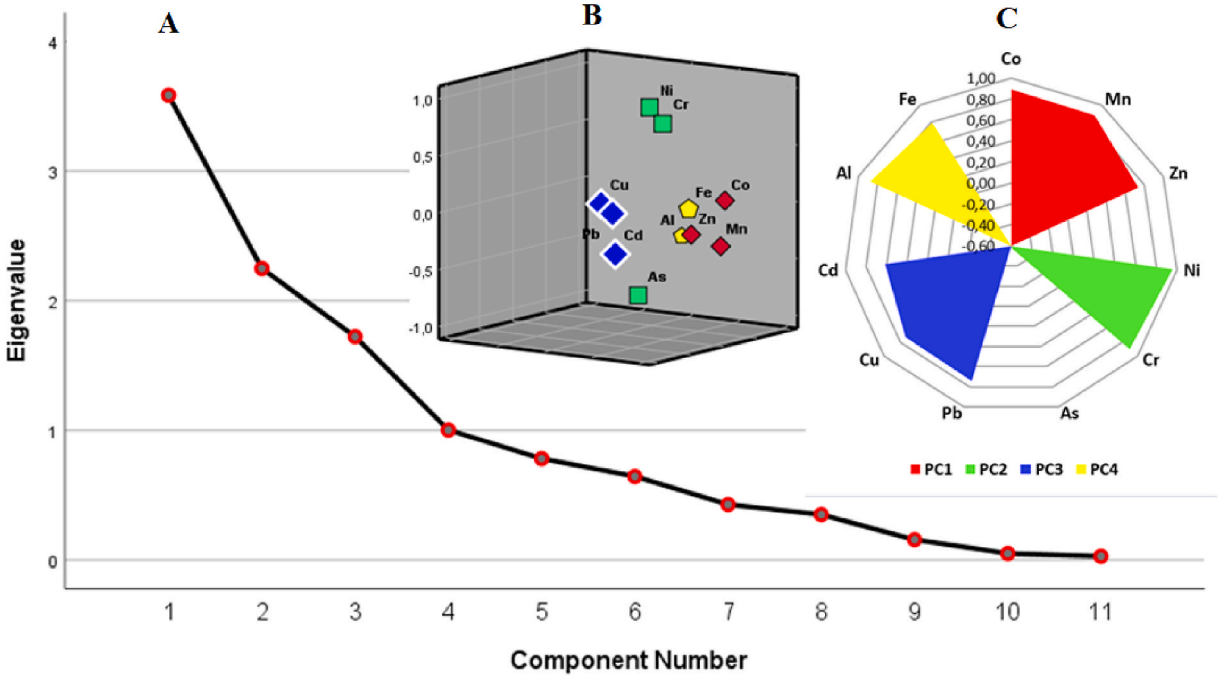


Fig. 5. PCA of HMs by (A) scree plot of the characteristic roots (Eigen values), (B) component plot in rotated space, and (C) radar chart of HMs.

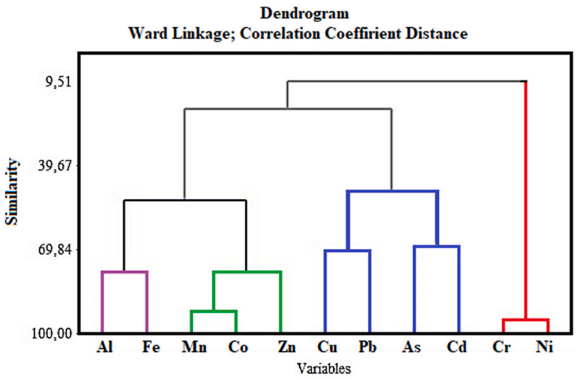


Fig. 6. Hierarchical cluster analysis (HCA) of HMs in the Giresun coasts of Southeast Black Sea.

four clusters found in HCA. In winter, EF and CF values of Pb at station S3 were found to be at very high risk level. In addition, I_{geo} values of Pb in the winter and Cu in the spring which are in the "heavily polluted" class, and "moderately to heavily polluted" were also recorded in station S3, respectively. In short, Pb and Cu were the HMs of concern in the study area. Moreover, in line with the consensus-based SQGs, Ni, Cu, and Pb were expected to cause adverse effect to demersal organisms in the coastal zone of Giresun. HMs were mostly originated from natural and crustal sources and at a lesser extent from anthropogenic such as wastewater and industrial effluent, river plumes, and vehicle traffic. In addition to the natural Pb and Cu deposits in the region, industrial emissions, fuel combustion, and pollution from vehicles can also cause Pb, Cu and Zn accumulation in sediments [42]. Moreover, enrichment of Zn and Cu may result from overuse of fertilizers, fungicides and pesticides [43].

These baseline findings are requisite to plan monitoring programs, take remedial actions, and encourage prospective research. At larger extend, it also provides baseline information to all Black Sea coastal countries for further relevant studies and policy-making initiatives to protect the marine ecosystem.

Author contribution statement

Murat Kodat, MSc: Performed the experiments; Analyzed and interpreted the data.

Yalçın Tepe, PhD: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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