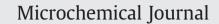
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Heavy metal contamination of surface soil around Gebze industrial area, Turkey

Gülten Yaylalı-Abanuz*

Department of Geological Engineering, Karadeniz Technical University, 61080 Trabzon, Turkey

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ABSTRACT

An increase in heavy metal pollution in the soils of Gebze (Turkey) due to intense industrialization and urbanization has become a serious environmental problem. There are two large organized industrial zones in Gebze; the Gebze Organized Industrial Zone (GOIZ) and the Dilovası Organized Industrial Zone (DOIZ). The region hosts several industrial facilities which are the main source for hazardous wastes which include paint, plastic, electric, metal, textile, wood, automotive supply industry, food, cosmetics, packing, machinery, and chemicals. Soil samples were collected from these two industrial zones and analyzed for their metal contents. Results of the analysis show that the soils are characterized by high concentrations of Cd, As, Pb, Zn, Mn, Cu, Cr and Hg. Since concentrations of other elements do not exceed the permissible levels, they are not evaluated. Concentrations are 0.05-176 mg/kg of Cd, 10-1161 mg/kg of Cr, 7.87-725 mg/kg of Cu, 1.50-65.60 mg/kg of As, 17.07-8469 mg/kg of Pb, 1.96-10,000 mg/kg of Mn, 29.5-10,000 mg/kg of Zn, and 9-2721 µg/kg of Hg. Application of factor, cluster and correlation analysis showed that heavy metal contamination in soils originates from industrial activities and heavy traffic which are of anthropogenic origin. Contaminations in soils were classified as geoaccumulation index, enrichment factor, contamination factor, and contamination degree. Integrated pollution index (IPI) values indicate that heavy metal pollution levels of soils collected from industrialization sites are greater than those from distal parts of industrialization. Spreading of hazardous wastes from industrial facilities in the study area via rain or wind is the main source of soil pollution. In addition, traffic-related metal pollution is also observed.

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1. Introduction

With rapid development in industrialization, soil contamination has become a serious problem in many countries. Contamination and negative impact on the quality of air, water, and soil by population growth, rapid urbanization, and industrial activities have been stated by several works [1,2]. Among the most significant soil contaminants resulting from both natural and manmade sources, heavy metals are of prime importance due to their long-term toxicity effect.

Soil is not only a geochemical reservoir for the contaminants but also a natural buffer for transportation of chemical materials and elements in the atmosphere, hydrosphere, and biomass and, thus, it is the most important component of the biosphere [3]. Due to their contaminant effect, heavy metals are the main focus of recent works [4–7]. Metal content in soils is the combination of metals arising from human activities and natural processes. Addition of anthropogenic metals to the soil is much greater than contribution of metals from natural sources [8,9]. Increase in metal content in soils is generally observed in areas of intense industrial activity. Metal accumulation in these areas is a few times higher than uncontaminated sites. However, due to long-distance atmospheric transport, high metal concentrations may also be detected in distal parts of industrial centers [10–12].

Unlike some organic materials, heavy metals do not vanish in time and although at certain levels they are essential for living they show toxic effect if they exceed the limit values. The most important impact of soil pollution on environmental health is that contaminants in soil can be introduced into the food chain by plants and by their direct use or consumption by animals feeding on them. Heavy metals taken into the human body at doses higher than the limit values proposed by the World Health Organization (WHO) are known to cause carcinogenic, teratogenic, toxic, or cardiovascular problems. Therefore, metal pollution in areas of agricultural activities is of great concern.

Gebze is one of the regions intensely affected by soil contamination of industrial origin. The region is one of the largest industrial regions in Turkey where the impact of rapid population growth and industrialization on limited natural sources and agricultural lands is progressively high and as a result the size of uncontaminated areas is getting diminished. Due to expanding industrialization and urbanization in Gebze and the unrestrained disposal of factory wastes to soil or waters and their transport by air, it is thought that heavy metal contents of soils in this region are extremely high. Therefore, monitoring of this change and determination of contamination in soils has gained importance. Heavy metal contents in the soils of the Gebze industrialization area, their contamination levels, and pollution sources have not been investigated. Therefore, the aim of this work is

^{*} Tel.: +90 462 3772073; fax: +90 462 3257405. *E-mail address:* gultenyaylali@yahoo.com.

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to examine the heavy metal contents in the soils of Gebze and investigate their possible origins.

2. Materials and methods

2.1. Index of geoaccumulation (Igeo)

The geoaccumulation index allows estimation of contamination comparing preindustrial and recent metal concentrations [13]. This method which has been used by Müller [14] since the late 1960s was applied to several trace metal studies in Europe. The geoaccumulation index is computed from the following Eq. (1):

$$I_{\text{geo}} = \log_2(Cn / 1.5Bn) \tag{1}$$

where Cn is the measured concentration of the element in the pelitic sediment fraction and Bn is the geochemical background value in fossil argillaceous sediment. The constant 1.5 allows us to analyze the natural fluctuations in the content of a given substance in the environment and very small anthropogenic influences. In the present work, geoaccumulation index was computed from the equation modified by Loska et al. [13], where Cn is the measured concentration of the element in the soil sampled and Bn is the geochemical background value in the Earth's crust [15].

Müller [14] divided the geoaccumulation index into seven classes, they are: ($I_{\text{geo}} \le 0$) practically uncontaminated; ($0 < I_{\text{geo}} < 1$), uncontaminated to moderately contaminated; ($1 < I_{\text{geo}} < 2$) moderately contaminated; ($1 < I_{\text{geo}} < 2$) moderately contaminated; ($3 < I_{\text{geo}} < 4$) heavily contaminated; ($4 < I_{\text{geo}} < 5$) heavily to extremely contaminated, and ($5 \le I_{\text{geo}}$) extremely contaminated.

2.2. Enrichment factor (EF)

The equation of Buat-Menard and Cherselet [16] which was later modified by Loska et al. [13] was used in the calculation of enrichment factor. This method is based on standardization of an element tested against a reference element. The most common reference elements are Sc, Mn, Ti, Al, Ca, and Fe [17–21]. If enrichment factor is <1, the element is depleted in the environment, while in the case of >1 the element is relatively enriched in the environment [22].

In this study Sr was used as the reference element. Strontium is one of the most important components in the Earth's crust and its concentration in soil varies with respect to matrix. Similar to I_{geo} , the reference environment adopted was the average concentration of elements in the Earth's crust. Enrichment factor was calculated using the modified formula based on Eq. (2) suggested by Buat-Menard and Chesselet [16].

$$EF = C_n(\text{sample}) / C_{ref}(\text{sample}) / \left(B_n(\text{background}) / B_{ref}(\text{background}) \right)$$
(2)

where C_n (sample) is the content of the examined element in the examined environment, C_{ref} (sample) is the content of the reference element in the examined environment, B_n (background) is the content of the examined element in the reference environment; and B_{ref} (background) is the content of the reference element in the reference element in the reference element.

Enrichment factor (EF) is divided into five groups [21]:

EF<2	Deficiency to minimal enrichment
EF = 2-5	Moderate enrichment
EF = 5-20	Significant enrichment
EF = 20-40	Very high enrichment
EF >40	Extremely high enrichment

2.3. Contamination factor, contamination degree and integrated pollution index

In the determination of soil contamination, enrichment factor and contamination degree are used. In the present study, the modified form [13] of the method for calculation of contamination factor by Hakanson [23] was utilized. The contamination factor is computed from the following Eq. (3):

$$C_f = C_o / C_n \tag{3}$$

where C_o is the mean content of metals of at least five sampling areas, C_n is the concentration of elements in the Earth's crust.

Hakanson [23] divided the contamination factor into four categories:

C _f <1	Low contamination factor indicating low contamination
$1 \le C_f < 3$	Moderate contamination factor
$3 \le C_f < 6$	Considerable contamination factor
$6 \ge C_f$	Very high contamination factor

The contamination factor reveals contamination of only one element. The sum of the contamination factors of all the elements yields the contamination degree (C_{deg}) of the environment investigated. The contamination degree is divided into four groups [23]:

C _{deg} <8	Low degree of contamination
$8 \leq C_{deg} < 16$	Moderate degree of contamination
$16 \le C_{deg} < 32$	Considerable degree of contamination
$32 \ge C_{deg}$	Very high degree of contamination

Integrated pollution index is another method used for the determination of heavy metal contamination in individual samples in the area of interest, rather than revealing a general contamination degree of the whole area. This value yields the average of the contamination factors computed for each sample. Integrated pollution index subsequently helps to illustrate the distribution of the sample contamination. IPI \leq 1: low level of pollution, 1<IPI \leq 2: moderate level of pollution, 2<IPI \leq 5: high level of pollution and IPI>5: extremely high level of pollution [6].

2.4. Statistical analysis

In order to determine relationships among the elements and the element groups, Cluster Analysis (CA) and Factor Analysis (FA) were employed. Results of the analyses were evaluated with EXCEL 2007, SPSS 10.0, and STATISTICA programs.

2.5. Study area

Gebze town of the Kocaeli City is located northwest of the İzmit Peninsula in the Marmara region. Economy of the district is mainly based on industry and it is one of the rapidly growing and developing regions in Turkey. Gebze town with an area of 438,65 km² is between 40° 45′ 08″ and 41° 02′ 38″ North latitudes and 29° 19′ 56″ and 29° 45′ 14″ East longitudes (Fig. 1). The rapid expansion of industrial activities, particularly after the 1980s has given rise to a jump in the population of the town as well.

Hosting several plants belonging to various industrial sectors, Gebze has grown prodigiously in the recent years. There are two large organized industrial zones in Gebze; the Gebze Organized Industrial Zone (GOIZ) and the Dilovası Organized Industrial Zone (DOIZ). Industrial facilities including paint, plastic, electric, metal, textile, wood, automotive supply industry, food, cosmetics, packing, machinery, and chemical sectors are currently in operation in these organized industrial zones.

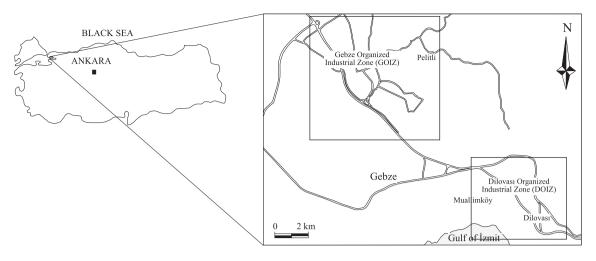


Fig. 1. Location map of the study area.

In Gebze winter is warm and rainy while summer is hot and less rainy; and annual precipitation is between 768 and 1153 mm. Soils in the region are well-developed acidic (pH<7), dark-colored, and organic-material rich and are included in the brown forest soil group.

2.6. Sampling and analysis

A total of 57 soil samples were collected from the outer surface (5–10 cm) after removing surface contamination. Fig. 2 shows the location of the soil samples collected from the area. Use of metal tools was avoided and a plastic spatula was used for sample collection. Soil samples were dried at room temperature and ground before analysis. The materials under 80-mesh sieve were sent to Acme Laboratories (Canada) for analyses. During the analysis, 1 g of soil sample was left in 2 ml HNO₃ solution for 1 h. The samples were then added to 6 ml of 2:2:2 HCl–HNO₃–H₂O solution, dissolved at 95 °C for

1 h, and analyzed with ICP-MS. Internal standard DS7 was used during the analytical run for trace elements in soils.

3. Results and discussion

3.1. Heavy metal concentrations of soil samples

Descriptive statistics such as minimum, median, mean, maximum, standard deviation and percentiles (25, 75, and 95%) for eight elements used in this study are shown in Table 1. Reference values (Earth crust averages) of the studied metals [15] are also included this table. Most of the elements have a wide range of variations of several magnitudes. This was evident for Cd, whose concentrations vary from 0.05 to 176 mg/kg with a median of 0.49 mg/kg and a significantly higher mean of 4.41 mg/kg. Similar variability was also found for Pb, Zn, and Hg.

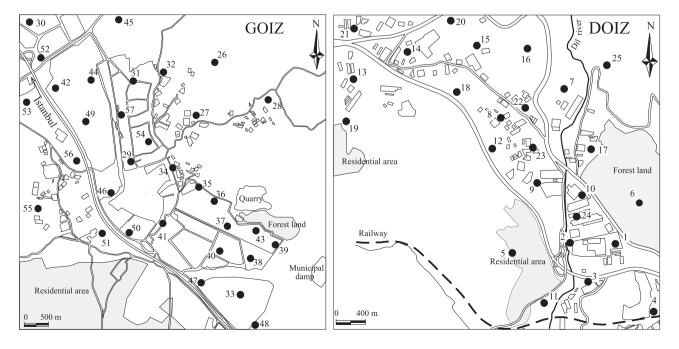


Fig. 2. Sampling location in Gebze area (GOIZ: Gebze Organized Industrial Zone; DOIZ: Dilovasi Organized Industrial Zone).

	Earth's crust		Med.	Range	Skw.	Kur.	Percentiles			
	average value						25	50	75	90
As mg/kg	1.6	9.53 ± 9.25	7.60	1.50-65.60	4.26	24.11	4.35	7.60	11.25	17.00
Cd mg/kg	0.1	4.41 ± 23.37	0.49	0.05-176	7.36	54.95	0.18	0.49	1.38	2.70
Cr mg/kg	69	118 ± 236	37.20	10.00-1161	3.25	10.37	21.30	37.20	77.30	418
Cu mg/kg	39	95.88 ± 157	42.33	7.87-725	2.89	7.97	22.70	42.33	68.34	300
Hg ^a	80	102 ± 371	29.00	9.00-2721	6.62	46.29	18.00	29.00	52.50	88.00
Mn mg/kg	580	1824 ± 2523	1009	196->10,000	2.50	5.20	478	1009	1567	7104
Pb mg/kg	17	246 ± 1120	60.10	17.07-8469	7.32	54.56	34.02	60.10	107.66	174.00
Zn mg/kg	67	632 ± 1562	193.40	29.50->10,000	4.770	25.12	97.45	193	418	1147

Table 1

^a $\mu g/kg$.

3.2. Arsenic

The mean arsenic content in the soil is 9.53 mg/kg ranging from 1.50 to 65.60 mg/kg (Fig. 3). Arsenic concentration in uncontaminated Poland soils has a range of 0.9 to 3.4 mg/kg [24,25]. Arsenic concentration in Turkish soils was found to be from 1.9 to 51 mg/kg with an average of 8 mg/kg [5].

High As concentrations in Gebze soils are due to industrial activities. Significant anthropogenic sources of As are related to industrial activities such as metallurgical and chemical industries and the use of arsenical sprays. Heavily As polluted soils are reported to be located in the vicinity of a former As and Pb-Zn smelter with increase up to 200 and 45 mg/kg, respectively [24,26].

The I_{geo} calculated for As changes from -0.68 to 4.77 (Fig. 4). The average I_{geo} classifies the soil as uncontaminated while maximum values classify the soil as heavily to extremely contaminated [14]. The EF for As ranges from 2.3 to 173 (Fig. 5). The minimum values point to moderate enrichment, whereas maximum values imply extremely high enrichment of soils with As.

3.3. Cadmium

There is a growing environmental concern about Cd as being one of the most ecotoxic metals, which exhibits highly adverse effects on soil biological activity, plant metabolism, and the health of humans and animals [24]. Cadmium pollution in soils is accepted to be a serious environmental problem. Cadmium concentration in topsoils is attributed to metal smelting, sewage waters, and the use of phosphate fertilizers [27.28].

The Cd concentrations in Gebze soils vary from 0.05 to 176 mg/kg and the average is 4.41 mg/kg. High Cd concentrations are recorded particularly in DOIZ (Fig. 6). The average Cd concentration in northern Poland soils is 0.80 mg/kg [13] which is significantly lower than that in Gebze soils. The average Cd concentration in soils of the Thrace region in the northwest part of Turkey was recorded to be 0.2 mg/kg [5].

The I_{geo} ranges from -1.58 to 10.20 (Fig. 4). The average I_{geo} (1.62) denotes moderate contamination while maximum values classify the soil as extremely contaminated. The average EF is 109 which points to extremely high enrichment with Cd.

3.4. Chromium

The Cr content of topsoil is known to increase due to pollution from various sources of which the main ones are several industrial wastes (Cr pigment and tannery wastes, electroplating sludges, and leather manufacturing wastes) and municipal sewage sludge. Chromium behavior in soil is controlled by soil pH and redox potential. Under moderately oxidizing and reducing conditions and nearneutral pH values Cr is a low-mobility element [24]. Chromium

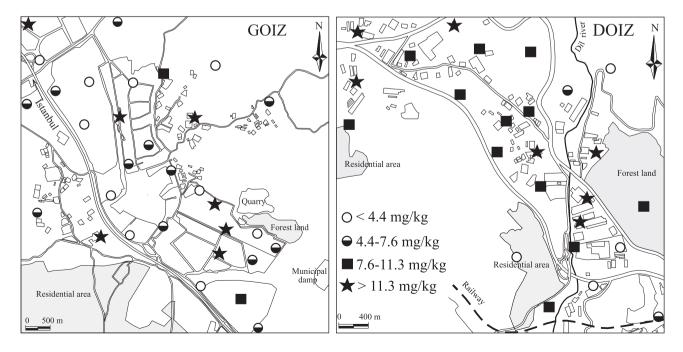


Fig. 3. Distribution of As in Gebze soil.

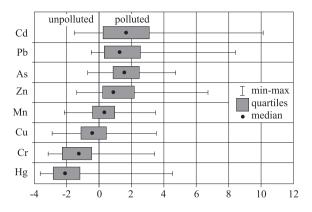


Fig. 4. Indexes of geoaccumulation for metals in soil of Gebze.

adsorption by clay minerals largely depends on pH, and Cr^{+6} adsorption decreases with increasing pH whilst Cr^{+3} adsorption increases with increasing pH [24]. Wastes and sewage waters unrestrainedly disposed from steel and textile industry facilities are the source of Cr in the study area. High doses of Cr cause liver and kidney damages and chromate dusts are known to be carcinogenic.

The values obtained in Gebze soils range from 10 to 1161 mg/kg (Fig. 7) with an average of 118 mg/kg as shown in Table 1. Uminska [29] determined that Cr concentrations around a Cr smelting facility in Poland exceed 10.000 mg/kg. Likewise, Cr concentrations in soils contaminated by sewage wastes are found to be from 214 to 727 mg/kg [30]. The I_{geo} reveals that nearly all the samples examined fall into class 0 practically uncontaminated (ranging from -3.37 to 3.49) (Fig. 4). The EF for Cr is high in comparison to other elements that range from 0.37 to 63. This is an extremely high enrichment [21].

3.5. Copper

Copper contamination in soils is due to fertilizers, sprays, or agricultural or municipal wastes and industrial emissions as well. Small-scale and local Cu contamination in soils originates from corrosion of construction materials with Cu alloys (e.g. electric cables). The average Cu concentration in soils from northwest Turkey is 20 mg/kg [5]. Copper content of soils in the Gebze region are between 7.87 and 725 mg/kg with an average of 95.88 mg/kg which is applicably greater than that in uncontaminated soils (Fig. 8). In some other works Cu concentrations lower than in Gebze soils were recorded [13,24].

The I_{geo} values for Cu range from -2.89 to 3.63 with a mean of -0.32 (Fig. 4). The minimum I_{geo} denotes practically no contamina-

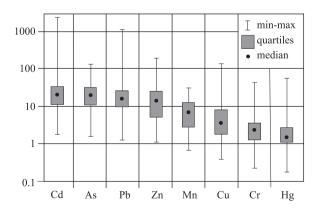


Fig. 5. Enrichment factors for metals in soil of Gebze.

tion while maximum values classify the soil as heavily contaminated [14]. The EF values for Cu range from 0.63 to 137 (Fig. 5) with a mean value of 11.26 which falls under the class of significant enrichment.

3.6. Mercury

Base-metal processing and some chemical industrial activities are the main source for Hg contamination in soils. Mining activities, sewage wastes, and the use of fungicides also result in Hg pollution. Previous works show that soils in the vicinity of coal power plants yield high Hg contents. For example, Hg contents in soils at such sites in Poland were found to be from 0.4 to 7.55 mg/kg [31]. Similarly, extremely high Hg concentrations were recorded in a study performed around a former battery-recycling facility [24].

Mercury concentrations in Gebze soils are between 9 and 2721 µg/kg with an average of 102 µg/kg (Fig. 9). Mercury concentrations in uncontaminated soils are found to be from 0.06 to 0.24 mg/kg in Japan [32], from 0.04 to 0.08 mg/kg in Israel [33], and from 0.03 to 1.14 mg/kg in Canada [34]. Mercury concentrations in Gebze soils are much greater than these values. I_{geo} values for Hg are from -3.74 to 4.50 with an average of -1.81. The lowest I_{geo} value indicates that soils are practically uncontaminated while the highest value shows that soils are heavily to extremely contaminated. EF values vary from 0.24 to 72.6 with an average of 4.18, indicating that soils are of moderate enrichment class. The lowest value is indicative of an extremely high enrichment [21].

3.7. Manganese

Manganese is one of the commonly found elements in the lithosphere. Mn content in the Gebze soils varies from 196 to 10.000 mg/kg (upper limit) with an average of 1824 mg/kg (Fig. 10). Mn concentration of three samples is greater than the upper limit. The average Mn content in uncontaminated soils in Turkey is reported as 600 mg/kg [5].

 I_{geo} values for Mn are from -2.15 to 3.52 with an average of 0.29. Based on the lowest value, soils are practically uncontaminated while the highest value implies that they are heavily contaminated [14]. The average EF value is 12.64 indicating a significant enrichment. The highest EF value (38.7) corresponds to very high enrichment.

3.8. Lead

Lead contamination in soils is seriously emphasized in recent years since this metal is very toxic for humans and animals. Lead enters to human or animal metabolism either via food chain or by intake of soil dust. Gasoline vehicles are the main source of lead pollution. Lead production and operation facilities without waste-gas treatment system, battery production and scrap battery recovery facilities, thermal power plants, and iron–steel industries are the other lead sources. Among the heavy metals, lead is the most immobile element and Pb content in soil is closely associated with clay minerals, Mn-oxides, Al and Fe hydroxyls, and organic material [35]. In general, the highest Pb concentrations are recorded in organic-material-rich soils and Pb behaves as adsorbent in soils contaminated by organic material [24].

Lead concentrations in Gebze soils are between 17.07 and 8469 mg/kg with an average of 246 mg/kg which is noticeably higher than values reported in the literature (Fig. 11). Kaljonen [36] found Pb concentration as 17 mg/kg in soils. In another study by Shacklette et al. [37], the upper limit for Pb in uncontaminated soils was given as 50 mg/kg. The average Pb concentration in the soils of the Thrace region northwest part of the study area was recorded to be 33 mg/kg [5].

 I_{geo} values for Pb vary from -0.58 to 8.38 with an average of 1.44. Based on the average value, Gebze soils are moderately contaminated while the maximum value implies that soils are extremely contaminated. The average EF value is 45 indicating that soils collected from the study area correspond to extremely high enrichment.

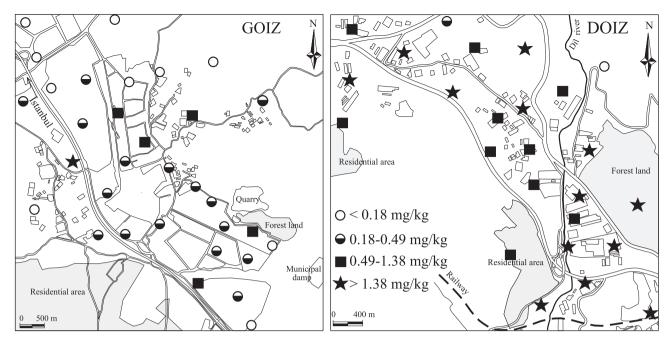


Fig. 6. Distribution of Cd in Gebze soil.

3.9. Zinc

The anthropogenic sources of Zn are related to the nonferric metal industry and agricultural practice [24]. Zinc is a most readily mobile element. High doses of zinc show toxic and carcinogenic effects and result in neurologic complications, hypertension, and kidney and liver function disorders [38].

The minimum Zn concentration in Gebze soils is 29.50 mg/kg and the maximum value is >10,000 mg/kg (upper limit) (Fig. 12). The average Zn concentration is 632 mg/kg which is higher than Zn concentrations reported in the literature (45 mg/kg, [5]; 191.3 mg/kg, [39]; 62.47 mg/kg, [13]). The average I_{geo} values vary from -1.77 to 6.64. The lowest value indicates that soils are practically uncontaminated and the highest value is indicative of extreme contamination. The average value is included to second class, which shows moderate contamination. The average EF value is 32, which indicates very high enrichment.

3.10. Correlation between heavy metals

Basic statistical parameters (Table 1) of the elements show that all elements are represented by high skewness and kurtosis coefficients and due to their positive skewness character a suitable data transformation is required. Logarithmic transformation is a commonly used

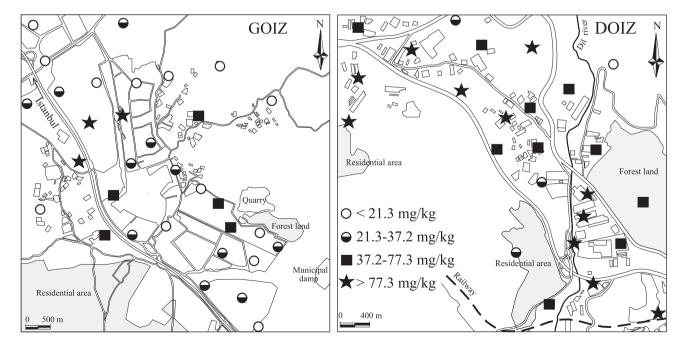


Fig. 7. Distribution of Cr in Gebze soil.

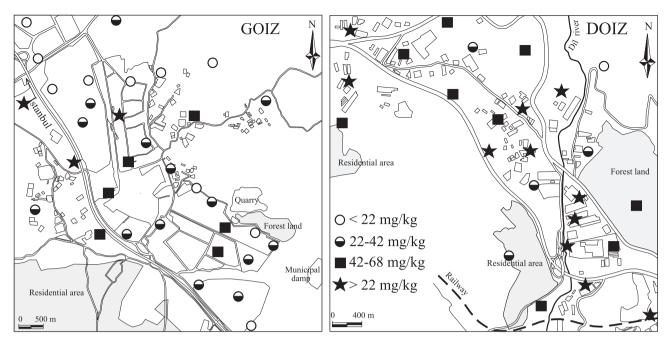


Fig. 8. Distribution of Cu in Gebze soil.

method for normalization of positive-skewed data sets [40]. As a result of logarithmic transformation, skewness coefficients smaller than the raw data were obtained and log-data were used in the statistical works. Correlation analysis for the studied elements in soil samples is very useful for determination of multi-element relations.

Pearson correlation analysis [41] between all the variables was performed. Heavy metals are generally closely associated with each other. Table 2 shows that all elements under investigation are significant at a level of $p \le 0.01$. Significant and high correlations between these metals indicate that contaminants and hazardous metals in the Gebze soils have a similar source which originates from industrial activities.

The absence of any geologic factor to yield high correlations could indicate that these elements are of anthropogenic origin.

The highest correlations coefficients are found between Cd–Zn (r=0.91), Cd–Pb (r=0.91), Pb–Zn (r=0.88), Cd–Hg (r=0.87) and Pb–Hg (r=0.86). Arsenic is weakly correlated with other elements at a significance level of $p \le 0.01$.

3.11. Cluster and factor analysis

In order to reveal relationship between elements and element groups some multivariate analysis techniques such as cluster and factor analysis were performed.

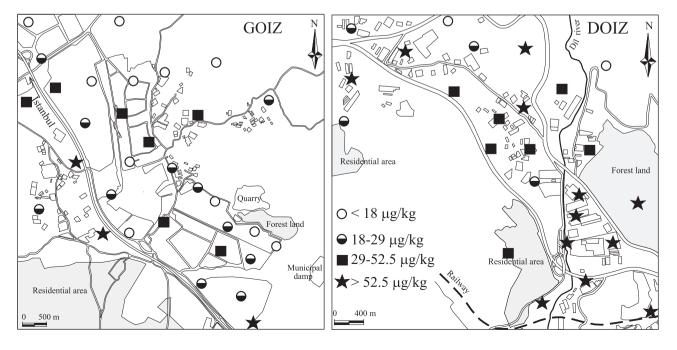


Fig. 9. Distribution of Hg in Gebze soil.

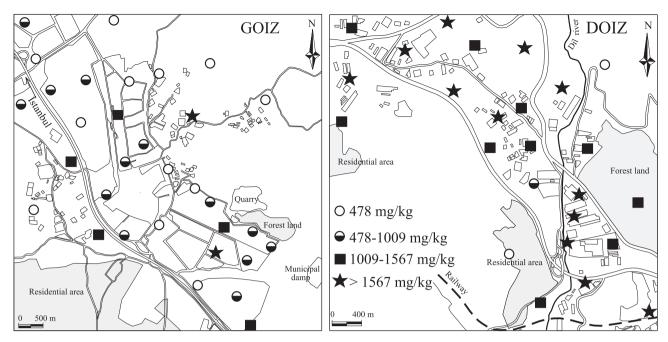


Fig. 10. Distribution of Mn in Gebze soil.

Using single-linkage and Pearson's correlation coefficients R-mode cluster analysis (hierarchical cluster analysis) was carried out and the results are given in a dendogram (Fig. 13).

Results of cluster analysis indicate that the elements comprise two main groups. The first group is composed of two subgroups: subgroup 1 consisting of Cu, Pb, Zn, Cd and Hg and subgroup 2 consisting of Mn and Cr. The second group is composed of only arsenic. Both groups coincide with low correlation coefficients.

The factor analysis was carried out with the Principal Component method which is, rather than the original data, based on the examination of dependency among the artificial variables which are computed from covariance and correlation coefficient matrixes. In other words, eigenvalues and eigenvectors of covariance and correlation coefficient matrixes are interpreted. In the meantime, to strengthen the factor loads Varimax rotation was performed and the results are shown in Table 3. Cluster and factor analyses yield similar results indicating three different factors responsible for the distribution of heavy metal concentrations in the Gebze soils.

Factor 1 consisting of Cu, Pb, Zn, Cd and Hg comprises 75% of all factors. The second factor corresponds to Cr and Mn enrichment in the soils. These two elements were most probably derived from steel and textile industry wastes and therefore, they can be described as anthropogenic components which mostly originated from industrial activities and heavy traffic.

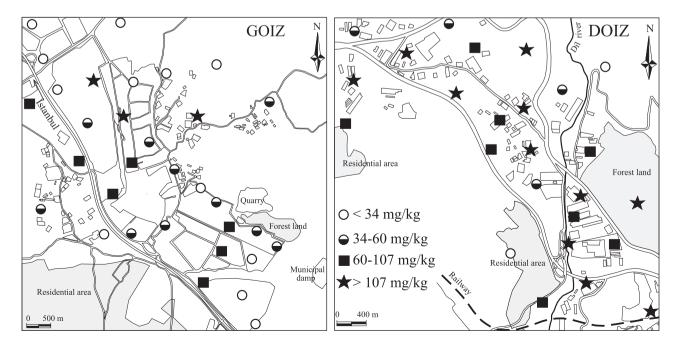


Fig. 11. Distribution of Pb in Gebze soil.

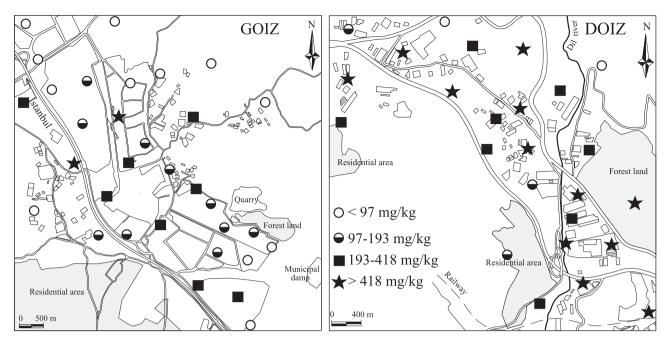


Fig. 12. Distribution of Zn in Gebze soil.

The third factor comprising 10% of all factors represents As enrichment in the soils. Arsenic contamination is largely derived from wastes from coal-burning industrial facilities. The highest As concentration in the study area is from samples collected in the vicinity of coal facilities.

3.12. Assessment of contamination in Gebze

In order to determine the general contamination in Gebze soils, the contamination factor (C_f) and contamination degree (C_{deg}) were used. Contamination factor and contamination degree values computed for each element are provided in Table 4. The elements in the Gebze soils

Table 2 Pearson correlation coefficient matrix for elements in the soil samples (*: $p\!\le\!0.01).$

Cu Pb Zn Mn As Cd Cr Hg	Cu 1.00 0.74* 0.80* 0.67* 0.58* 0.76* 0.78* 0.72*	Pb 1.00 0.88* 0.78* 0.43* 0.91* 0.76* 0.86*	Zn 1.00 0.71* 0.35* 0.91* 0.73* 0.79*	Mn 1.00 0.46* 0.79* 0.85* 0.76*	As 1.00 0.40* 0.48* 0.45*	Cd 1.00 0.77* 0.87*	Cr 1.00 0.77*	Hg 1.00
Hg	0.72*	0.86*	0.79*	0.76*	0.45*	0.87*	0.77*	1.00

(*: $p \le 0.01$).

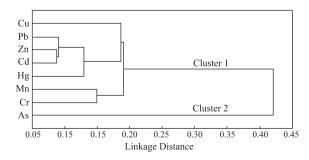


Fig. 13. Dendogram depicting the hierarchical clustering of the heavy metals (Single linkage; 1-Pearson r).

were classified on the basis of the contamination factor calculations. Accordingly, Gebze soils are contaminated moderately with respect to Cu, Cr, and Hg; considerably with respect to Mn and As; and extremely–heavily with respect to Zn, Pb, and Cd. The sum of the contamination factors determined for each element yields the contamination degree. The contamination degree for the Gebze soils is found as 82.59 which is noticeably higher compared to the classification proposed by Hakanson [23]. The contributions of each element to the contamination degree in Gebze soils are 53.44% by Cd, 17.54% by Pb, 11.43% by Zn, 7.22% by As, 3.81% by Mn, 3.2% by Cu, 2.07% by Cr, and 1.55% by Hg.

Using IPI values of metals in the Gebze soils, distribution diagrams were prepared (Fig. 14). The results show that 22.8% of

Table 3

Factor loads which were subjected to Varimax rotation and calculated based on correlation coefficient matrix of elements from soil samples in the Gebze area.

Metals	Factor 1	Factor 2	Factor 3	
Cu	0.684	0.311	0.357	
Pb	0.832	0.371	0.212	
Zn	0.797	0.264	0.082	
Mn	0.486	0.793	0.241	
As	0.151	0.187	0.952	
Cr	0.389	0.752	0.225	
Hg	0.786	0.410	0.265	
Cd	0.827	0.390	0.146	
Total variance %	75.43	5.05	10.13	

Table 4

Contamination factors and contamination degree for metals in the Gebze soils.

Metals	Minimum	Maximum	Average
Cu	0.20	18.61	2.46
Pb	1.00	498	14.49
Zn	0.44	149	9.44
Mn	0.34	17.24	3.15
As	0.94	41	5.96
Cr	0.14	16.83	1.71
Hg	0.11	34.01	1.28
Cd	0.50	1762	44.14
Contamination degree (C_{deg})	3.67	2537	82.59

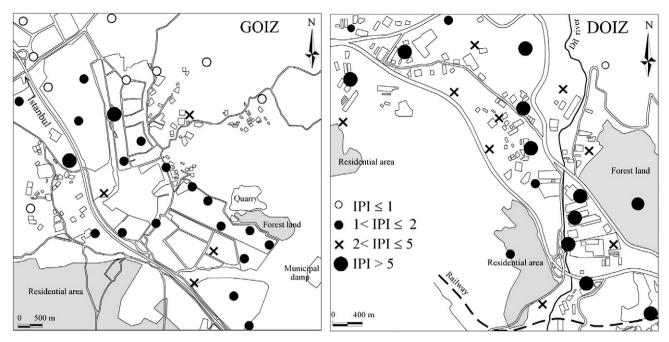


Fig. 14. Spatial distribution of the integrated pollution index (IPI) in Gebze area.

samples are heavily–extremely contaminated; 21% are extremely contaminated, 38.6% are moderately contaminated; and others are slightly contaminated. This indicates that the Gebze region is strongly affected by industrial activities and soils in this region are seriously contaminated by heavy metals. In addition to industrial activities, traffic-related pollution is also significant. In other words, Gebze soils have been notably affected by heavy metal contamination arising from anthropogenic activities such as industrial activities and traffic.

4. Conclusions

Soil is an important constituent of human biosphere. Any harmful change to occurring in this environment seriously affects human life and life quality. The most adverse effect of heavy metals is that they can be introduced into the food chain and threaten human health. Agricultural products growing on soils with high metal concentrations are represented by metal accumulations at levels harmful to human and animal health and bioenvironment.

The Gebze industrial zone has been extremely contaminated for many years because of unrestrained disposal of hazardous wastes from industrial facilities and exhaust gasses. As a result of the index of geoaccumulation, enrichment factor, contamination degree, and integrated pollution index applications, very high Cd, Pb, Zn, Mn, Cu, As, and Cr concentrations were found in the soils of the Gebze industrial zone. In addition, these soils are also slightly contaminated by Hg. These element concentrations can be introduced into the food chain via soil and may be a serious threat for human and animal health. These metals with high concentrations in the Gebze soils may be mixed with groundwater by leaching.

High concentrations of Cd, Pb, Zn, Mn, Cu, Hg, Cr, and As in soils around the industry facilities originate from an anthropogenic source which is associated with unrestrained solid and fluid wastes of industry facilities and heavy traffic. Based on environmental health criteria the Gebze area needs a remediation. Remediation techniques such as phytoremediation can be used to mitigate pollution [42].

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