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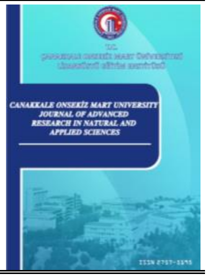

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Soil Contamination by Metals/Metalloids around an Industrial Region and Associated Human Health Risk Assessment

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Research Article

Abstract − Industrial, agricultural, transportation, and waste management activities cause soil contamination by metals/metalloids. Soil contamination is an essential global concern since it poses a significant risk to human health. Particularly in areas near heavy industry, people are more prone to exposure. This study aims to determine current metal/metalloid contamination levels in soil from Aliağa industrial region and assess associated health risks. Five surface soil samples were collected from the region, representing residential, agricultural areas, and downwind of possible sources. Pollution indices were calculated to determine the metal(loid)s with anthropogenic inputs, and a human health risk assessment was conducted. As a result, significant to extreme enrichment of arsenic (As), moderate to significant enrichment of zinc (Zn) and manganese (Mn), and very high enrichment of lead (Pb) and cadmium (Cd) were observed in soil samples. Possible sources of contamination were iron and steel facilities with electric arc furnaces and oil combustion. Non-carcinogenic risk assessment revealed acceptable risks of exposure to Aliağa soils, while exposure scenarios had a great impact on estimated risks. Arsenic, chromium (Cr), and Pb appeared to be significant contributors to non-carcinogenic risk. Carcinogenic risks associated with exposure to As, Pb, Cr, cobalt (Co), and Cd in soils were evaluated to be at an acceptable level. This study only considered soil exposure pathways; hence, a comprehensive risk assessment is deemed necessary not to underestimate the risk of living around an industrial region. Nevertheless, the study provided crucial information for the current hot spots for metal(loid)s in the region and human exposure level.

Keywords − *Carcinogenic risk, hazard quotient, industrial sources, soil, trace elements*

1. Introduction

Anthropogenic activities such as industrial, mining, and agricultural activities, combustion of fuels, improper waste management practices, and release/use of wastewater/sewage on land lead to contamination of soil [1-3]. Among the contaminants, metals, and metalloids constitute an important class due to their resistance to degradation [1], ability to infiltrate through the soil and reach groundwater [4], and bioaccumulation in the food crops grown in the contaminated soil [5]. The presence of metal(loid)s in the soil, and accordingly, in groundwater and food crops, poses a risk to human health via several exposure pathways. Particularly due to contaminated soil, exposure can be via accidental soil ingestion, inhalation of soil fine particulates, and dermal contact with soil. Some metals are essential for body health (e.g., Zn, Cu, Mn) [1]; however, exposure to some metals, such as lead (Pb) and cadmium (Cd), has been reported to have reproductive, renal, hepatic, neurological, developmental, immunological, and hematological effects [6,7]. Arsenic (As) and cadmium (Cd) are known carcinogens (International Agency for Research on Cancer IARC-Group 1), while Pb and cobalt (Co) are probable human carcinogens [8-10]. Arsenic has also been reported to cause diabetes in children and adults and has respiratory, dermal, cardiovascular, gastrointestinal, neurological, developmental, and

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immunological effects [11,12]. Therefore, exposure to these metal(loid)s requires an in-depth investigation.

People living in regions near anthropogenic metal(loid) sources are more prone to exposure [13]. Under the influence of heavy industrial activities and traffic, the metal(loid) composition of soils has been shown to be altered compared to background soils [14-16]. Aliağa industrial region is an example of such industrial regions in Türkiye. The regional industrial activities include iron and steel plants, scrap processing plants, shipbreaking yards, a fertilizer plant, and a petrochemical plant. The region also involves ports, a railway, and a highway where heavy transportation activities exist. Due to these activities, heavy metals have been emitted to the environmental media. Previous studies conducted in the region demonstrated metal(loid) contamination of atmospheric particles [17,18], soil [14,16,19], sediments [20-23], and seawater [24], and accumulation of metals in biological matrices as well [19,25-28]. The region has another importance since three residential areas are very close to the Aliağa industrial region (Horozgediği, Çakmaklı, Bozköy), and agricultural activities, including olive tree fields, are ongoing. A study conducted to observe heavy metal contamination in soils of olive fields showed Ni, Cr, and Pb contamination in the Aliağa region [29]. The researchers also found that higher Al, Ni, and Pb levels measured in the olive leaves were possibly linked to higher soil levels of these metals [29]. This finding indicated that determining soil metal(loid) contamination is essential to assess the impacts of industrial sources on their surroundings and the associated human exposure.

This study aims to evaluate current metal(loid) contamination levels in soils around the Aliağa industrial region and assess human health risks associated with soils in the region. To the author’s knowledge, the last study on soil contamination by metal(loid)s in the region was conducted in 2011 [19]. and there is no human health risk assessment study on this scope.

2. Materials and Methods

2.1. Soil Sampling and Physical-Chemical Analyses

Aliağa industrial region is located in İzmir, in western Türkiye. The region consists of several industrial facilities, including scrap processing iron-steel production facilities, steel rolling mills, a petroleum refinery, a petrochemical plant, a fertilizer plant, a natural gas-fired power plant, ship dismantling facilities, and scrap storage sites. The region also includes small residential areas (Figure 1). Soil sampling locations were selected according to the prevailing wind direction (northwest in summer, southeast in winter [14]), location of major sources, and potential receptors. Soil samples #1 and #2 were representative samples for residential areas (i.e., Horozgediği) close to the iron-steel production facilities and scrap storage sites. Soil sample #3 is downwind of major scrap processing iron and steel facilities. Lastly, soil samples #4 and #5 were collected from downwind of ports and near the road towards the port site. These two samples were also representative of agricultural areas in the region since they were collected from olive tree fields. The sampling points are depicted in Figure 1.

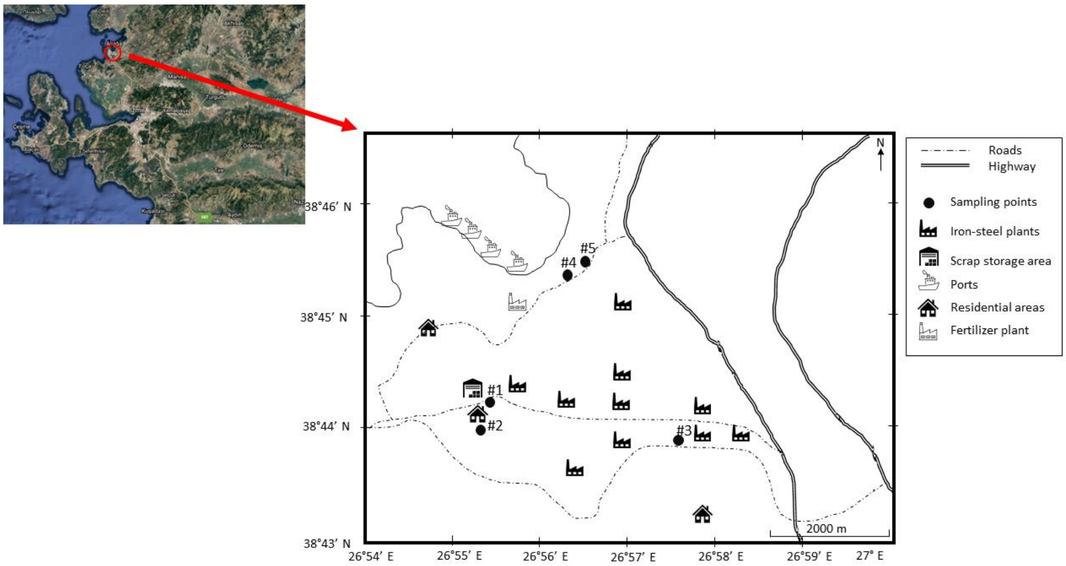

Figure 1. Location of sampling points in the Aliağa industrial region

Surface soil samples (from 0 – 10 cm) were collected in August 2021 (dry period). From every sampling location, at least five subsamples were collected from ~50 m^2 area. After removal of vegetation where necessary, the subsamples were combined to obtain a composite sample in pre-cleaned glass jars. Collected samples were transported immediately to the laboratory at 4°C. After sieving through a 2 mm sieve, some portions of the samples were allocated for moisture content, total organic carbon and particle size analyses, and other portions for metal analysis. The moisture content of soil samples was analyzed by drying 10 g of samples in an oven at 105°C overnight. The organic matter contents were then analyzed by igniting the samples after measuring moisture content in a muffle furnace at 600°C for 4 hours. Total organic carbon analysis was conducted with Shimadzu TOC-Vcph (TNM-1 / SSM-5000A). Particle size analysis was performed by Horiba La-960 Particle Size Distribution Analyzer using the laser diffraction method. pH of the soil samples was measured in a 1:2.5 soil: water suspension using a pH meter after being soaked overnight.

2.2. Analysis of Metals/Metalloids

The soil samples were dried at room temperature overnight. Then, they were grounded by an agate mortar. Approximately 0.5 g of samples were digested in a microwave digestor (MARS CEM6) after being soaked in 10 mL of HNO_3 for half an hour. The microwave program was as follows: the temperature was increased to 180°C in 15 minutes, then held there for 20 minutes and cooled back. Digested samples were analyzed for 18 metal(loid)s in an Inductively Coupled Plasma-Mass spectrometer (ICP-MS, Agilent 7500ce Octopole Reaction System). The metal(loid)s studied were lead (Pb), cadmium (Cd), molybdenum (Mo), strontium (Sr), selenium (Se), arsenic (As), zinc (Zn), copper (Cu), nickel (Ni), cobalt (Co), iron (Fe), manganese (Mn), chromium (Cr), calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), and boron (B). The limits of detection for metal(loid)s were between 0.0112 µg/L (Cr) and 109 µg/L (Ca), and limits of quantitation were in the range 0.0037 µg/L (Cd) and 364 µg/L (Ca). The certified reference material analyses yielded recoveries in the range 79% (Ca) – 151% (Sr) for Supelco SQC001 and 58% (Mn) – 106% (Pb) for RTC CRM051.

2.3. Pollution Indices Calculation

Pollution indices have been mainly used to assess the degree of metal contamination in soils and sediments [15]. The most widely used pollution indices were calculated as given in (2.1)-(2.4).

$$Enrichment\ factor(EF) = \frac{C_n/C_{ref}}{B_n/B_{ref}} \tag{2.1}$$

$$Contamination\ factor(CF) = \frac{C_n}{B_n} \tag{2.2}$$

$$Pollution\ load\ index(PLI) = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{\frac{1}{n}} \tag{2.3}$$

$$Geoaccumulation\ index(I_{geo}) = \log_2 \frac{C_n}{1.5 \times B_n} \tag{2.4}$$

where C_n is the concentration of metal(loid) in the sample, C_{ref} is the concentration of reference metal(loid) in the sample, B_n is the concentration of metal(loid) in background soil (i.e., Earth's crust), and B_{ref} is the concentration of reference metal(loid) in the Earth's crust, and n is the number of metal(loid)s analyzed. In this study, Fe was chosen as the reference metal, similar to previous studies [22,23,31], and the elemental concentrations of Earth's crust were taken from [32]. EF was commonly used to assess the degree of anthropogenic effects on soil [33]. CF was proposed by [34] to determine the pollution level of metal compared to background levels. PLI was developed by [35] as another index for pollution assessment. Lastly, I_{geo} was used to evaluate soil contamination by comparing the current levels with pre-industrial levels [36]. Table 1 represents the criteria to evaluate the pollution levels of soil samples in this study.

Table 1. Criteria to assess soil metal(loid) pollution level

Indices	Value	Assessment
EF	EF < 2	Minimal enrichment
	2 < EF < 5	Moderate enrichment
	5 < EF < 20	Significant enrichment
	20 < EF < 40	Very high enrichment
	EF ≥ 40	Extremely high enrichment
CF	CF < 1	Low contamination factor
	1 ≤ CF < 3	Moderate contamination factor
	3 ≤ CF < 6	Considerable contamination factor
	CF > 6	Very high contamination factor
PLI	PLI < 1	Not polluted
	PLI = 1	Baseline levels of pollution
	PLI> 1	Polluted
I_{geo}	I_{geo} <0	Uncontaminated
	0< I_{geo} < 1	Uncontaminated to moderately contaminated
	1 < I_{geo} < 2	Moderately contaminated
	2 < I_{geo} < 3	Moderately to strongly contaminated
	3 < I_{geo} < 4	Strongly contaminated
	4 < I_{geo} < 5	Strongly to extremely contaminated
	I_{geo} ≥ 5	Extremely high contaminated

2.4. Human Health Risk Assessment

The presence of metal(loid)s in soil poses a risk for human health since several interaction mechanisms are possible between soil and humans. Hence, human health risk assessment (HHRA) was conducted using the methodology proposed by the United States Environmental Protection Agency (US EPA) [37]. Three exposure pathways were considered: i) accidental soil ingestion, ii) inhalation of soil particulates, and iii) dermal contact with soil. HHRA was conducted for i) children between 6 and 12 years of age, ii) female adults, and iii) male adults. For the dermal contact pathway, two scenarios were developed for children and adults: exposure during outdoor sports and gardening or farming activities for adults and exposure during playing in dry and wet soil for children. These scenarios provided evaluating one order of magnitude difference in the level of contact with soil, i.e., soil adherence to skin. The daily exposure doses (DED) were estimated for each pathway using (2.5)-(2.7), the mean of the metal(loid) concentrations, and the values presented in Table 2. Then, non-carcinogenic risk was estimated for the metal(loid)s listed in Table 3 using (2.8) since these metal(loid)s had toxicity reference values (TRVs) defined for modes of action other than cancer. TRV is the maximum dose of a pollutant that a human can intake daily without having a health risk. Several regulatory agencies have reported TRV under various names such as no-observed adverse effect level, tolerable daily intake, and derived no or minimum effect level [38-41]. CompTox database established by the US EPA was used primarily for TRVs since this database reports data from many resources, allowing the users to select the most appropriate one [41]. When no data was available in the CompTox database, other sources (e.g., ECHA, Health Canada, and OEHHA) were used. For As, Cd, Cr, Co, and Pb, which are known and probable human carcinogens, the carcinogenic risk was assessed using (2.9). For As and Pb, oral and inhalation exposure routes were evaluated separately, while for Cd, Cr, and Co, inhalation cancer risk was estimated. Slope factors were obtained from various sources and presented in Table 3.

$$DED_{ing}\left(\frac{mg}{kg\ body\ weight \times day}\right) = \frac{C_n \times IngR \times EF \times ED}{BW \times AT} \tag{2.5}$$

$$DED_{inh}\left(\frac{mg}{kg\ body\ weight \times day}\right) = \frac{C_n \times InhR \times EF \times ED}{PEF \times BW \times AT} \tag{2.6}$$

$$DED_{derm}\left(\frac{mg}{kg\ body\ weight \times day}\right) = \frac{C_n \times TBSA \times SA \times DAF \times EF \times ED}{BW \times AT} \tag{2.7}$$

$$Hazard\ quotient\ (HQ_i) = \frac{DED_i}{RfD_i} \tag{2.8}$$

$$CR_i = DED_i \times SF_i \tag{2.9}$$

Table 2. Parameters used in estimating daily exposure dose due to ingestion, inhalation, and dermal contact exposure routes

Parameter	Value	Reference
Ingestion rate (IngR – mg/day)	20 (adults)	[37]
	50 (children)	[37]
Inhalation rate (InhR – m^3/day)	15 (adults)	[37]
	12 (children)	
Total body surface area (TBSA – m^2)	2.10 (adult male)	[37]
	1.86 (adult female)	
	1.08 (children)	
Soil adherence to skin (SA – mg/cm^2)	0.01 (adults – outdoor sports-soccer)	[42]
	0.1 (adults – gardeners, farmers)	
	0.2 (children – playing in wet soil)	
	0.04 (children – playing in dry soil)	
Dermal absorption factor (DAF)	0.03 (for As)	[39,42]
	0.01 (for Cd)	
	0.1 (for Cr, Zn)	
	0.06 (for Cu)	
	0.091 (for Ni)	
	0.001 (for all other metal(loid)s	
Particle emission factor (PEF – m^3/g)	$1.36 \cdot 10^6$	[43]
Exposure duration (ED – years)	24 (adults)	
	6 (children)	[37]
Exposure frequency (EF – days)	350 (adults & children)	[37]
Average time	365·ED (for non-carcinogenic)	[37]
	365·Lifetime (for carcinogenic)	
Lifetime	75 years	[37]
Body weight (BW – kg)	80 (male adults)	[37]
	70 (female adults)	
	31.8 (children)	

Table 3. Toxicity reference values and slope factors of metal(loid)s to be used in risk assessment

Metal(loid)	Toxicity reference value (TRV) (mg/kg.day)	Slope factor (mg/kg.day)$^{-1}$	
		oral	inhalation
As	0.0003 [41]	1.5 [41]	27 [39]
Cd	0.001 [41]		42 [39]
Cr (total)	0.001 [39]		46 [39]
Co	1 [41]		27 [44]
Cu	0.041 [38]		
Fe	0.7 [38]		
Mn	0.14 [41]		
Ni	0.02 [41]		
Pb	0.0015 [41]	0.0085 [40]	0.042 [40]
Zn	0.9 [41]		

2.5. Data Analysis

Statistical analyses of the data were conducted using SPSS 25. Non-parametric tests were applied for correlations (Spearman correlation, r_s) due to a low number of samples. Correlations were considered significant if $p < 0.05$.

3. Results and Discussion

3.1. Physical Characteristics of Soil Samples

The collected soil samples had a moisture content of 2.86 – 5.39%, organic matter content of 6.08 – 12.4%, TOC content of 0.91 – 3.51%, and pH of 7.80 – 8.65. Sample #3 has the lowest moisture and organic contents and the highest pH (Table 4). The particle size analysis results revealed that samples #1 and 2 had silt, and others had silt loam texture, according to USDA classification. A previous study identified the soil groups in the study area [45]. According to the classification, samples #1 and #2 belonged to the non-calcareous brown soil group, #3 belonged to the colluvial soil group, and samples #4 and #5 belonged to the brown forest soil group [45].

Table 4. Moisture, organic matter, and total organic carbon content of soil samples (% w/w)

Sample #	Moisture content	OM content	TOC	pH
1	5.39	12.4	2.61	7.80
2	4.06	10.7	3.51	7.88
3	2.86	6.08	0.91	8.65
4	3.23	9.44	2.53	8.20
5	3.49	9.82	2.04	8.00

3.2. Metal(loid) Concentrations in the Soil Samples

The concentrations of metal(loid)s in soil samples are presented in Table 5. The lithophilic elements, such as Fe (mean ± standard deviation: 26320±15105 μg/g dry weight (dw), Ca (18936±11952 μg/g dw), Mg (4910±1442 μg/g dw) and K (3047±1633 μg/g dw), dominated the soil composition in Aliağa region, while they were lower than crustal elemental concentrations [32]. This finding was also noted by [16], who discussed the variation concerning site-specific geological formations. Other than the lithophilic elements, Mn, Zn, Pb, and Sr had one or two orders of magnitude higher concentrations than other metal(loid)s. The industrial region has several scrap processing iron and steel facilities operating electric arc furnaces. Previous studies demonstrated that these facilities emit Zn, Fe, Pb, Mn, and Cd from their stacks [46]. Kara et al. [14] study also showed the dust emitted from the region's paved and unpaved roads, slag piles, and coal piles caused the emission of particles involving these metals into the atmosphere. Then, dry and wet deposition of atmospheric particles result in their sinking into the soil around the region. Considering the prevailing wind directions, i.e., northwest in summer, and southeast in winter [14], all sampling locations were influenced by iron and steel facilities throughout the year. Nevertheless, sampling points #1 and #2 showed the highest concentrations for Zn, Fe, Pb, Mn, and Cd, indicating the hot spots in the region. Essentially, these two sampling points showed the highest concentrations for all metal(loid)s analyzed, except for Cu, whose concentration was highest in sampling point #4.

B concentrations in the Aliağa region were previously reported by [14] as 25.5 ±17.8 µg/g dw around Nemrut Bay, where the samples of the present study were also collected. The present study found a very similar mean value for B (22.7 ± 7.77 µg/g dw) to [14] study in which samples were collected in 2009. The researchers discussed this high value of B compared to other industrial and non-industrial areas of Aliağa that geothermal interferences due to groundwater use in some plants might be the reason [14]. Hence, it can be speculated that groundwater use and geothermal influences continue in the region.

Table 5. Metal(loid) concentrations in soil samples from Aliağa region (µg/g dry weight)

Sample #	1	2	3	4	5	Mean	Median	Standard deviation
Zn	423.9	375.6	201.9	266.4	227.3	299.0	266.4	96.30
Sr	159.6	170.8	125.9	102.6	128.9	137.6	128.9	27.49
Se	0.22	0.09	ND	0.13	0.18	0.12	0.13	0.09
Pb	187.0	186.9	84.45	182.7	144.2	157.1	182.7	44.39
Ni	27.54	50.82	23.00	23.56	30.11	31.01	27.54	11.46
Na	110.8	455.1	398.9	297.1	215.1	295.4	297.1	138.5
Mo	3.08	1.85	1.77	1.67	2.55	2.18	1.85	0.61
Mn	1463	2306	1525	934.9	1066	1459	1463	536
Mg	6626	2671	5252	4662	5341	4910	5252	1442
K	1678	1622	2523	5406	4006	3047	2523	1633
Fe	24582	52371	22960	15475	16213	26320	22960	15105
Cu	34.79	45.38	25.73	87.41	30.67	44.80	34.79	24.90
Cr	42.26	98.82	34.94	37.61	39.88	50.70	39.88	27.04
Co	9.50	11.38	8.83	4.30	6.29	8.06	8.83	2.78
Cd	2.27	2.26	1.03	1.01	1.20	1.55	1.20	0.65
Ca	21153	4935	19135	12414	37043	18936	19135	11952
B	34.54	14.36	25.78	20.09	18.79	22.70	20.10	7.77
As	49.76	30.08	10.92	16.75	45.29	30.56	30.08	17.05

Although the number of samples was low, correlations between elements were investigated to observe possible common sources. Cr and Ni; Pb and Zn; Mn with Fe; As and Cd, Mo, Se; Sr with Fe, Co, and Cr correlated significantly and strongly (r_s>0.90). Cr and Ni are commonly used in industries such as steel production and metal plating [47], while it is worth noting that Ni concentrations in the samples were lower than the crustal concentrations. Correlations of Pb with Zn and Mn with Fe might show their common source being iron-steel production facilities in the area, while traffic may be another source for Pb and Zn [16]. Arsenic correlation with Cd might indicate their common source to be vehicular or industrial oil combustion [48]. Another source for As and Cd contamination might be the possible use of phosphate fertilizers, which contain these metal(loid) [49]. Moisture and organic matter contents of soil samples significantly correlated with Pb, Zn, Cr, and As concentrations (r_s=0.90). The organic matter content of soil influences the sorption of metals to soil, which is also dependent on soil pH and the presence of other metal ions [50]. Correlations of pH with Pb, Cd, As, Zn, and Cr were significant and strong but negative (r_s=-0.90). In general, as the soil pH decreases, the solubility and, hence, the mobility of metal(loid)s increases. A previous study also reported lower concentrations of Cd, Pb, and Zn in soils with a pH >8.2 than at a pH around 7.7 [51]. The inverse relationship between pH and concentration found in the present study indicated that redox potential, soil clay content, presence of competing ions, and complexation potential of metal(loid)s were essential parameters to understand the mobility and behavior of metal(loid)s in soil [51]. Nevertheless, Pb, Zn, Cr, and As can be considered the most affected metal(loid)s by the soil organic content and pH. A more precise result can be achieved by increasing the number of soil samples.

Pollution indices were calculated to assess the anthropogenic effects of metal(loids) on soil composition in the region (Figure 2). EFs calculated for As revealed extreme enrichment of soil samples #1 and 5, while significant to very high enrichment of As was observed for other samples. For soil samples #1, 4, and 5, very high enrichment of Pb and Cd were observed. Zn and Mn were moderately to significantly enriched in all samples. The contamination factor was very high for Pb, Cd, and As for all samples. Additionally, for samples #1, 2, and 4, considerable contamination of Zn was observed. Interestingly, B and Mo had moderate contamination factor for all samples. Lastly, according to geoaccumulation index calculations, soil sample #5 was extremely highly contaminated by Mn. Strong to extreme contamination by As was observed for soil sample #1, while strong contamination by Pb and Cd was observed for samples #1 and 2. To sum up, As, Pb, Cd, Zn, and Mn were evaluated as the metal(loid)s of anthropogenic origin in the Aliağa industrial region. This finding was also supported by previous studies conducted in the region [14,16]. High enrichment of metal(loid)s in soil samples #1 and 2, collected from the residential area, suggested a high potential for human exposure. PLI of samples #1 and 2 were higher than one, which supported this hypothesis. Additionally, soil samples #4 and 5 were collected from olive tree fields, and their high enrichment with these metal(loid)s can be considered a threat to agricultural products grown in the area.

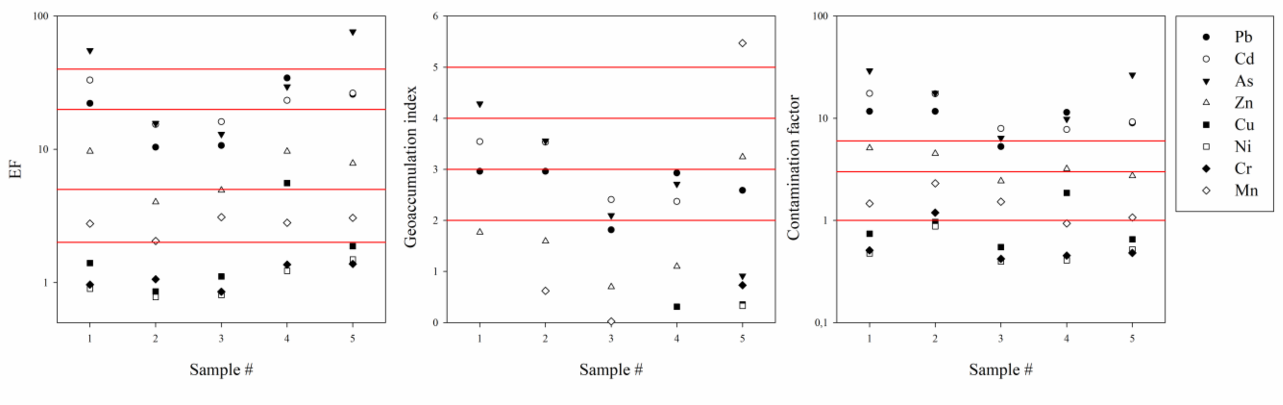

Figure 2. Enrichment factor, geoaccumulation index, and contamination factor for sampling locations in the Aliağa industrial region

Compared to the soil concentrations in Türkiye and around the world (Table 6), this study's metal(loid) concentrations were generally in the range of minimum and maximum observations. Goren et al. [52] presented a comprehensive review of soil metal concentrations from various parts of Türkiye. Compared to Turkish levels, Pb and Fe concentrations found in this study were greater than the Turkish average but lower than that of Türkiye's industrial sites. Also, the Zn and Mn concentrations of this study were greater than that of the Turkish general and industrial average. On the other hand, As, Cu, Co, Ni, and Cr concentrations were lower than the Turkish general and industrial average. Among the previous studies from the region, [16] demonstrated similar concentrations of Fe and Cu but higher concentrations of Cd, Co, Cr, Ni, and Zn. Mn and Pb levels found in this study were higher than those found by [16]. Only As concentration was comparable to that found in [14,19], while other metals were lower in this study. Another study conducted in the region focused on soil concentrations in olive tree fields [29]. Lower levels of Cd and Pb but comparable levels of Cr and Ni were observed by [29]. Two other regions where heavy industrial activities are ongoing in Türkiye, i.e., İskenderun (Hatay) and Dilovası (Kocaeli), showed higher concentrations of metal(loid)s than that of this study, except for As and Pb [30,53]. When compared to the levels from locations where industrial activities such as a Cu-smelter [13], coal-fired power plants [54], petrochemical plants [55,56], and steel production plants [57] affect environmental metal(loid) concentrations in different parts of the world, soil samples from Aliağa region showed consistently higher Pb, Zn, and Mn concentrations. For other metal(loid)s, case-specific observations have been recorded (Table 6).

Table 6. Comparison of mean metal(loid) concentrations in soil samples from around the world (µg/g dry weight)

Location	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	References
Aliağa, Türkiye (n=5)	30.56	1.55	8.06	50.7	44.8	26320	1459	31.01	157.1	299	This study
Aliağa, Türkiye (n=9)	-	2.3	23	163	45	27800	864	62	85	1092	[16]
Aliağa, Türkiye (n=13)	25.5	23.5	16.7	2	237	50900	3148	71.9	1309	6065	[14]
Aliağa, Türkiye (n=21)	27.1	2	-	-	55.7	-	-	-	237	933	[19]
Hatay, İskenderun, Türkiye (n=17)	9	2	-	798	61	-	-	1154	109	531	[30]
Dilovası, Kocaeli, Türkiye (n=49)	11	2.1	8	125	59	34628	2684	44	129	535	[53]
Konya, Türkiye (n=17)	-	0.15	-	24.98	-	-	-	34.29	20.48	-	[58]
Turkish average	188	1.55	13.9	133	72.9	18918	555	89.2	78.7	162	[52]
Türkiye's industrial soils average	500	4.25	21.1	333	588	35579	992	125	248	248	[52]
Hubei, China (n=102)	35.84	4.87	-	-	195.26	-	-	-	92.65	-	[13]
Jiangsu, China (n=105)	7.46	0.11	12.76	86.38	31.6	11600	352.8	34.93	31.41	61.16	[59]
Rostov Region, Russia (n=12)	-	0.8	-	23.64	53	-	827	58.4	41.9	108.7	[54]
Mahshahr, Iran (n=47)	0.37	3.58	-	23.64	20.88	-	-	70.89	39.65	62.98	[56]
Ulsan, Phang, Gwangyang, S.Korea (n=50)	8.3	2	9.2	30.4	24.8	28800	588.6	16.4	23.7	119	[55]
Smederevo, Serbia (n=48)	-	2.75	25.5	56.3	31.8	24620	740	80.2	40.6	77.6	[57]

3.3. Human Health Risk Assessment

HHRA was conducted to understand how soil contamination by metal(loid)s might affect local people through three main exposure pathways: accidental ingestion of soil, inhalation of soil particulates, and dermal contact with soil. Non-carcinogenic risks (HQ) have been estimated for children and adults for each metal separately. Figure 3 presents HQ values estimated for all exposure pathways where two scenarios were generated for dermal contact. The results suggested that HQs varied significantly by exposure scenario, metal(loid) species, and age. Among the exposure pathways, inhalation had the lowest HQs for all metals. A general factor of particulate emission from soil [43] was used to estimate inhalation exposure; hence, sampling of particulate matter and dust right above soil might better represent local emissions and, accordingly, the exposure dose via inhalation of soil particulates in the region. As can be seen from Figure 3, dermal contact during playing with dry and wet soil for children and during outdoor sports and farming for adults completely changed the HQ profiles. The ingestion pathway was the most significant contributor to non-carcinogenic risk for all metal(loid)s when playing with dry soil, and outdoor sports scenarios were considered. In contrast, HQ of dermal contact with soil exceeded that of ingestion pathway for As, Zn, Cr, Cu, and Ni when playing with wet soil, and farming scenarios were considered. The hazard index (HI) was also calculated by summing up the HQs of each exposure pathway for each metal(loid). For dermal contact during playing with dry soil and outdoor sports scenarios, the highest HIs of metal(loid)s were in the order: As (0.20) > Pb (0.17) > Cr (0.15) for children and As (0.04) > Pb (0.03) > Cr (0.027) for adults. However, for dermal contact during playing with wet soil and farming scenario, HI order has changed to Cr (0.41) > As (0.36) > Pb (0.17) for children and Cr (0.14) > As (0.11) > Pb (0.03) for adults. Therefore, it was recommended that exposure scenarios were carefully defined while conducting HHRA.

Examining the above-given HI values, no metal(loid) exceeded the unacceptable risk level of 1. Hence, the non-carcinogenic risk of exposure to Aliağa soil was evaluated to be acceptable under all scenarios. Comparatively, children always had a higher risk than adults due to their lower body weight and higher accidental soil ingestion rate, indicating that children are more susceptible to environmental contamination.

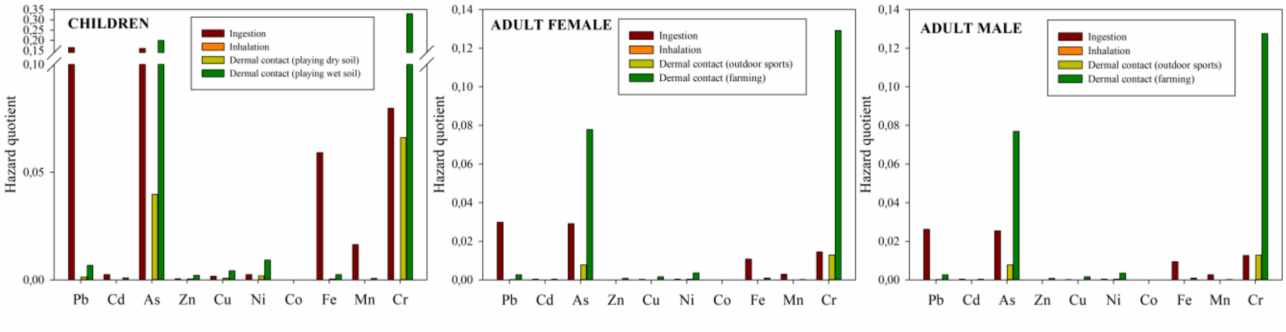

Figure 3. Hazard quotients of metal(loid)s' exposure via various pathways for children and adults

This study also estimated the carcinogenic risks of exposure to metal(loid)s in soil, considering only ingestion and inhalation pathways. CR for children via ingestion and inhalation pathways were $2.21 \cdot 10^{-5}$ and $1.76 \cdot 10^{-8}$ for As, and $1.61 \cdot 10^{-7}$ and $1.40 \cdot 10^{-10}$ for Pb, respectively. Since there are only slope factors of inhalation route for Cr, Co, and Cd, their CR for children were $4.96 \cdot 10^{-8}$, $6.35 \cdot 10^{-9}$, and $1.39 \cdot 10^{-9}$, respectively. CRs for adults were lower than those for children through the ingestion pathway, yet they were approximately two times higher than those for children through the inhalation pathway. Since all CRs estimated in this study were lower than 10^{-4}, which is the threshold for unacceptable cancer risk, the carcinogenic risk of exposure to soil metal(loid)s was evaluated to be acceptable. While As was the most important contributor to CR via the ingestion pathway, Cr became the prominent metal(loid) in CR via the inhalation pathway. The interchange of important metal(loid)s, As, and Cr between exposure scenarios was also observed in non-carcinogenic risk assessment.

4. Conclusion

The metal(loid) concentrations of five soil samples collected from the Aliağa industrial region were dominated by lithophilic elements. However, pollution indices demonstrated moderate to extreme enrichment and strong to extremely high soil contamination of Pb, Cd, Mn, Zn, and As. Scrap processing iron and steel facilities with electric arc furnaces were the possible sources of these metal(loid)s together with oil combustion in the region. The study was deemed a pre-screening of soils in Aliağa industrial region after a ten-year research gap to understand the current hot spots. As a result, samples from residential and agricultural areas pointed out the possibility of human exposure to metal(loid)s in soil. HHRA suggested that both carcinogenic and non-carcinogenic risks were at an acceptable level. However, a considerable increase in HQ values has been observed when dermal exposure scenarios were changed. Hence, exposure scenarios should be clearly defined when conducting HHRA. Additionally, this study only considered soil exposure pathways and did not include inhalation of metal accumulating air particles or ingestion of locally grown food. It is important to conduct a comprehensive risk assessment not to underestimate the risk of living close to an industrial region. Furthermore, a more extensive sampling and analysis strategy would be essential for continuously monitoring soil contamination and assessing the risk in the area.

Author Contributions

The author read and approved the final version of the paper.

Conflicts of Interest

The author declares no conflict of interest.

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