

Environmental, Ecological and Human Health Risk Assessment of Heavy Metals in Sediments at Samsun-Tekkeköy, North of Turkey

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Abstract

A detailed study was conducted in order to evaluate the effects of heavy metal pollution in the sediments in terms of environmental, ecological and human health. Sediment samples were collected from 5 different points in two seasons, namely summer (August 2017) and winter (December 2017), to determine the distribution of heavy metals, potential pollutants, toxic and ecological risks in the river sediments in Samsun - Tekkeköy district located in the Mid-Black Sea Region of Turkey and to evaluate the human health risk. The distribution of heavy metals at the sampling points was $Fe > Al > Mn > Zn > Cu > Cr > Ni > Pb > Cd$ based on their averages. According to the toxic risk index (TRI) results, sampling point OIZ (Organized Industrial Zone) Channel (T3) was also found to have a moderate risk, and it was determined that the highest contribution was from $Cu > Ni > Cd > Cr$, respectively. Potential ecological risk (PERI) results revealed a low risk except for Cd metal at all sampling points. While the sediment enrichment factor (EF) did not show much metallization at many points, the highest enrichment was observed in Cd, Cu, and Zn metals and at sampling point T3. According to the geoaccumulation index (I_{geo}) and contamination factor (C_F), sampling point T3 showed contamination with Cd, Cu, Cr, and Zn. Evaluation of human health risk showed that the hazard index (HI) results of carcinogenic and non-carcinogenic risks were higher among children than adults. The total lifetime cancer risks (TLCR) of heavy metals were within the limits determined by USEPA. However, the risk was ranked as $Cr > Cd > Pb$. Sediment Quality Guidelines (SQG) and pollution index results showed that heavy metal contamination was due to anthropogenic and industrial activities since the region was an industrial zone. It was determined that heavy metals posed ecological risks and that Samsun-Tekkeköy region was moderately and significantly contaminated.

1. Introduction

Industrial zones have remained within the city along with the improvement of urbanization and the increase in population in recent years and could not get far away from the city since they should be intertwined with city life for economic reasons. While enterprises located in industrial zones use fertile lands due to their activities, they discharge a significant amount of pollutants into rivers, estuaries, and coastal regions. Pollution caused by industry is usually due to the deficiencies in investment planning and location selection rather than the size of applications. Metals and their derivatives, which are excessively used for production in these regions, enter the water ecosystem as heavy metals and constitute the main source of pollution. Heavy metals enter the ecosystem not only through industrial activities but also through natural processes, anthropogenic inputs such as sediment erosion, atmospheric accumulation, and discharge of domestic, agricultural, and industrial wastewater (Bat and Özkan 2019).

Along with the entry of heavy metals into the aquatic environment, while some part of the metals remains in the water column, the other amount is distributed between the sediment and biota. Heavy metals are bound to the sediment by complexing with surface adsorption, ion exchange, co-precipitation and organic matter, and they accumulate in it. Most of the metals bound to the sediment are dropped back into the water column by suspension, desorption, reduction, and oxidation reactions. While the released particles create a habitat for many aquatic organisms, heavy metals accumulated in the sediment may lead to potential long-term effects on human and aquatic organisms health owing to the food chain due to their extensive resources, non-degradability, bio-use, bioaccumulation, toxicity, and cumulative effects. Therefore, sediments are very important in the distribution, accumulation, and transport of heavy metals while reflecting the current quality of the system (Bakan and Özkoç 2007; Zhuang et al. 2018; Li et al. 2019).

Since the accumulation of metals in the sediment poses hazards to the aquatic ecosystem, it is necessary to evaluate the potential ecological risk caused by metal pollutants to which the organism in the aquatic environment is exposed. To this end, it is necessary to review the sediment quality guidelines and determine the quality indicators (Ding et al. 2019). Sediment quality indicators (indices) are enrichment factor (EF), potential ecological risk index (PERI), contamination factor (C_F), geoaccumulation index (I_{geo}), toxic risk index (TRI), and similar sediment assessment indices (Duodo et al. 2016). Sediment quality markers focus on either a qualitative threshold qualitative or an ecological risk assessment of a metal. The determination and assessment of these quality markers are very important in determining the risks caused (which may be caused) by the sediment in the relevant region.

In this study, it was aimed to evaluate the distribution of heavy metals in sediment samples collected from streams in Samsun-Tekkeköy district of the Mid-Black Sea Region since it is a region with many industrial enterprises and a high pollution potential. The concentrations of nine heavy metals (Fe, Al, Mn, Zn, Cu, Cr, Ni, Pb, Cd) in the sediments in Tekkeköy Industrial Zone were determined, the contamination level and the ecological and environmental risks of heavy metals in the sediment were calculated, and the pollutant potential in the sediment was evaluated statistically by the Pearson correlation index. By determining the levels of contamination due to heavy metals in Samsun-Tekkeköy region with the study results, the environmental risks to be caused by the region in the ecosystem and therefore the risks for human health were determined, and recommendations have been made for preventions to be taken.

2. Materials And Methods

2.1 Definition of the Study Area

The study area is located between 37° east and 35° west longitudes and between 41° north and 40° south latitudes in Tekkeköy District of Samsun province. The population of the district is around 50000. The primary stream resources in the district are the Abdal Stream, Büyüklü Stream, Saryurt Stream, Kirazlık Stream, Şabanoğlu and Tekkeköy Stream, and there are also other streams.

Tekkeköy is located 1 km inland from the 13th km of the Samsun - Ordu highway towards the south. The district is surrounded by the Black Sea in the north, Çarşamba District in the east and south, Asarcık District in the southwest, and Canik District in the west. It has a surface area of 321 km² and an altitude of 4 m. The continuation of the Çarşamba Plain constitutes one-third of its soil. Industry, agriculture, and animal husbandry constitute the economy of the district. There are a total of five organized industrial zones consisting of two large and three small zones in Tekkeköy. Industrial enterprises in the region lead to significant environmental pollution, and thus, the population of living creatures is adversely affected by pollution.

In this study, the Akkiraz Stream (T1), Şabanoğlu Channel (T2), OIZ (Organized Industrial Zone) Channel (T3), Hidrellez Stream (T4) and Selyeri Stream (T5) discharging into the Black Sea in Tekkeköy district located in the Mid-Black Sea Region were selected as the sampling points (Fig. 1).

Among the sampling points, the coordinates of which are given in Table 1, the Akkiraz stream (T1) consists of clayey, sandy, and silty soils consisting of alluviums carried by the rivers by its soil structure. Due to the continuous currents and sediments coming from the upper basins, the stream bed is contaminated and narrows and contains flood hazard. The Şabanoğlu stream (T2) and the Hidrellez stream (T4) are contaminated by the wastes from industrial areas and the Haciosman and Çırakman channels that feed them. The OIZ channel (T3) is in the Central Organized Industrial Zone, and the occupancy rate of the OIZ is 100%. One hundred eleven companies are operating in the Central OIZ covering an area of 160 hectares. There are enterprises operating mainly in the hardware, non-electrical machinery, non-ferrous metals, food and furniture sectors. Since the production wastes of all these industrial enterprises are discharged to the OIZ Channel, they constitute a significant source of contamination. The Selyeri sampling point (T5) was one of the points with the highest risk of flood and is exposed to domestic wastes of the environment and emission pollution caused by traffic due to its proximity to the Samsun-Ordu highway (URL-1).

Table 1
Samsun - Tekkeköy sampling points and their coordinates

		Coordinates	
	Stations	Latitude	Longitude
Akkiraz	T1	41° 14' 30.6"	36° 24' 44.3"
Şabanoğlu	T2	41° 14' 13.8"	36° 25' 0.0"
OIZ Channel	T3	41° 14' 32.5"	36° 26' 0.4"
Hidrellez	T4	41° 13' 57.8"	36° 26' 1.1"
Selyeri	T5	41° 13' 45.6"	36° 28' 51.7"

2.2 Sediment Sampling and Analyses

Sediment samples were collected from five sampling points in the Samsun - Tekkeköy industrial zone in two seasons, namely August 2017 (summer) and December 2017 (winter), using a Van Veen grab sediment sampler in accordance with the USEPA (2001) technical manual standards. Sediment samples were collected from a depth of 0–20 cm and placed in polyethylene containers. The samples were brought to the laboratory with coolers (< 4 C°) to prevent deterioration before analysis. First, sediment samples were allowed to dry at 103°C for 24 hours. The dried sediment was sieved, and the samples below < 63 were digested according to the USEPA (2007) standard method 3051A. The silt fraction (approximately < 63 µm) of the sediment is considered to be important for the determination of pollutants, especially for metals. Due to the solubility of larger particles, pollutants are attached to the finer sediment fraction and can be an effective carrier in particles below 63 µm (Simpson 2005). A Milestone Digestion Stard D digestion device was used for the digestion process. 0.2 g of sediment samples below 63 µm were weighed and placed in Teflon containers. In the first step, 4 mL of 96% H₂SO₄ and 3 mL of 85% H₃PO₄ were added, and the device was operated at 220°C for 20 minutes and then for 15 minutes. After the time was over, in the second step, 5 mL of 67% HNO₃ and 6 mL of 40% HF were added, and Teflon containers were closed, and the device was operated for a total of 35 minutes, as in step 1. All chemicals were purchased from Sigma Aldrich (Saint Louis, USA). When both steps were completed and the device cooled down, the digestion process was completed, and the digested sediment samples were passed through a 0.45 µm porous Whatman WHA69722504 filter and made ready for heavy metal analysis. For heavy metal analyses, the samples were diluted to 50 ml with reagent water, and heavy metal measurements were performed by ICP-MS (Bruker 820-MS).

2.3 Evaluation of Sediment Contamination According to the Sediment Quality Guidelines (SQGs)

The Sediment Quality Guideline (SQG) has been developed to assess many environmental uncertainties and to support regulatory programs. In general, sediment pollution was determined by evaluating the chemical concentrations of the compositions and comparing them with background or reference values (Thomas 1987; USEPA 1987). SQGs are commonly used to determine contamination in the sediment by comparing the effects of the concentrations of sediment pollutants in the aquatic ecosystem with relevant quality guidelines (MacDonald 2000; Iqbal et al. 2013).

2.3.1 Toxic Risk Index (TRI)

In recent years, the toxic risk index (TRI) has been developed to determine the potential toxic risks of aquatic organisms (Zhang et al. 2016). The TRI method provides an integrated assessment of the toxic effects of heavy metals in the sediment, depending on both TEL and PEL values. In this study, the TEL and PEL values recommended by Macdonald et al. (2000) were selected. TRI_i was calculated using the following formula:

$$TRI = \sum_{i=1}^n TRI_i = \sqrt{\frac{\left(\frac{C_i}{TEL}\right)^2 + \left(\frac{C_i}{PEL}\right)^2}{2}} \quad (1)$$

where C_i represents a single metal concentration, and n represents the number of metals. Toxic risk effects were classified by five different categories (Table 2) (Kükrer et al. 2020).

2.3.2 Modified Hazard Quotient (mHQ)

The mHQ was proposed by Benson (2018) to evaluate the effects of contamination in the sediment depending on the level of contamination caused by heavy metals. This new approach is a tool for determining the level and risk of any metal for organisms (Mortazavi 2018). The determination of the modified hazard quotient (mHQ) is an important assessment guiding that indicates the risk level of each heavy metal for the biota, and this indice is obtained from the assessment of the compounds of metals in sediments by quantitative effect thresholds (TEL, PEL, and SEL) and the distribution of undesirable ecological synoptic effects (Mortazavi 2018). It was calculated using Eq. (2) (Benson 2018):

$$mHQ = \sqrt{\left| C_i \left(\frac{1}{TEL_i} + \frac{1}{PEL_i} + \frac{1}{SEL_i} \right) \right|} \quad (2)$$

where C_i is the measured metal concentration, TEL_i , PEL_i , and SEL_i are the abbreviations of threshold effect level, probable effect level, and severe effect level, respectively, for metal i . mHQ is interpreted by eight different classifications given in Table 2.

Table 2
Toxic risk and contamination classifications based on mHQ and TRI values

mHQ	Contamination level	TRI	Toxic risk level
$mHQ \leq 0.5$	Absence of contamination	< 5	No toxic
$0.5 < mHQ \leq 1.0$	Very low contamination	5–10	Low toxic
$1.0 < mHQ \leq 1.5$	Low contamination	10–15	Moderate toxic
$1.5 < mHQ \leq 2.0$	Moderate contamination	15–20	Significant toxic
$2.0 < mHQ \leq 2.5$	Considerable contamination	> 20	Very high toxic
$2.5 < mHQ \leq 3.0$	High contamination		
$3.0 < mHQ \leq 3.5$	Very high contamination		
$mHQ > 3.5$	Excessive contamination		

2.4 Potential Ecological Risk Index (PERI)

The PERI is recommended for determining the contaminating effect of heavy metals in coastal sediments, their environmental behavior and potential risks associated with toxicity (Hakanson 1980). The primary purpose of this index is to identify contaminating agents and to determine where to focus in cleaning and removal efforts (Maanan et al. 2015). PERI refers to the sum of the potential risk (E_r^i) of each metal and is calculated based on equations (3) and (4) below:

$$PERI = \sum E_r^i \quad (3)$$

$$\sum E_r^i = T_r^i \times (C_n^i \times C_{ref}^i) \quad (4)$$

where E_r^i is the ecological risk index of each metal, T_r^i is the toxic risk factor for a single metal, C_n is the metal concentration measured in this study, and C_{ref} is the mean background value of the measured metal (Smith and Huyck 1999). T_r (toxic response factor) was taken as 5 for Cu, Pb and Co, 1 for Zn and 30 for Cd (Guo et al. 2012; Islam et al. 2015). Table 3 includes the risk classifications of the E_r^i and PERI values (Mamat et al. 2016; Kükrer 2020).

Table 3 Potential ecological risk index classification

E_r^i	Risk classification	PERI
$E_r^i \leq 40$	Low Risk	PERI ≤ 150
$40 \leq E_r^i < 80$	Moderately Risk	$150 < PERI \leq 300$
$80 \leq E_r^i < 160$	Considerable Risk	$300 < PERI \leq 600$
$160 \leq E_r^i < 320$	High Risk	PERI > 600
$E_r^i \geq 320$	Severe High Risk	

2.5. Environmental Risk Assessment

The enrichment factor, geoaccumulation index, and contamination factor were used for environmental risk assessment. The classifications for risk assessment are presented in Table 4.

2.5.1 Enrichment Factor (EF)

EF is used as a method of controlling whether the enrichment of heavy metals in the sediment is anthropogenic or of natural origin (Iqbal et al. 2013). It is a normalization method proposed by Sinex and Helz (1981) and is used in the standardization of the heavy metal content obtained from the sediment relative to a reference metal selected as Fe, Al, or Mg. EF was calculated according to Eq. (5) as follows:

$$EF = \frac{(C_n/Fe)_{\text{sample}}}{(B_n/Fe)_{\text{background}}} \quad (5)$$

In this study, Fe was used as the reference metal. C_n is the measured metal concentration, B_n is the background value of the metal used in the calculation.

2.5.2 Geoaccumulation Index (I_{geo})

The I_{geo} is a method used to evaluate the level of heavy metal contamination in the sediment. It is found by comparing the measured heavy metal concentration in the sediment with the relevant geochemical background data (Varol 2020). I_{geo} is calculated according to the following Eq. (6) (Müller 1981):

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 \times B_n} \right) \quad (6)$$

C_n is the heavy metal concentration measured in the study, and B_n is the geochemical background concentration of the relevant metal.

2.5.3 Contamination Factor (C_F)

C_F is commonly used to identify the level of potential contamination in the sediment. In the method developed by Hakanson (1980), the metal concentration measured to determine the contaminant level of each metal was found by comparing it with the reference metal concentration as follows, in Eq. (7):

$$C_F = C_n / B_n \quad (7)$$

Where C_n is the concentration of each metal measured in the study and B_n is the background concentration of the metal.

Table 4
Environmental risk assessment classifications, EF, I_{geo} and C_F

EF	Enrichment level	I_{geo}	Contamination level	C_F	Contamination level
EF < 2	Minimum enrichment	$I_{geo} < 0$	Uncontaminated	$C_F \leq 1$	Low contamination
$2 \leq EF < 5$	Medium enrichment	$0 \leq I_{geo} < 1$	Uncontaminated to moderately contaminated	$1 \leq C_F < 3$	Moderate contamination
$5 \leq EF < 20$	Significant enrichment	$1 \leq I_{geo} < 2$	Moderately contaminated	$3 \leq C_F < 6$	Significant contamination
$20 \leq EF < 40$	Very high enrichment	$2 \leq I_{geo} < 3$	Moderately to severely contaminated	$C_F \geq 6$	Very high contamination
EF ≥ 40	Excessive enrichment	$3 \leq I_{geo} < 4$	Very contaminated		
		$4 \leq I_{geo} < 5$	Strong to heavily contaminated		
		$I_{geo} \geq 6$	Highly contaminated		

2.6. Human Health Risk Assessment

Human health risk assessment is the process of predicting the possibility of negative health effects in people who may be exposed to contaminants in a contaminated environment at present or in the future. People can be exposed to heavy metals in three ways: oral ingestion, inhalation and exposure of the skin to contaminants by dermal contact (Luo et al., 2012; Kusin et al., 2018). Risk assessment was performed using the USEPA RAGS methodology (USEPA 1989, 2004; Filipsson et al. 2009).

In general, the health risk through ingestion, inhalation and dermal route for both adults and children is predicted by chronic daily exposure (CDE) (mg/kg/day), and it is formulated as follows:

$$CDE_{ing} = \frac{C_{sed} \times IngR \times EF \times ED \times CF}{BW \times AT} \quad (8)$$

$$CDE_{inh} = \frac{C_{sed} \times InhR \times EF \times ED}{PEF \times BW \times AT} \quad (9)$$

$$CDE_{der} = \frac{C_{sed} \times SA \times AF \times ABS \times EF \times ED \times CF}{BW \times AT} \quad (10)$$

where C_{sed} is the heavy metal concentration in the sediment sample (mg/kg), CDE_{ing} is the exposure through ingestion (mg/kg/day), CDE_{inh} is the exposure through inhalation, and CDE_{der} is the dermal exposure (mg/kg/day). Table 5 includes other exposure definitions used in CDE prediction.

Table 5
Exposure factors used in CDE prediction (USEPA 2002)

Parameter	Specification (unit)	Amount
IngR	Ingestion rate (mg/day)	100 (adult), 200 (children)
InhR	Inhalation rate (mg/ cm ²)	20
EF	exposure frequency (days/year)	350
ED	exposure duration (years)	24 (adult), 6 (children)
CF	conversion factor (kg/mg)	1×10^{-6}
PEF	particle emission factor (m ³ /kg)	1.36×10^9
BW	body weight (kg)	70 kg (adult), 15 kg (children)
AT	averaging time (days)	2190
SA	surface area (cm ²)	5700
AF	adherence factor (mg/cm ²)	0.07
ABS	dermal absorption factor (unitless)	0.01

The health risks related with exposure to heavy metals in the sediment are defined as hazard quotients (HQ) according to the USEPA (2004) health risk assessment guidelines, and HQ characterizes non-carcinogenic risks. The hazard index (HI) representing accumulative non-carcinogenic risks is obtained by summing the exposed hazard quotients, as in Eq. 12 below (Wang 2015; Kusin et al. 2018; Ustaoğlu and Islam 2020a).

$$HQ = \frac{CDE}{RfD} \quad (11)$$

$$HI = \sum HQ = HQ_{ing} + HQ_{inh} + HQ_{derm} \quad (12)$$

The *RfD* value in Eq. 11 represents the reference dose used to predict human health risk determined by the USEPA (2020).

The total lifetime cancer risk (TLCR) was calculated to predict health risk caused by carcinogenic metals. The sum of cancer risks was determined using Eq. 14 for each exposure route.

$$TLCR = CDE \times CSF \quad (13)$$

$$\sum TCLR = CLR_{ing} + CLR_{inh} + CLR_{derm} \quad (14)$$

CSF is the cancer slope factor and was 6.3, 0.5, and 0.0085 mg/kg/day for Cd, Cr, and Pb, respectively (USEPA 2012). The threshold value of TLCR is considered as 1×10^{-4} by the USEPA, and the acceptable range was given as $1 \times 10^{-6} - 1 \times 10^{-4}$.

In this study, Cr, Cd, and Pb metals were used in the calculation for predicting the carcinogenic health risk for both children and adults, and Fe, Al, Mn, Cr, Cu, Ni, Zn, Pb and Cd metals were used in the calculation for predicting the non-carcinogenic health risks.

2.7 Statistical Analysis

Commonly used methods to determine the contaminating effects of heavy metals include element types, profile dispersion and spatial dispersion. However, it is not possible to distinguish between metal sources on their own and they must be associated with additional data. (Boruvka et al. 2005). Multivariate statistical methods supply an alternative direction for identifying sources of pollution and understanding the anthropogenic and natural contribution of pollutants. Statistical methods can be used to evaluate complex ecotoxicological processes by demonstrating correlations and differences between variables and their relative weights in the study (Iqbal et al. 2013; Ustaoğlu and Tepe 2019). In this study, the correlation between heavy metals in sediment samples was determined using the Pearson correlation index (PCI). SPSS 22.0 statistical software program was used for PCI analysis. PCI is a statistical method used to determine the correlations between metals and metalloids and the extent of the correlation between variables.

3. Results And Discussions

3.1 Distribution of Heavy Metals in the Sediment and Assessment According to SQG

The investigation of the accumulation of heavy metals in the sediment caused by industry is one of the important points in understanding inorganic contamination in aquatic ecosystems. Therefore, it is extremely important to determine the anthropogenic source metal input in the sediment and the toxic

effect of this input on all ecosystems (Balık and Tunca 2015). The concentrations of heavy metals in sediment samples collected from Samsun-Tekkeköy Region are presented in Table 6. According to the mean concentrations in August and December 2017 given in Table 5, the accumulation of heavy metals was Fe > Al > Mn > Zn > Cu > Cr > Ni > Pb > Cd.

Table 6
Heavy metal concentrations in the sediment samples in Samsun-Tekkeköy (mg/kg)

mg/kg	Fe	Mn	Cr	Cu	Zn	Pb	Ni	Al	Cd
August 2017									
T1	14082.50	181.05	11.60	47.00	26.50	3.05	11.45	9114.50	0.05
T2	11913.00	254.50	13.95	53.25	64.35	8.30	9.90	10788.00	0.55
T3	11275.50	260.10	177.05	102.05	390.10	5.10	92.75	6965.00	1.15
T4	9153.50	172.70	15.30	28.25	231.00	5.25	8.00	5921.00	1.30
T5	10885.00	194.65	22.15	46.40	64.05	7.20	11.75	8945.50	0.45
Mean	11461.90	212.60	48.01	55.39	155.20	5.78	26.77	8346.80	0.70
December 2017									
T1	12124.50	274.40	14.75	34.65	62.75	7.40	9.95	6267.50	0.70
T2	11657.00	221.20	12.95	37.90	32.65	5.35	9.30	6113.50	0.75
T3	9660.00	247.60	127.25	103.65	300.55	5.30	60.30	6671.00	0.80
T4	11980.00	231.30	31.15	47.45	58.80	5.45	14.35	6386.00	0.35
T5	13147.50	235.15	19.80	37.00	30.85	5.05	13.95	5796.00	0.45
Mean	11713.80	241.93	41.18	52.13	97.12	5.71	21.57	6246.80	0.61
^a TEL	-	-	37.3	35.7	123	35	18	-	0.6
^a PEL	-	-	90	197	315	91.3	36	-	3.53
^a SEL	-	-	110	110	820	250	75	-	10
^b Background value	50000	950	100	70	132	13	68	79000	0.2
^a : Mac Donald et al. (2000)									
^b : Smith and Huyck (1999)									

Fe and Al are the main metals found at higher concentrations in the soil and sediment compared to other metals. Mn is known as the third metal with a lower but generally high concentration compared to Fe and Al (Diami et al. 2016; Kutty and Al-Mahaqeri 2016; Kusun et al. 2018). In this study, the highest Fe and Mn concentration (14082.50 mg/kg – 274.40 mg/kg, respectively) was observed in the Akkiraz stream, and the highest Al concentration was observed at the Şabanoğlu sampling point. The lowest Fe, Al, and Mn concentrations (9153.50; 5921.00; 172.70 mg/kg, respectively) were observed at Abdal river sampling point T4. Al, Fe, and Mn concentrations did not exceed the earth crust reference value at any sampling point. When other metals were examined, Pb did not exceed the background value at any sampling point, and Cd was above the background value in both seasons except for the sampling point T1 (Akkiraz). While Cr and Cu were above the earth crust reference value at sampling point T3 (OIZ Channel) in both seasons, Zn was above it at sampling points T3 and T4 (the Şabanoğlu stream) in summer and at sampling point T3 in winter, and Ni was above it at sampling point T3 only in summer.

When the threshold effect level (TEL), severe effect level (SEL), and probable effect level (PEL) values given in Table 6 were examined according to the SQG, Cr metal exceeded all effect levels at sampling point T3 in both seasons. Cu was above the TEL at sampling points T1, T2, T3, and T5 (the Hidrellez Stream) in summer (August 2017) and at sampling points T2, T3, T4, and T5 in winter (December 2017), PEL was not exceeded at any point, and SEL was exceeded only at sampling point T3 in summer. For Zn, SEL was not exceeded in both seasons, TEL was exceeded at sampling points T3 and T4 in summer and at sampling point T3 in winter, and PEL was exceeded at sampling point T3 only in summer. Pb was found to be below the effect levels at all points. For Ni, PEL and SEL levels were not exceeded, and TEL was exceeded only at point T3 in both seasons. Finally, Cd metal was below the PEL and SEL levels. However, the TEL effect level was exceeded at points T3 and T4 in summer and at points T1, T2, and T3 in winter.

When the metal results were evaluated in general, sampling point T3 was found to be above the standard values for almost every metal according to both the background values and the SQG values. High amounts of heavy metals in ecosystems are usually described in the literature due to the discharge of wastewater from agriculture (pesticides and fertilizers), industrial activities and domestic wastewater (Yang et al. 2009; Hedayatzadeh and Hassanzadeh 2020). Accordingly, the fact that sampling point T3 was the channel sample within the industry of Tekkeköy District and the industrial and domestic wastewater discharges in the environment led to an increase in metal contamination at this sampling point. On the other hand, the distribution of heavy

metals differed between different sampling points in two seasons. However, it was observed that the increase in contamination was generally higher in summer. The differences in the source of heavy metals are due to many conditions such as dominant physicochemical state, adsorption, redox potential and flocculation of the sediment (Jain et al. 2008). Furthermore, the dilution caused by the effect of the entry of rainwater to the sampling points in the winter season, during which precipitation is high, led to a decrease in metal concentrations. These results are similar to the results of the studies conducted by Kir et al. (2007), Ntakirutimana et al. (2013), Hedayatzadeha and Hassanzadehb (2020).

3.1.1 Evaluation of the Toxic Risk Index (TRI)

TRI was used to evaluate ecotoxic risks (Zhang et al. 2016). When the toxic risk index of each metal was calculated for two seasons, it was observed that there was no toxic risk due to contamination close to negative. When the total risks of metals were evaluated in Fig. 2, the TRI value was calculated to be 13.65 at sampling point T3 in August 2017. Since the TRI value was in the range of $10 < TRI \leq 15$, it was found to be a moderate risk in summer, and sampling point T4 was found to have a low toxic risk with a value of 6.12 in the range of $5 < TRI \leq 10$. In December 2017, sampling point T3 had a moderate toxic risk with a value of 10.27. The highest contribution to TRI comes from Cu, Ni, followed by Cd and Cr, respectively.

3.1.2 Evaluation of the Modified Hazard Quotient

The mHQ is an index, which was developed by Benson et al. (2018) and is used to determine the degree of contamination caused by heavy metals one by one in the sediment. This index compares the concentration of individual metals with the sediment quality guidelines (TEL, PEL and SEL) levels to calculate and rank the exceeding magnitude of each heavy metal. The modified hazard quotient values calculated for both seasons are presented in Table 7.

Table 7
Modified Hazard Quotient values of the sediment samples in Samsun- Tekkeköy

	mHQ									
	August 2017					December 2017				
	T1	T2	T3	T4	T5	T1	T2	T3	T4	T5
Cr	0.74	0.81	2.89	0.85	1.02	0.83	0.78	2.45	1.21	0.96
Cu	1.41	1.50	2.07	1.09	1.40	1.21	1.26	2.09	1.41	1.25
Zn	0.58	0.90	2.21	1.70	0.90	0.89	0.64	1.94	0.86	0.62
Pb	0.36	0.60	0.47	0.48	0.56	0.57	0.48	0.48	0.49	0.05
Ni	1.05	0.98	2.99	0.88	1.07	0.98	0.95	2.41	1.18	1.16
Cd	0.32	1.06	1.54	2.40	0.96	1.20	1.24	1.28	0.85	0.96

mHQ indicates moderate contamination in the range of $1.5 < mHQ < 2.0$, at which contamination begins to increase according to Table 2. Accordingly, when Table 7 was evaluated, all metals except Pb were in and above this value range at sampling point T3 in the August 2017 sampling period. While Cd showed moderate contamination with a value of 1.54, other metals showed significant and high contamination with a value above 2. Values above 1.5 are marked in bold. In the same season, only at sampling point T4 except for T3, moderate and significant contamination was observed in Zn and Cd metals, respectively. In December 2017, it was observed that there was contamination in Cr, Cu, Zn, Ni, and Cd metals at sampling point T3.

3.2 Evaluation of the Potential Ecological Risk Index (PERI)

Table 8 shows data on the potential ecological risk of the sampling points in the study calculated in two seasons. This index is an index that includes the toxicity effect of metals in the calculation in addition to the measured sediment concentration compared to the background value of the heavy metal in the earth's crust (Diimi et al. 2016). Accordingly, when the results were examined, all metals except for Cd had a low risk according to the risk classification given in Table 3. Cd was at a serious risk level in both seasons according to the PERI values of the metal, this is because Cd is one of the largest discharges from human activities. (Cheng et al. 2015).

Table 8 E_r^i and PERI values in Samsun-Tekkeköy Region

	E_r^i August 2017					PERI	E_r^i December 2017					PERI
	T1	T2	T3	T4	T5		T1	T2	T3	T4	T5	
Cr	0.23	0.28	3.54	0.31	0.44	4.8	0.3	0.26	2.55	0.62	0.4	4.13
Cu	3.36	3.8	7.29	2.02	3.31	19.78	2.48	2.71	7.4	3.39	2.64	18.62
Zn	0.2	0.49	2.96	1.75	0.49	5.89	0.48	0.25	2.28	0.45	0.23	3.69
Pb	1.17	3.19	1.96	2.02	2.77	11.11	2.85	2.06	2.04	2.1	1.94	2.19
Cd	7.5	82.5	172.5	195	67.5	525	105	112.5	120	52.5	67.5	457.5

3.3 Environmental Risk Assessment

The evaluation of the enrichment factor (EF), geoaccumulation (I_{geo}) factor and contamination factor (C_F) results is provided for environmental risk assessment (Fig.3). EF geochemical normalization is used to attain the enrichment factor and evaluate the anthropogenic effects of the metals in the

sediments examined (Aloupi and Angelidis 2001; Figueroa et al. 2006; Alkan et al. 2015). In this study, Fe metal was used for geochemical normalization. The geo-accumulation index (I_{geo}) allows the evaluation of contamination by comparing the current and past earth crust concentrations of metals (Iqbal et al. 2013). According to the EF classification given in Table 4, there was a minimal metal enrichment in the case of $EF < 2$. When the results given in Fig. 3 were examined, the EF values of Mn, Cr, Pb, Ni, and Al metals were below 2 in both seasons and showed little metal enrichment. Cu was above the minimal enrichment level in both seasons and at all sampling points. However, it showed a significant enrichment at sampling point T3 with a value of 7.85 in summer and 6.59 in winter. Zn was below the minimal enrichment value only at sampling point T1 and showed a significant enrichment at sampling points T3 and T4 during the August 2017 period; however, during the December 2017, it was in the range of significant enrichment value only at sampling point T3. Cd showed enrichment at all points except for sampling point T1 only in August 2017. A very high metal enrichment was observed at sampling point T3 in both seasons.

When I_{geo} values were examined, all metal results ($I_{geo} < 0$) except for Cd were negative at the "non-contaminated" level in December 2017, and Cd was negative only at sampling point T1 and was at "moderately to severely contaminated" levels, showing positive values at other points in August 2017. Furthermore, it was observed that Cr was at the level of "non-contaminated to moderately contaminated" with a value of 0.24 at sampling point T3 in August 2017, and Zn was "non-contaminated to moderately contaminated" at sampling points T3 and T4 as in Cr metal.

Finally, similar to C_F , I_{geo} and EF values, Fe, Mn, Pb and Al metals showed "a low level of contamination" below 1. Cr, Cu, and Zn were in the range of " $1 \leq C_F \leq 3$ moderate contamination" at sampling point T3 in both seasons. Cd showed "a low level of contamination" with a value of 0.25 at sampling point T1 in August 2017, "a significant contamination" at sampling point T3 in both seasons, and "considerably high contamination" at sampling point T4 only in August 2017.

3.4 Human Health Risk Assessment

As a result of heavy metal contamination, the environment and, therefore, living beings are affected, and heavy metal contamination in the environment poses a risk to human health stemming from the food chain. Metals such as Cr, As, Cd and Pb have high toxicity and are among the primacy metals that should be evaluated for public health. Even at the lowest levels of immunity, they are considered to be toxic, which may affect multiple organ damage, and these elements are classified as human carcinogens (IARC 2012; Paul et al. 2014; Kusin et al. 2018). Therefore, in this study, carcinogenic and non-carcinogenic human health risks were evaluated. Eq. (8) for CDE_{ing} , Eq. (9) for CDE_{inh} and Eq. (10) for CDE_{der} were calculated separately for each metal. Results are given at Table 9 and Table 10.

Table 9
Samsun-Tekkeköy Region August 2017 chronic daily exposure (CDE), hazard quotient (HQ), and hazard index (HI) for non-carcinogenic risks

Adults(Agu17)								
Metal Element	RfD	CDEing	CDEinh	CDEderm	HQing	Hqinh	HQderm	HI
Fe	7.00E-01	1.570E-02	2.309E-06	6.265E-05	2.243E-02	3.299E-06	8.950E-05	2.252E-02
Mn	1.40E-01	2.912E-04	4.283E-08	1.162E-06	2.080E-03	3.059E-07	8.300E-06	2.089E-03
Cr	3.00E-03	6.575E-05	9.670E-09	2.624E-07	2.192E-02	3.223E-06	8.745E-05	2.201E-02
Cu	4.00E-02	7.589E-05	1.116E-08	3.028E-07	2.046E-03	3.008E-07	8.162E-06	2.054E-03
Zn	3.00E-01	2.126E-04	3.127E-08	8.483E-07	7.087E-04	1.042E-07	2.828E-06	7.116E-04
Pb	3.00E-03	7.945E-06	1.168E-09	3.170E-08	2.270E-03	3.338E-07	9.058E-06	2.279E-03
Ni	2.00E-02	3.671E-05	5.399E-09	1.465E-07	1.836E-03	2.699E-07	7.324E-06	1.843E-03
Al	1.00E + 00	1.143E-02	1.681E-06	4.562E-05	1.143E-02	1.681E-06	4.562E-05	1.148E-02
Cd	1.00E-03	9,589E-07	1,410E-10	3,826E-09	9,589E-04	1,410E-07	3,826E-06	9,629E-04
Children(Agu17)								
Fe	7.00E-01	1.465E-01	1.078E-05	2.924E-04	2.093E-01	1.539E-05	4.177E-04	2.098E-01
Mn	1.40E-01	2.718E-03	1.999E-07	5.423E-06	1.942E-02	1.428E-06	3.873E-05	1.946E-02
Cr	3.00E-03	6.137E-04	4.512E-08	1.224E-06	2.046E-01	1.504E-05	4.081E-04	2.050E-01
Cu	4.00E-02	7.083E-04	5.208E-08	1.413E-06	1.909E-02	1.404E-06	3.809E-05	1.913E-02
Zn	3.00E-01	1.984E-03	1.459E-07	3.959E-06	6.614E-03	4.863E-07	1.320E-05	6.628E-03
Pb	3.00E-03	7.416E-05	5.453E-09	1.479E-07	2.119E-02	1.558E-06	4.227E-05	2.123E-02
Ni	2.00E-02	3.426E-04	2.519E-08	6.836E-07	1.713E-02	1.260E-06	3.418E-05	1.717E-02
Al	1.00E + 00	1.067E-01	7.847E-06	2.129E-04	1.067E-01	7.847E-06	2.129E-04	1.069E-01
Cd	1.00E-03	8,950E-06	6,581E-10	1,785E-08	8,950E-03	6,581E-07	1,785E-05	8,968E-03

The total lifetime cancer risks (TLCR) of heavy metals are presented in Table 11. Similarly, in both seasons, heavy metal exposure showed a higher potential risk in children than adults because children are more likely to be exposed to heavy metals through skin, inhalation, or ingestion (Luo et al. 2012). All TLCR values were in the range of $(1 \times 10^{-6} - 1 \times 10^{-4})$ recommended by USEPA. Similar results were also reported in the studies conducted in Turkey and other countries (e.g. Luo et al. 2012; Karim and Qureshi 2014; PerezVazquez et al. 2016; Kusin et al. 2018; Ustaoglu and Islam 2020a; Varol 2020).

Table 10
Samsun-Tekkeköy Region December 2017 chronic daily exposure (CDE), hazard quotient (HQ), and hazard index (HI) for non-carcinogenic risks

Adults(Dec17)								
Metal Element	RfD	CDEing	CDEinh	CDEderm	HQing	Hqinh	HQderm	HI
Fe	7.00E-01	1.605E-02	2.360E-06	6.402E-05	2.292E-02	3.371E-06	9.146E-05	2.302E-02
Mn	1.40E-01	3.314E-04	4.874E-08	1.322E-06	2.367E-03	3.481E-07	9.445E-06	2.377E-03
Cr	3.00E-03	5.641E-05	8.296E-09	2.251E-07	1.880E-02	2.765E-06	7.503E-05	1.888E-02
Cu	4.00E-02	7.141E-05	1.050E-08	2.849E-07	1.925E-03	2.831E-07	7.680E-06	1.933E-03
Zn	3.00E-01	1.330E-04	1.956E-08	5.308E-07	4.435E-04	6.522E-08	1.769E-06	4.453E-04
Pb	3.00E-03	6.452E-06	9.488E-10	2.574E-08	1.843E-03	2.711E-07	7.355E-06	1.851E-03
Ni	2.00E-02	2.955E-05	4.345E-09	1.179E-07	1.477E-03	2.173E-07	5.895E-06	1.484E-03
Al	1.00E+00	8.557E-03	1.258E-06	3.414E-05	8.557E-03	1.258E-06	3.414E-05	8.593E-03
Cd	1.00E-03	8.356E-07	1.229E-10	3.334E-09	8.356E-04	1.229E-07	3.334E-06	8.391E-04
Children(Dec17)								
Fe	7.00E-01	1.498E-01	1.101E-05	2.988E-04	2.140E-01	1.573E-05	4.268E-04	2.144E-01
Mn	1.40E-01	3.093E-03	2.274E-07	6.171E-06	2.209E-02	1.625E-06	4.408E-05	2.214E-02
Cr	3.00E-03	5.265E-04	3.871E-08	1.050E-06	1.755E-01	1.290E-05	3.501E-04	1.759E-01
Cu	4.00E-02	6.665E-04	4.901E-08	1.330E-06	1.797E-02	1.321E-06	3.584E-05	1.800E-02
Zn	3.00E-01	1.242E-03	9.130E-08	2.477E-06	4.139E-03	3.043E-07	8.257E-06	4.148E-03
Pb	3.00E-03	6.022E-05	4.428E-09	1.201E-07	1.721E-02	1.265E-06	3.432E-05	1.724E-02
Ni	2.00E-02	2.758E-04	2.028E-08	5.502E-07	1.379E-02	1.014E-06	2.751E-05	1.382E-02
Al	1.00E+00	7.987E-02	5.873E-06	1.593E-04	7.987E-02	5.873E-06	1.593E-04	8.003E-02
Cd	1.00E-03	7.799E-06	5.735E-10	1.556E-08	7.799E-03	5.735E-07	1.556E-05	7.815E-03

Table 11
Samsun-Tekkeköy Region exposure assessment for carcinogenic risks

	Adults				Children			
(Agu17)	LCRing	LCRinh	LCRderm	TLCR	LCRing	LCRinh	LCRderm	TLCR
Cr	3,288E-05	4,835E-09	1,312E-07	3,301E-05	3,068E-04	2,256E-08	6,122E-07	3,075E-04
Pb	6,753E-08	9,932E-12	2,695E-10	6,781E-08	6,303E-07	4,635E-11	1,257E-09	6,316E-07
Cd	6,041E-06	8,884E-10	2,410E-08	6,066E-06	5,638E-05	4,146E-09	1,125E-07	5,650E-05
(Dec17)								
Cr	2,821E-05	4,148E-09	1,125E-07	2,832E-05	2,633E-04	1,936E-08	5,252E-07	2,638E-04
Pb	5,484E-08	8,065E-12	2,188E-10	5,507E-08	5,119E-07	3,764E-11	1,021E-09	5,129E-07
Cd	5,264E-06	7,742E-10	2,100E-08	5,286E-06	4,913E-05	3,613E-09	9,802E-08	4,924E-05

3.5 Pearson Correlation Matrix

A statistical evaluation was performed using the correlation matrix values of the metals in the sediments in Samsun-Tekkeköy Region (Table 12) to further evaluate the extent of metal contamination in the study area and to determine its sources. The correlation analysis between metals can reflect whether the sources of pollution are similar. A significant or extremely significant correlation between elements indicates that these metals may have the same source of

contamination (Kükrer et al. 2014; Ustaoğlu et al. 2020b). In the Pearson Correlation Index (PCI), values (r) close to “-1” indicate a strong negative correlation and values close to “+1” indicate a strong positive correlation.

Table 12
Pearson Correlation matrix of the heavy metals in the Samsun Tekkeköy District Sediment (Lower part of the diagonal August 2017 - upper part December 2017)

	Fe	Mn	Cr	Cu	Zn	Pb	Ni	Al	Cd
Fe	1	-0.093	-0.883	-0.906	-0.911	-0.472	-0.868	-0.884	-0.652
Mn	0.100	1	0.117	0.072	0.238	0.449	0.126	0.279	0.305
Cr	-0.086	0.634	1	0.997**	0.988**	0.101	0.997**	0.760*	0.416
Cu	0.183	0.789*	0.939**	1	0.984**	0.129	0.992**	0.780*	0.426
Zn	-0.497	0.393	0.857*	0.647	1	0.211	0.987**	0.798*	0.518
Pb	-0.377	0.458	-0.159	-0.056	-0.166	1	0.058	0.679	0.457
Ni	-0.030	0.640	0.998**	0.950**	0.837*	-0.190	1	0.717*	0.446
Al	0.630	0.309	-0.407	-0.074	-0.751	0.457	-0.380	1	0.388
Cd	-0.849	-0.243	0.079	-0.234	0.581	-0.043	0.041	-0.812	1
* Significant coefficient at a level of $p < 0.05$									
** Significant coefficient at a level of $p < 0.01$									

The values close to “0” mean that there is no significant linear correlation (Ustaoğlu and Tepe, 2019). According to the values of the Pearson correlation coefficients given in Table 12, many metals were considerable correlated ($p < 0.01$ and $p < 0.05$). Quite strong correlations were found between Cr, Cu, Zn, and Ni.

In August 2017, highly strong positive correlations were found between Cr-Cu, Ni; Cu-Ni (r above 0.93; $p < 0.01$) and strong correlations were found between Mn-Cu; Cr-Zn, Zn-Ni (r above 0.78; $p < 0.05$). When the data for December 2017 were examined, it was observed that there was a high correlation between Cu-Cr; Zn-Cr, Cu; Ni-Cr, Cu, Zn (r above 0.98; $p < 0.01$) and a high correlation between Al- Cr, Cu, Pb and Ni (r above 0.70; $p < 0.05$).

4. Conclusions

The results of heavy metal concentrations show that the sediment from Tekkeköy ranges from contaminated to moderately toxic and poses a significant risk in some assessments. The Tekkeköy Coast is contaminated with heavy metals, which is an effect of industrial and domestic wastes in the area and is found to be strongly dependent on their sources.

The highest concentrations of heavy metals measured were observed at station T3 (OIZ channel). The OIZ channel is in the Central Organized Industrial Zone, and there are enterprises operating in the hardware, non-electrical machinery, non-ferrous metals, food and furniture sectors. Since the production wastes of all these industrial enterprises are discharged to the OIZ Channel, they constitute a significant source of contamination. When the SQG values at point T3 were compared with the standard values, while heavy metal concentrations were lower in winter, they were higher in summer. These results may be due to the dilution of surface waters with the entry of rainwater into surface water in winter.

As a result of the ecotoxicological risk assessment according to the contamination effects of heavy metals on the coastal sediment, TRI showed that there was a hazard at point T3 but did not pose too much risk, and according to the mHQ index, a significant and high degree of contamination was determined in all metals except for Pb at point T3. In the evaluation of PERI, EF and Igeo, Cd showed considerable risk values and main pollutants at T3 due to the effect of direct outer sources such as agricultural flows, industrial activities and other anthropogenic resources. It is a stock pollutant and extremely harmful to marine life at high concentration levels.. When potential health risks for humans were evaluated, it was observed that exposure to sediment through ingestion or skin contact posed a low non-carcinogenic health risk for heavy metals.

While the heavy metal concentration measured in the sediments in the study area is listed as $Fe > Al > Mn > Zn > Cu > Cr > Ni > Pb > Cd$, environmental indices (enrichment factor, and contamination factor) followed the descending order as $Cd > Zn > Cu > Cr > Pb > Ni > Mn > Fe > Al$. The reason for this can be considered as transportation-based inputs and industrial processes, since the study area is an industrial area. According to the results obtained, the effect of industrial input as a heavy metal source in the study area was quite high due to the difficulty in overall sediment management because all industrial wastewater cannot be treated, and untreated water is discharged directly to the river and the sea from the sewers, especially after heavy rain. It is very important to improve the loads and cumulative concentrations of heavy metals and to implement timely contamination monitoring and improvement strategies in order to prevent heavy metal contamination in the study area, especially in the area around sampling point T3 exposed to agricultural and industrial loads. Furthermore, domestic and industrial wastewater should be discharged to the receiving environment after the receiving rate discharge standards are met. The results of the study may be precious for researchers in environmental quality and human health risk assessment, and the methods applied can also be used for contamination assessment in other environments.

Declarations

Ethics approval and consent to participate

No ethics approval or consent was required for this study.

Consent for publication

All authors agreed to submission of the manuscript.

Availability of data and materials

Not applicable.

Competing interests

The authors declare no competing interests.

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Author Contributions

AŞ: Writing- Original draft preparation, Formal analysis, Investigation, Conceptualization. HBÖ: Methodology , Writing - Review & Editing, Conceptualization. All authors read and approved the final manuscript. GB: Methodology, Supervision.

- All data generated or analysed during this study are included in this published article.

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Figures



Figure 1

The study area and locations of sampling points in Samsun-Tekkeköy District

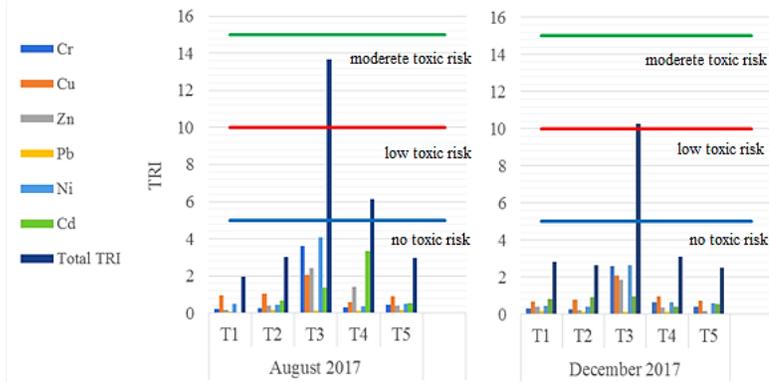


Figure 2

TRI classification according to heavy metal concentrations in Samsun-Tekkeköy

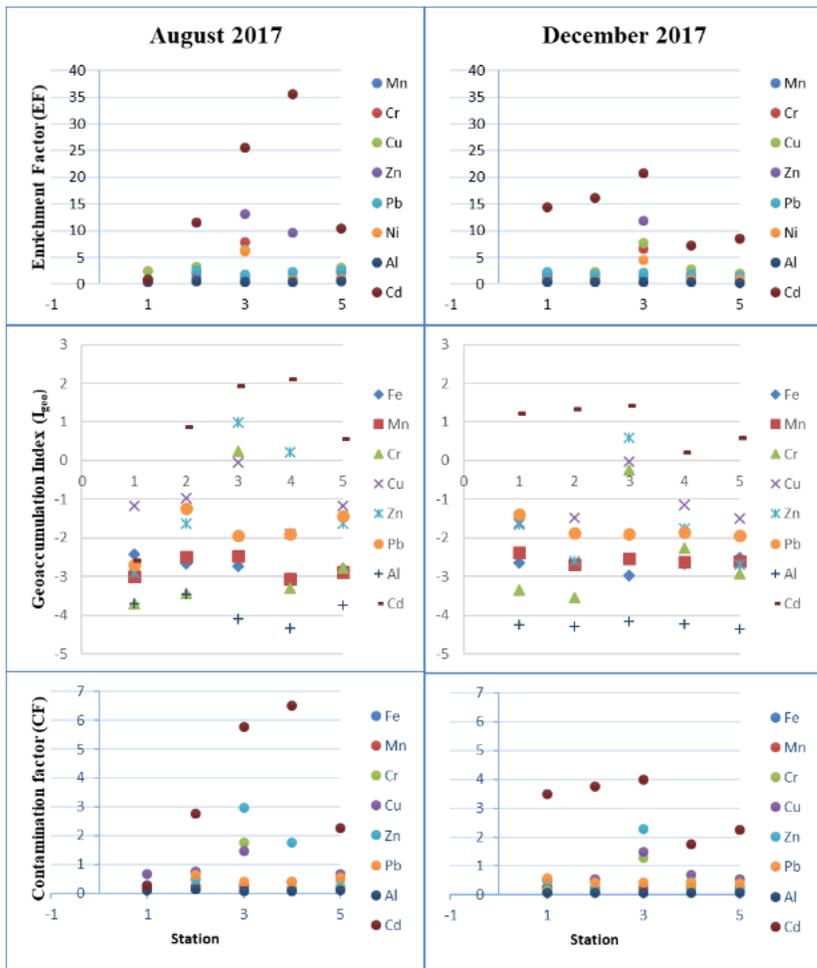


Figure 3
 Environmental indexes: 1) Enrichment Factor (EF) 2) Geoaccumulation Index (I_{geo}) 3) Contamination Factor (CF) values for heavy metals in Samsun-Tekkeköy sediments