



# Application of multivariate statistics in the source identification of heavy-metal pollution in roadside soils of Bursa, Turkey

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## Abstract

Bursa located within the western part of Turkey is a rapidly growing and heavily industrialized city, hence a considerable amount of pollutions reaching intolerable levels around the city caused especially by anthropogenic activities. This study aims at finding out causes, intensity, and extent of pollution around the D-90 highway and O-33 motorway. Soil sampling was invoked as the first method to identify and discuss the nature of the pollution. A total of 91 soil samples from 10 different locations were collected away from the roadsides. The samples were analyzed for As, Cd, Cr, Co, Cu, Hg, Mn, Ni, Pb, and Zn. The analytical results were evaluated to understand chemical variability of soil compositions using several multivariate statistical methods such as correlation analysis, principal component analysis (PCA), and cluster analysis (CA). Cluster analysis and PCA clearly reveal three distinct groups of elements as (a) Pb, As, and Cd; (b) Cu, Zn, and Hg; and (c) Ni, Cr, Co, and Mn. Two of these groups (Cd, Pb, and As and Cu, Zn, and Hg) are originated from anthropogenic sources (traffic and industrial activities). Ni, Co, Cr, and Mn elements are reflecting underlying lithology. Soil pollution was investigated with the use of enrichment factor (EF), pollution index (PI), and integrated pollution index (IPI) values. The results consistent with the multivariate statistical evaluations demonstrate that soils along the Bursa highway are seriously polluted by toxic trace elements. Lead, As, Cd, Zn, Hg, and Cu are ascertained to be of anthropogenic origin and derived from traffic and industrial activities.

**Keywords** Heavy-metal pollution · Multivariate statistics · Highways · Bursa · Turkey

## Introduction

As a result of industrialization and rapid urbanization, heavy-metal pollution in soils has been recently one of the most important problems. Pollutants are emitted to the nature by various ways which include emission from vehicles, industrial wastes, and coal burning. Urban traffic is one of the important sources of soil pollution. Soils along the road are important depots for vehicle-based pollution which affects pedestrians and people living in close proximity. Particles from exhausts of vehicles and particles from tires and arising from erosion of road surfaces are the main vehicle-based pollutants (Khan et al. 2011; Maher et al. 2008; Wawer et al. 2015). Soil pollution is a serious threat for the health of people living

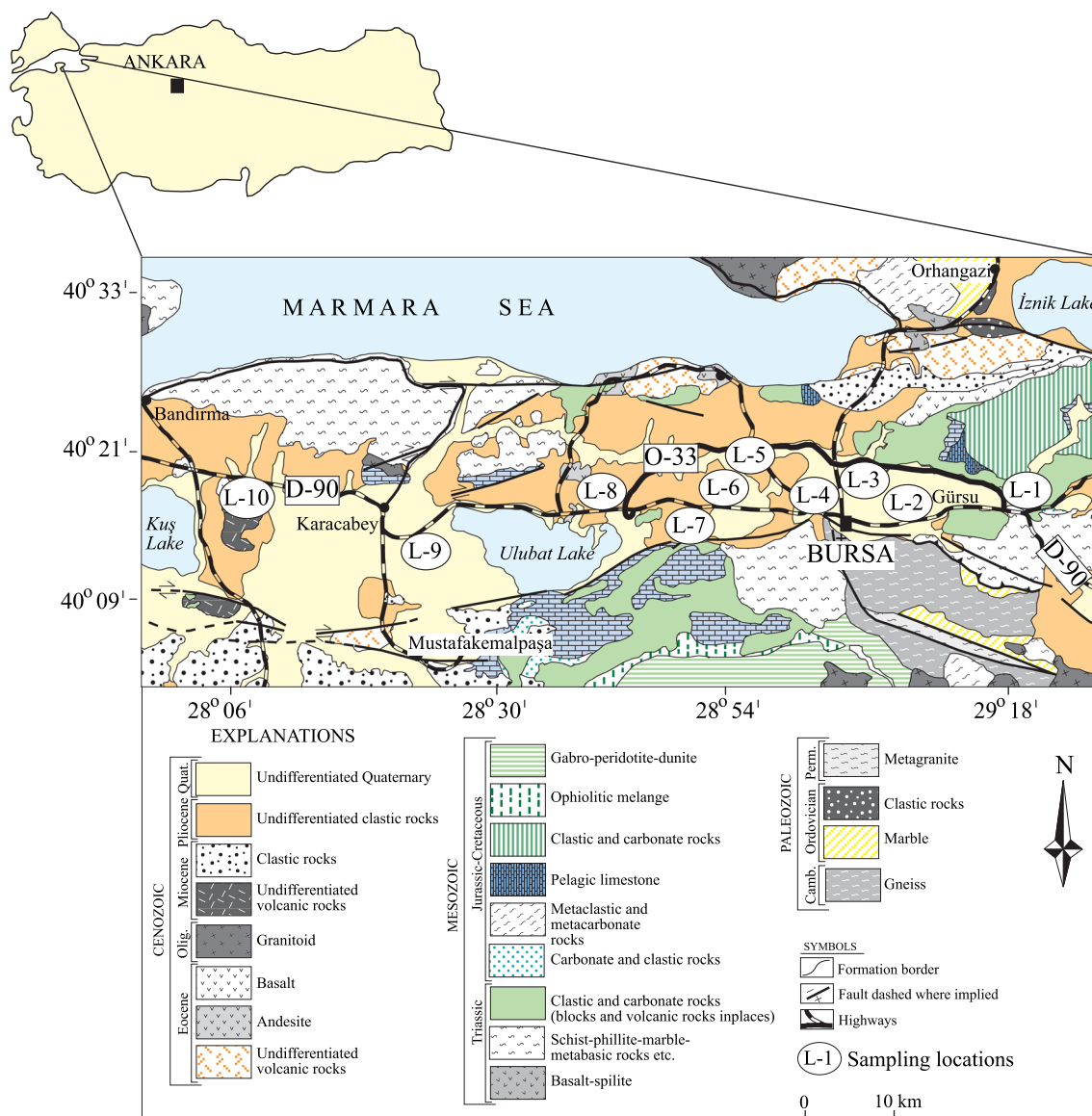
particularly in large residential districts. Soil not only is a geochemical reservoir for the pollutants but also serves as a natural buffer for transportation of chemical materials and elements between atmosphere, hydrosphere, and living things (Knox et al. 1999). Excess pollution of soils by heavy metals results in entrance of metals into food chain via plants and water and creates a potential risk for the human health. Unlike some organic materials, heavy metals are not vanished and, although certain levels are essential for the livings if their concentration exceeds the limit values, they show toxic effect. It is known that if the heavy-metal uptake by the human body exceeds the acceptable values suggested by the World Health Organization (WHO), carcinogenic, teratogenic, toxic, or cardiovascular problems are expected. Studies yield that children suffer the most from heavy-metal pollution and the degree of heavy-metal absorption is the highest in the digestive system of children. In addition, when compared to adults, sensitivity to hemoglobin is greater for the children. Lead is of particular concern because there is increasing evidence that relatively low concentrations of lead in the blood can affect children's mental development, an effect that persists into adulthood (Haley and Talbot 2004).

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**Fig. 1** Geological map of the study area (modified after (Türkecan and Yurtsever 2002))

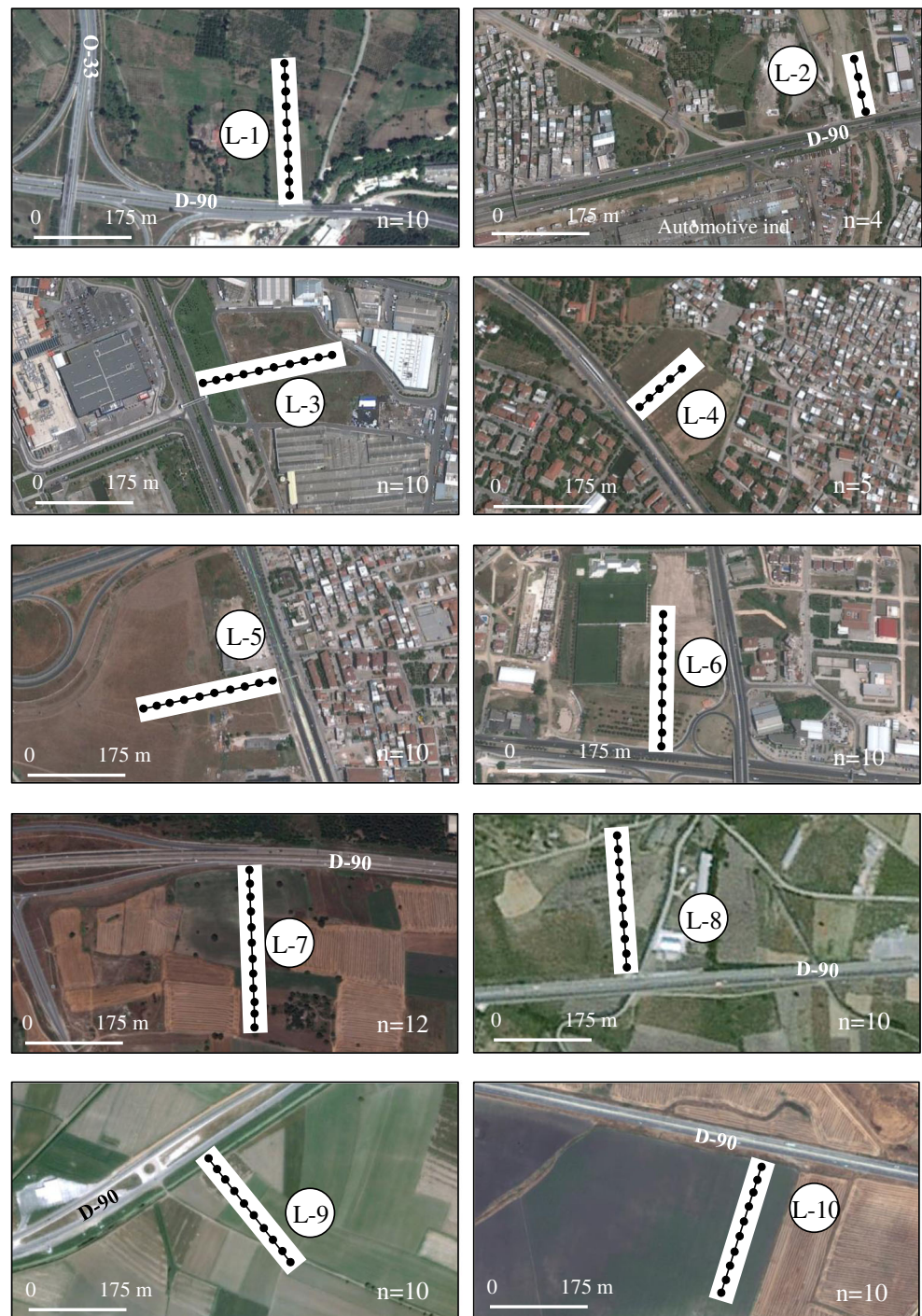
There are several studies to investigate Pb concentrations in soils along the highways (Archer and Barrett 1976; Biggins and Harrison 1980; Chow 1970; Day 1977; Day et al. 1975; Duggan and Williams 1977; Farmer and Lyon 1977; Harrison 1979; Lacasse 1970; Motto et al. 1970; Olson and Skogerboe 2000; Solomon and Hartford 1976); however, studies on pollution of soils along the highways by other metals are limited (Ferguson and Simmonds 1983; Ferguson et al. 1980; Harrison et al. 1971; Hopke et al. 1980; Ward et al. 1977; Werkenthin et al. 2014; Yongming et al. 2006). Lead originates from gasoline used in vehicles and about 200–600 mg lead are added to 1 L gasoline (Öztürk and Türkan 1982). A vehicle with a speed of 90 km/h expels 2 mg Pb per minute. For a traffic load of 200 vehicles per hour, 40–60 g/km-hour Pb is expelled to the air (Öztürk and Türkan 1982). As of June 1, 2000, the use of lead in gasoline was prohibited in

European Union and the amount of lead in gasoline produced by the Turkish Petroleum Corporation (TUPRAŞ n.d.) was lowered from the standard value and maximum Pb contents were allowed to be 0.15 g Pb/L in regular gas, 0.40 g Pb/L in premium gasoline, and 0.01 g Pb/L in unleaded gasoline (TUPRAŞ n.d.).

Cu, Zn, and Cd originated from corrosion of some parts of vehicles and tires and engine oil, thrust bearings, and bushing and corrosion of metal coatings, rocker arms, crank shafts, and rings as well (Christoforidis and Stamatis 2009; Markus and McBratney 1996).

The city of Bursa is one of the largest metropolitans in Turkey and regarding the population, it is the fourth largest city. The population of Bursa is 2.6 million and the area is 10.82 km<sup>2</sup>. Seventeen percent of lands in the Bursa city are covered with plains. In the city automotive, textile

**Fig. 2** Sampling locations in Bursa area



and furniture industries are well developed and other industrial branches include machinery, automotive supply industry, electronics industry, building materials, and metal industry. D-90 highway and O-33 motorway extend at north of Bursa. There are residential areas, parks, gardens, and agricultural sites at the sides of both roads. The traffic load on these roads is quite high and the number of vehicles attains 85.001 per day (KGM Turkish General Directorate of Highways 2016). Roadside soil has been

used as an indicator of heavy-metal pollution in our environment. In Bursa, determination of the heavy metals along the roadside soil is now a growing demand because of metal biomagnification in the food chain and their potential health impact. There has been no study on metal pollution in soils along the highways in the city of Bursa. This study focuses on the identification of heavy metals in the roadside surface soils of Bursa D-90 highway and O-33 motorway which will be served as a baseline study in



**Table 1** Mean for heavy, light, and total traffic counts for the selected study sites ( $n = 14$  days)

Location	Number of heavy vehicles	Number of light vehicles	Total number of vehicles
L-1	6026	13442	19468
L-2	11918	49698	61616
L-3	9629	40515	50144
L-4	2625	82356	85001
L-5	6309	33044	39333
L-6	13470	65491	78961
L-7	5188	13975	19161
L-8	8615	17876	26491
L-9	4586	15715	20301
L-10	1678	5166	7796

Turkey for future monitoring of heavy metals and their levels around the roadside areas. Therefore, the aim of this work is to (a) measure the concentrations of heavy metals in roadside soils of Bursa D-90 highway and O-33; (b) ascertain traffic-related metal pollution using enrichment factor (EF), pollution index (PI), and integrated pollution index (IPI); (c) evaluate the relation between metals with the use of various statistical methods; and (d) define their natural/anthropogenic contributions using multivariate statistical methods.

## Description of the area

The city of Bursa is located in 40° eastern meridian and 28–30° northern parallel of latitudes in the Marmara region. The study area lies between 40° 39' 99" and 39° 59' 79" North latitudes and 27° 57' 93" and 29° 26' 09" East longitudes (Fig. 1). About 35% of lands in Bursa are covered with mountainous areas. The mountains are in the form of mountain ranges extending in the E-W direction. The Uludağ Mountain (2.54 m asl) and İznik Lake (298 km<sup>2</sup> surface area), which are the tallest mountain and the largest lake in the Marmara region, respectively, are within the territory of this city. The Ulubat Lake (134 km<sup>2</sup> surface area) is another lake in Bursa.

Bursa with elevation of 155 m asl has a warm climate. However, climate changes for different regions. Dry summer and wet winter conditions of the Marmara Sea at the north and severe climate conditions of the Uludağ Mountain at the south are noticeable. July and September are the hottest months while February and March are the coldest months. Based on the 52-year meteorological record, the annual average precipitation in the region is 706 mm and the relative humidity is around 69% (BMM Bursa Metropolitan Municipality 2016). Most of

the rain falls during the winter. The soils in the region are calcimorphic soils with neutral and slightly alkaline character ( $\text{pH} > 7$ ) and contain rendzina, grumusol, and brown forest soils. Agricultural activity in Bursa is quite intense. Olive, wheat, barley, corn, oat, bean, horse bean, pea, tomato, tobacco, cotton, and sunflower are the main agricultural products grown in the region.

Various metamorphic, volcanic, plutonic, and sedimentary rocks with ages ranging from Paleozoic to Quaternary occur in and around the Bursa region (Fig. 1). The Uludağ massif consisting of gneiss, marble, and amphibolite is the oldest lithologic unit in the region. It is overlain by Triassic rocks composing of metabasite, marble, phyllite, and carbonate rocks which are covered by Jurassic-Cretaceous sedimentary sequence. This sequence is comprised at the bottom by sandstone, conglomerate, and siltstone which change at the top to limestones and ophiolitic mélange ultrabasic and ultramafic rocks. The Eocene rocks in the region are composed of andesite, basalt, and tuffs which are overlain by the Uludağ granite that cuts the Uludağ massif. Wolframite mineralization occurs at the contact between the Uludağ granite and marbles of the Uludağ massif. The alluvium and travertines comprise the Quaternary units (Ertürk 2010; Türkecan and Yurtsever 2002). Soil sample locations are covered by Quaternary unit composed of alluvium and travertines.

## Material and methods

### Soil sampling and analysis

Ten sites situated along the Bursa D-90 highway and O-33 motorway were selected for this study after a preliminary survey in June 2016. The major criterion for selecting the sampling sites was the presence of farming households, residential areas, parks, and gardens near the roads (Figs. 1 and 2). Ninety-one soil samples were collected from 10 locations. Samples were collected from a depth of 0–10 cm (A zone) in 25-m spacing from the roadside away from the road in each site. The distances of sample location from the main road are as follows: 225 m for L-1, L-3, L-5, L-6, L-8, L-9, and L-10; 75 m for L-2; 100 m for L-4; and 275 m for L-7. During the sampling, plastic spatula was used and metal tools were avoided. Samples were stored into paper bags and dried at room temperature. Samples were then grinded to maintain ideal size for analysis and samples under 80 meshes were sent for analyses at Acme Lab. in Canada. During the analysis, 1 g of soil sample was left in 2 mL HNO<sub>3</sub> solution for 1 h. The samples were then added to 6 mL of 2:2:2 HCl–HNO<sub>3</sub>–H<sub>2</sub>O solution, dissolved at 95 °C for 1 h and analyzed with ICP-MS. Internal standard DS9 was used during the analytical run for trace elements in soils.

**Table 2** Basic statistical parameters and critical levels (Lindsay 1979) of heavy-metal concentrations in soils of study area (mg/kg)

	As	Cd	Co	Cr	Cu	Hg*	Mn	Ni	Pb	Zn
Min.	7.60	0.07	8.80	27.90	14.61	5.00	339	21.00	6.88	34.90
Max.	59.90	0.87	37.90	214.90	424.68	193.00	1151	340.60	84.02	180.00
Mean	26.17	0.23	25.24	124.69	51.00	46.18	862	190.25	35.81	77.49
Median	26.20	0.22	25.70	116.20	32.78	35.00	891	191.70	34.14	73.10
SD	14.13	0.09	5.94	42.45	51.87	34.12	180	72.49	15.07	25.56
CV	0.59	0.39	0.24	0.34	1.01	0.74	0.21	0.38	0.43	0.33
Skw.	0.29	3.67	- 0.29	0.23	4.77	1.95	- 0.77	0.04	0.49	1.93
Kur.	- 1.09	23.79	0.28	- 0.70	30.06	4.53	- 0.13	- 0.49	- 0.02	4.94
Q1	12.90	0.18	21.90	100.40	29.46	23.00	732	143.70	25.22	59.70
Q3	36.10	0.27	28.30	164.60	50.03	61.00	1001	237.40	50.00	85.90
Critical level	5.00	0.06	8.00	100.00	30.00	30.00	600	40.00	10.00	50.00
DL	0.10	0.01	0.10	0.50	0.01	5.00	1.00	0.10	0.01	0.10
RSD %	2.00	5.00	1.00	0.80	3.40	3.60	2.40	10.80	1.50	4.90

SD: standard deviation, Q1: first quartile, Q3: third quartile, Skw.: skewness, Kur.: kurtosis, CV: coefficient of variation (SD/mean), DL: deduction limits, RSD: relative standard deviation

\*µg/kg

Heavy- and light-vehicle density values at the sampling sites for the year of 2016 are given in Table 1 (BMM Bursa Metropolitan Municipality 2016). Heavy vehicles represent medium commercial vehicles (vehicles with passenger capacity of 14–25 persons and trucks with total weight + load of 3.5 to 10 tons), bus, truck, trailer, and towing truck and light vehicles correspond to automobiles. The traffic density was determined by counting the number of motor vehicles passing the road at each site over a period of 18 h from 4:00 a.m. to 10:00 p.m. each day for 14 days between March and October 2016. It is seen from the Table 1 that the total number of vehicles at the locations range from 7796 to 85,001. L-4 is the most busy whereas L-10 is the least busy locations.

### Statistical analyses

In order to determine element relations in soil samples, correlation analysis was performed. Cluster (CA) and principal component analysis (PCA) were applied to ascertain element groups. In addition, regression and correlation analyses were carried out to examine relation between element concentrations and distance to the roads. The results of the analyses were evaluated with EXCEL 2007, SPSS 10.0, STATISTICA, and GRAPHER 5.0 programs.

### Assessment of soil pollution

The enrichment factor is a measure used for quantifying the pollution which is based on standardization of an element

**Table 3** Comparison of mean concentrations (mg/kg) of heavy metals in roadside soils in Bursa and other cities in the world.

	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn	References
Beijing (China)	8.10	0.22	-	61.9	29.7	-	-	26.7	35.4	92.1	Chen et al. (Chen et al. 2010)
Jeddah (S. Arabia)	13.90	-	-	53.3	-	-	-	46.7	47.5	222	Kadi (Kadi 2009)
Luanda (Angola)	5.00	1.10	2.90	26	42	0.13	258	10	351	317	Baptista and De Miguel (Baptista and De Miguel 2005)
Yozgat (Turkey)	-	2.54	24	33	38	-	852	51	69	-	Divrikli et al. (Divrikli et al. 2005)
Xian (China)	10.60	-	-	167	95	0.63	687	-	231	421	Yongming et al. (Yongming et al. 2006)
Qinghai (Tibet)	10.18	0.13	8.10	54.3	18.4	-	-	20.4	18.5	48.8	Zhang et al. (Zhang et al. 2015)
Murgia (Spain)	-	0.10	-	38	15	-	-	21	22	60	
Galway (Ireland)	-	-	5.40	-	16.6	-	650	22.1	40.8	81.8	Dao et al. (Dao et al. 2010)
Ottawa Canada	1.00	0.33	8.02	41.7	38.13	0.02	420	14.8	33.5	101	Rasmussen et al. (Rasmussen et al. 2001)
İstanbul (Turkey)	-	2.30	-	-	209	-	385	33.3	212	521	Sezgin et al. (Sezgin et al. 2003)
Bursa (Turkey)	26.20	0.23	25.20	125	51	0.05	862	190	35.8	77.5	Present work

**Table 4** Spearman correlation coefficients for elements in the soil samples

	Cu	Pb	Zn	Ni	Co	Mn	As	Cd	Cr	Hg
Cu	1									
Pb	-0.90	1								
Zn	0.70**	0.39**	1							
Ni	0.16	0.21*	-0.18	1						
Co	0.56**	-0.07	0.21*	0.66**	1					
Mn	0.19	0.25	0.10	0.32**	0.73**	1				
As	0.21*	0.47**	0.52*	0.13	0.17	0.33**	1			
Cd	0.38**	0.45**	0.64**	0.17	0.56	-0.13	0.39**	1		
Cr	0.29**	0.40**	0.28**	0.76**	0.64**	0.62**	0.55**	0.16	1	
Hg	0.71**	-0.04	0.64**	-0.13*	0.24**	0.03	0.46**	0.13**	0.20	1

\*Correlation is significant at the 0.05 level (2-tailed)

\*\*Correlation is significant at the 0.01 level (2-tailed)

tested against reference element. The most common reference elements are Al, Sc, Mn, Ti, Ca, and Fe (Pacyna and Winchesler 1990; Quevauviller et al. 1989; (Reimann and de Caritat 2000); Schiff and Weisbeg 1999; (Sutherland 2000)). In the present study, Al was used as the reference element. Aluminum is one of the most important components in the Earth's crust and its concentration in soil varies with respect to matrix. If the enrichment factor is < 1, element is depleted in the environment; if it is > 1, the element is relatively enriched in the environment (Brumsack 2006). In the calculation of enrichment factor, the equation suggested by Buat-Menard and Chesselet (Buat-Menard and Chesselet 1979) and later modified by Loska et al. (Loska et al. 2004) was used (1).

$$EF = [Cn(\text{sample})/Cref(\text{sample})]/[Bn(\text{background})/Bref(\text{background})] \quad (1)$$

where  $Cn$  (sample) is the concentration of the examined element in the examined environment,  $Cref$  (sample) is the concentration of the reference element in the examined environment,  $Bn$  (background) is the concentration of the examined element in the reference environment, and  $Bref$  (background) is the content of the reference element in the reference environment. The geochemical background values of the studied elements are taken by Taylor and McLennan (Taylor and McLennan 1995). EFs > 1 suggest possible anthropogenic origin.

EF is divided into five groups (Sutherland 2000):

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

As mentioned in several other studies, the enrichment factor depends on dissolution of a given element and therefore it is indirectly affected by environmental conditions (Blaser et al. 2000; Reimann and de Caritat 2000).

PI value is another measure used to determine metal pollution in soils. For each element studied, a PI value was computed using Eq. (2) (Wei and Yang 2010):

$$PI = C_i / S_i \quad (2)$$

where  $C_i$  is the measured concentration of each metal and  $S_i$  is the required standard of each metal. For  $S_i$  value, the critical value given by Lindsay (Lindsay 1979) was used.

PI value ≤ 1 refers to non-pollution, 1 < PI ≤ 2 indicates low level of pollution, 2 < PI ≤ 3 means moderate levels of pollution, and PI > 3 indicates high level of pollution (Wei and Yang 2010).

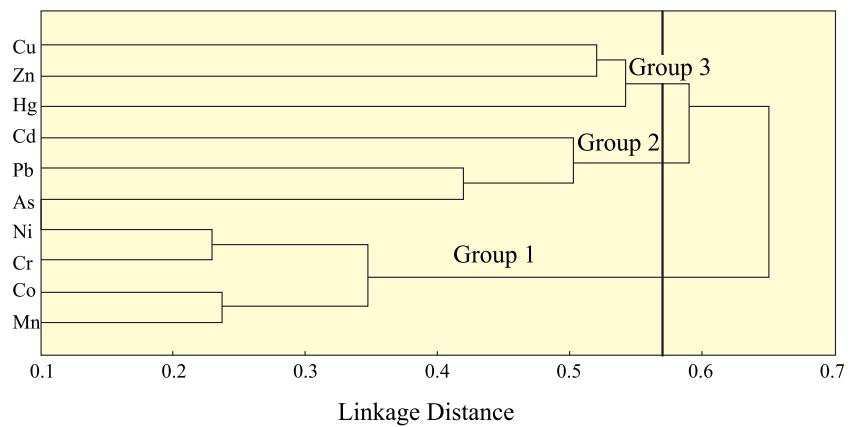
Integrated pollution index subsequently helps to illustrate the distribution of the sample contamination. Integrated pollution index (IPI) which shows the pollution value at each sampling location is the average of PI values computed for each sample. The IPI value was graded into four categories: IPI ≤ 1.0 low level of pollution, 1 < IPI ≤ 2 moderate level of pollution, 2 < IPI ≤ 5 very high pollution, IPI > 5 extremely high pollution (Wei and Yang 2010).

## Results and discussion

### Heavy-metal concentrations of soil samples

Table 2 shows descriptive statistical parameters such as mean, median, range, standard deviation, coefficient of variation, skewness, and kurtosis for As, Cd, Co, Cr, Cu, Hg, Mn, Ni,

**Fig. 3** Dendrogram depicting the hierarchical clustering of elements (single linkage; 1-Pearson *r*)



Pb, and Zn elements in all soil samples collected from the roadside.

Skewness values in this table show that As, Co, Cr, Mn, Ni, and Pb are close to normal distribution while Cd, Cu, Hg, and Zn yield a positive skewness. The coefficient of variation (CV) of studied elements is low and the highest variation coefficient belongs to Cu (1.01) indicating that elements in the soil show a homogeneous distribution.

Lead concentrations of soil samples are in the range of 6.88 to 84.02 mg/kg with an average of 35.81 mg/kg. The arithmetic means of As, Cd, Co, Cr, Cu, Mn, Ni, and Zn elements are 26.17, 0.23, 25.24, 124.69, 51, 862, 190.25, and 77.49 mg/kg and that of Hg is 46.18 µg/kg.

Heavy-metal concentrations in roadside soils in Bursa were compared to those in other cities in the World (Table 3)

**Table 5** Factor loads (with varimax rotation) prepared based on correlation coefficient matrix and total variance explained

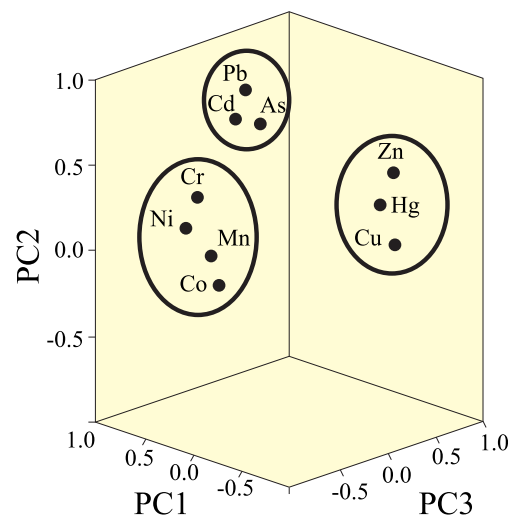
	Components		
	PC1	PC2	PC3
Cu	0.09	-0.19	<i>0.83</i>
Pb	0.19	<i>0.87</i>	-0.11
Zn	-0.18	0.49	<i>0.69</i>
Ni	<i>0.78</i>	0.22	-0.27
Co	<i>0.91</i>	-0.23	0.19
Mn	<i>0.84</i>	-0.03	0.06
As	0.33	<i>0.69</i>	0.13
Cd	-0.23	<i>0.63</i>	0.17
Cr	<i>0.85</i>	0.35	-0.08
Hg	0.00	0.18	<i>0.78</i>
Eigenvalues (total)	3.23	2.31	1.69
% of total variance	32.25	23.12	16.87
Cumulative % of variance	32.23	55.36	72.23

Extraction method: principal component analysis  
 Rotation method: varimax with Kaiser normalization  
 Italics indicate the elements most effected by factors

(Baptista and De Miguel 2005; Chen et al. 2010; Dao et al. 2010; Divrikli et al. 2005; Kadi 2009; Rasmussen et al. 2001; Sezgin et al. 2003; Yongming et al. 2006; Zhang et al. 2015). The mean concentrations of Pb, Cu, Zn, and Cd collected from the highways in Bursa were slightly lower than those in the samples from İstanbul (Turkey) (Sezgin et al. 2003). This may be because of the fact that the highway in İstanbul is one of the most heavily traveled roads in Turkey. The mean concentration of Pb in roadside soils sampled in Bursa is similar to those sampled in Ottawa, Galway, Beijing, Jeddah, and Yozgat, higher than those sampled in Qinghai and Murgia, lower than sampled in Luanda and Xian.

The mean concentrations of Cd, Cr, Cu, Ni, Pb, and Zn collected from Bursa were slightly higher than those in the samples from Murgia and Qinghai. The mean concentration of Cu and Cr in roadside soil of Bursa is high compared with several cities in the world except for Xian (Yongming et al. 2006).

The Pb concentrations in Luanda and Xian are almost 20–35 times as high as the critical Pb concentrations (Lindsay 1979). The Zn concentrations in Luanda, Xian, and Jeddah are much higher than the critical metal levels. These indicate



**Fig. 4** Distribution of factor loads of elements analyzed in the soils

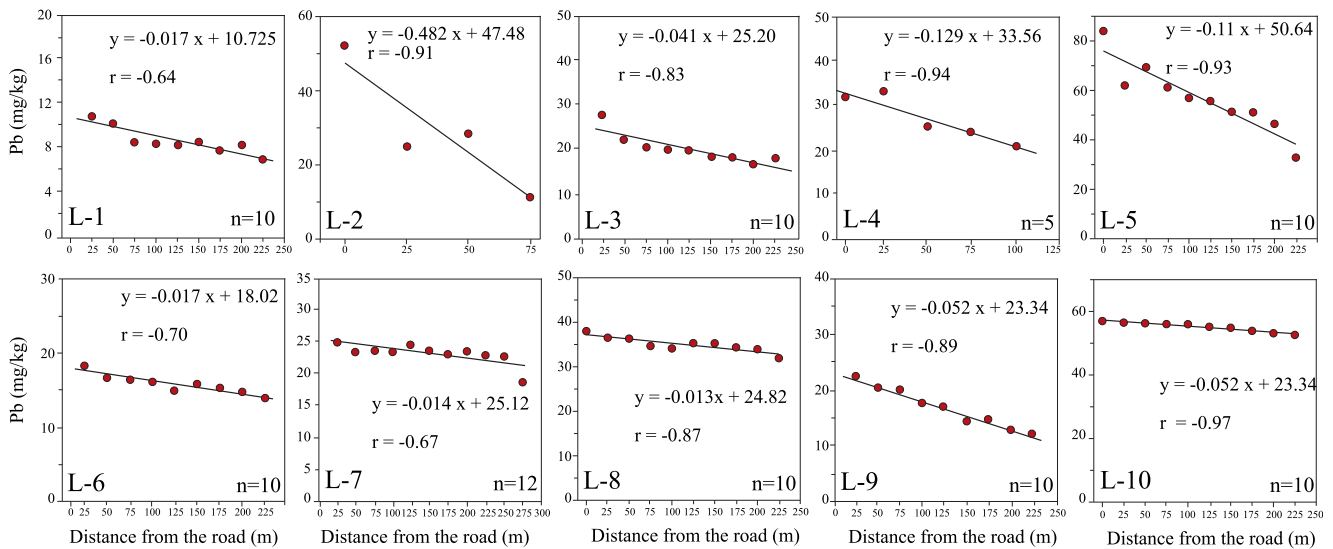


Fig. 5 Diagrams showing the relation between Pb content and distance to the road

the severe pollution from the local traffic and industrial activities.

### Interrelationship among elements in soils

With the application of Spearman correlation analysis (Edwards 1976), correlations of elements were examined at significance levels of  $p \leq 0.05$  and  $p \leq 0.01$ . Cr–Ni, Co–Mn, Co–Ni, and Cr–Co element pairs are represented by the highest correlations with respective correlation coefficients of 0.76, 0.73, 0.66, and 0.64 (Table 4). Pb, As, Cr, Ni, and Cd are significantly positively correlated with each other, which may suggest a common origin such as traffic. In addition, Pb shows negative correlations with Cu and Hg. The reason is the observed correlation for the various elements

based on the geochemical behavior of chemical species and/or the anthropogenic inputs.

In order to understand the nature element associations/relations, analytical data sets were subjected to cluster and principal component analysis.

In hierarchical cluster analysis, although several techniques are applied, the single-linkage clustering method is the most commonly used technique yielding the best results (Jardine and Sibson 1971). Based on single-linkage and Pearson’s correlation coefficients, hierarchical cluster analysis was applied to the soil samples and the results are shown on a dendrogram in Fig. 3. It is shown in this dendrogram that elements analyzed form 3 groups, as Ni–Cr–Co–Mn, Cd–Pb–As, and Cu–Zn–Hg. Concentrations of Pb, Zn, and Cd elements indicate significant decrease in concentrations away from the road. It is clear that these elements originate from traffic load. On the

Table 6 Pearson correlation coefficients between elements and distance from the road

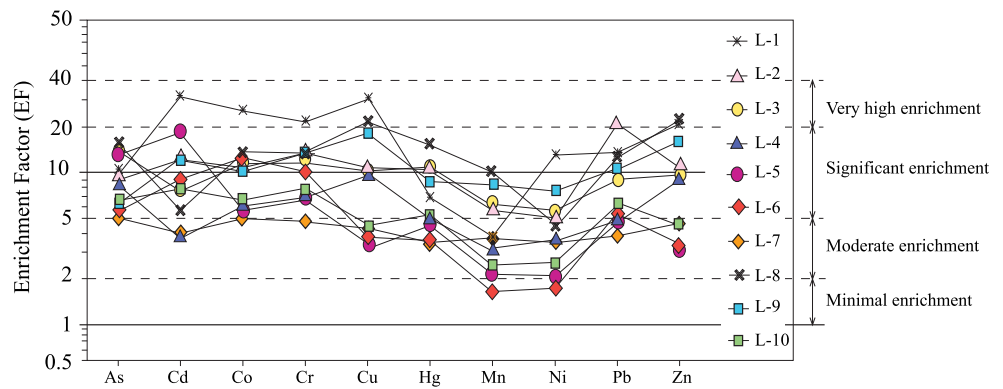
Location	Correlation coefficient ( <i>r</i> )									
	Pb	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Zn
1	-0.64*	0.30	-0.65*	0.49	0.59	0.61*	0.09	0.49	0.68*	-0.52
2	-0.91	0.38	-0.91*	-0.50	-0.52	-0.81*	-0.98*	-0.65	-0.50	-0.90*
3	-0.83**	0.06	-0.35	0.45	0.44	-0.49	-0.70*	0.32	0.68*	-0.58
4	-0.94*	-0.22	-0.55	0.30	0.29	-0.78**	-0.60*	0.25	0.59	-0.66*
5	-0.93**	-0.34	-0.53	-0.63	-0.22	-0.72*	0.09	-0.60	-0.49	-0.87**
6	-0.70*	-0.09	-0.51	0.20	0.23	-0.54	0.35	0.20	0.18	-0.54
7	-0.67*	0.35	-0.68*	-0.12	-0.11	-0.04	-0.39	-0.11	-0.11	-0.37
8	-0.87**	0.16	-0.51	-0.06	-0.05	-0.29	-0.16	0.10	-0.21	-0.07
9	-0.89**	-0.03	-0.38	0.40	0.50	-0.60	-0.59	0.03	0.47	-0.85**
10	-0.97**	-0.63	0.03	-0.72*	-0.46	-0.85**	-0.23	-0.63	-0.67*	-0.23

\*Correlation is significant at the 0.05 level (2-tailed)

\*\*Correlation is significant at the 0.01 level (2-tailed)



**Fig. 6** Diagram of enrichment factor for trace elements in soil



other hand As, Cu, and Hg elements are associated with industrial activities around the study area. Two of these groups, Cd–Pb–As and Cu–Zn–Hg, are indicative of anthropogenic source. Mn, Cr, Co, and Ni from the 3rd group are lithogenic.

Principal component analysis (PCA) was performed to distinguish the associations among the 10 elements analyzed in soils along the Bursa D-90 highway and O-33 motorway. PCA is used to reduce a large number of variable parameters to a small number of principal components (Aste et al. 2008; Nazzal et al. 2014; Zaharescu et al. 2009; Zhang et al. 2015). By extracting the eigenvalues and eigenvectors from the correlation matrix, the number of significant factors and the percent of variance explained by each of them are calculated.

Using varimax rotation with Kaiser Normalization, PCA was performed on the data set maximizing the sum of the variance of the component coefficients. This technique clusters variables into different groups. Table 5 displays the factor loadings with varimax rotation, eigenvalues and the variance explained by the components. Three components were obtained, accounting for 72.23% of the total variance; in other words, elements in soil samples are affected by three major components. The results are fully consistent with the attribution of the elements in the three groups and defined with the CA.

Distribution diagram of PCA loadings is presented in Fig. 4. As shown from this figure, elements form three groups which are prominently separated from each other. Component 1, accounting for 32.25% of total observed variance, positively corresponded to Ni, Co, Mn, and Cr elements (Table 5). The source of this component is lithologic origin and controlled by mafic bedrocks in the field. Mn is generally accumulated as oxide or hydroxide in areas of sedimentary rocks. Cobalt has a strong tendency to make compounds with Mn oxides. Distributions of Ni, Co, and Cr elements in the earth crust are very similar and these elements are derived from soils generated on the mafic rocks of the undifferentiated Quaternary units. Ni, Co, and Cr concentrations are increased in mafic environments particularly where the bedrock is composed of mafic components of Quaternary units.

The 2nd component corresponds to 23.12% of total observed variance. The Pb, As, and Cd elements are positively and significantly related to component 2. The source of this component may be contributions mainly from traffic. The 3rd component is correlated very strongly with Cu, Zn, and Hg. This component corresponds to 16.87% of total observed variance. The source of this component may be anthropogenic because automotive, textile, furniture, electronics, building materials, and metal industry are well developed in Bursa city.

**Table 7** Average enrichment factors of trace element for soil samples

Location	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
L-1 (n = 10)	10.07	9.91	13.34	8.14	13.88	5.75	5.19	15.71	6.14	6.05
L-2 (n = 4)	32.73	12.38	7.83	3.85	17.73	9.16	4.13	6.03	12.53	7.74
L-3 (n = 10)	25.55	11.27	11.18	6.16	5.78	12.47	4.96	12.93	11.09	5.92
L-4 (n = 5)	23.33	13.33	11.6	6.59	6.72	10.01	4.95	13.41	12.97	6.92
L-5 (n = 10)	29.47	11.06	10.48	10.09	3.30	3.72	4.62	22.57	17.57	4.68
L-6 (n = 10)	7.74	11.09	9.48	5.25	4.34	2.92	3.65	17.35	9.10	5.05
L-7 (n = 12)	3.90	5.75	6.42	3.35	2.09	1.55	3.00	9.95	7.90	2.58
L-8 (n = 10)	12.47	5.03	5.79	3.84	1.98	1.69	3.61	5.48	7.44	2.57
L-9 (n = 10)	13.15	19.31	9.26	5.11	4.41	5.16	4.08	13.77	10.89	6.46
L-10 (n = 10)	21.31	11.35	9.61	8.54	3.11	3.32	4.71	19.66	15.77	4.73

**Table 8** Pollution index (PI) values of elements for all locations

Location	Range As	Mean	Range Cd	Mean	Range Co	Mean	Range Cr	Mean	Range Cu	Mean
L-1	2.12–3.60	3.11	1.67–6.83	3.25	1.76–4.74	4.21	1.11–1.68	1.54	2.12–5.97	4.38
L-2	4.88–9.18	7.02	1.17–5.67	3.42	1.10–2.61	1.78	0.28–0.90	0.52	0.49–14.2	4.27
L-3	6.94–8.68	7.46	3.00–4.33	3.87	3.10–3.63	3.28	1.03–1.22	1.11	1.45–2.11	1.70
L-4	6.88–7.62	7.30	4.33–5.33	4.90	3.40–3.94	3.65	1.20–1.38	1.27	1.01–1.94	1.26
L-5	4.22–11.9	9.55	2.17–5.83	4.23	2.38–4.09	3.38	1.80–2.15	1.92	0.75–1.24	1.07
L-6	1.66–3.10	2.28	3.00–4.83	3.87	1.75–3.65	3.02	0.67–1.20	1.01	0.97–2.46	1.22
L-7	1.52–2.48	1.73	2.67–4.00	3.03	1.64–3.53	3.08	0.64–1.13	0.97	0.82–1.06	0.98
L-8	4.66–6.32	5.82	2.33–3.50	2.78	2.49–2.85	2.72	0.70–1.31	1.09	0.83–1.01	0.93
L-9	2.12–6.34	3.42	2.33–14.5	5.18	1.64–3.30	2.52	0.57–1.06	0.85	0.81–1.78	1.15
L-10	4.86–9.52	7.45	3.50–5.83	4.65	2.26–3.78	3.37	1.68–1.87	1.82	0.97–1.19	1.09
	Hg		Mn		Ni		Pb		Zn	
L-1	1.27–2.50	1.78	0.92–1.79	1.63	1.70–5.91	5.01	1.03–4.78	1.65	1.41–3.47	1.71
L-2	0.17–4.07	2.24	0.57–1.10	0.93	0.53–2.83	1.35	1.13–5.25	2.94	0.70–3.60	1.80
L-3	2.37–6.43	3.64	1.35–1.58	1.46	3.48–4.15	3.80	2.52–5.40	3.25	1.57–1.96	1.74
L-4	2.20–5.07	3.14	1.43–1.62	1.56	3.94–4.48	4.23	3.14–5.00	4.07	1.85–2.52	2.18
L-5	0.80–1.50	1.18	1.00–1.85	1.50	5.94–8.52	7.24	3.28–8.40	5.71	0.94–1.76	1.52
L-6	0.50–1.67	0.89	0.78–1.39	1.15	2.79–6.98	5.59	2.11–4.61	2.61	1.05–3.30	1.37
L-7	0.50–1.10	0.69	0.74–1.72	1.44	2.97–5.68	4.75	2.78–5.52	3.63	1.11–1.31	1.18
L-8	0.23–1.27	0.77	1.47–1.84	1.70	2.40–2.83	2.59	3.19–3.80	3.51	1.14–1.29	1.20
L-9	0.40–2.20	1.29	0.79–1.41	1.10	2.16–4.98	3.80	1.81–5.13	2.78	0.99–2.68	1.67
L-10	0.93–1.53	1.16	1.09–1.92	1.65	4.04–7.99	6.91	5.26–5.70	5.51	1.46–1.91	1.66

### Relationship between the metals and traffic

Regression and correlation analyses were carried out to examine variations in metal concentrations regarding distance to the road. In regression analyses, outliers are removed from the data set.

Regression equations and correlation coefficients revealing the relation between Pb concentration in the soil and distance to the road were computed for each location and relevant graphics are shown in Fig. 5 and Table 6. For all the locations, negative correlations were obtained between Pb concentration and distance to the road and the highest correlation coefficient ( $r = -0.97$ ) was for location 10. The slope at locations 8 and 10 are relatively lower than others.

At all locations, Pb concentration is decreased with distance to the road, and this might indicate the presence of traffic-related Pb pollution. Lead concentrations of location 1 are lower than those of other locations. This might be attributed to the protection of the sampling area by the surrounding woods and trees.

For all locations, the relation between element concentrations and distance to the road were determined with the use of Pearson correlation coefficients. With the exception of a few locations, there is no significant correlation between Cd, Cu, and Zn concentrations in the soil samples and distance to the road (Table 6). The relation is negative and element

concentrations are decreased away from the road. Cadmium concentrations were found between 0.16 mg/kg (L-7) and 0.41 mg/kg (L-1) for road edge (0 m); Cu and Zn concentrations lie between 24.52–424.68 mg/kg and 180–58.30 mg/kg respectively. Like the case for Pb, this also indicates that vehicular emission played a significant role in the levels of Cd, Cu, and Zn. Mercury concentration is negatively correlated with the distance except for locations 1, 5, and 6 and Hg concentrations in the soil are decreased away from the road.

Arsenic concentration is decreased at locations 4, 5, 6, 9, and 10 with increasing distance from the road and it is increased at other locations. Likewise, Co, Cr, Mn, and Ni concentrations at some locations are decreased with increasing distance from the road and increased at some others. Consequently, element concentrations are found to significantly vary away from the road.

### Pollution indices

Enrichment factors of soil samples were computed and using the average element enrichment values for each location, graphic was prepared (Fig. 6). According to Fig. 6, EF ratios suggest that all metals are minimal to very high enriched. Pb, Cd, and Co are notably enriched at all locations and Ni shows very high enrichment at location 5 and significant enrichment at other locations. The average enrichment values are 6.1–17.6

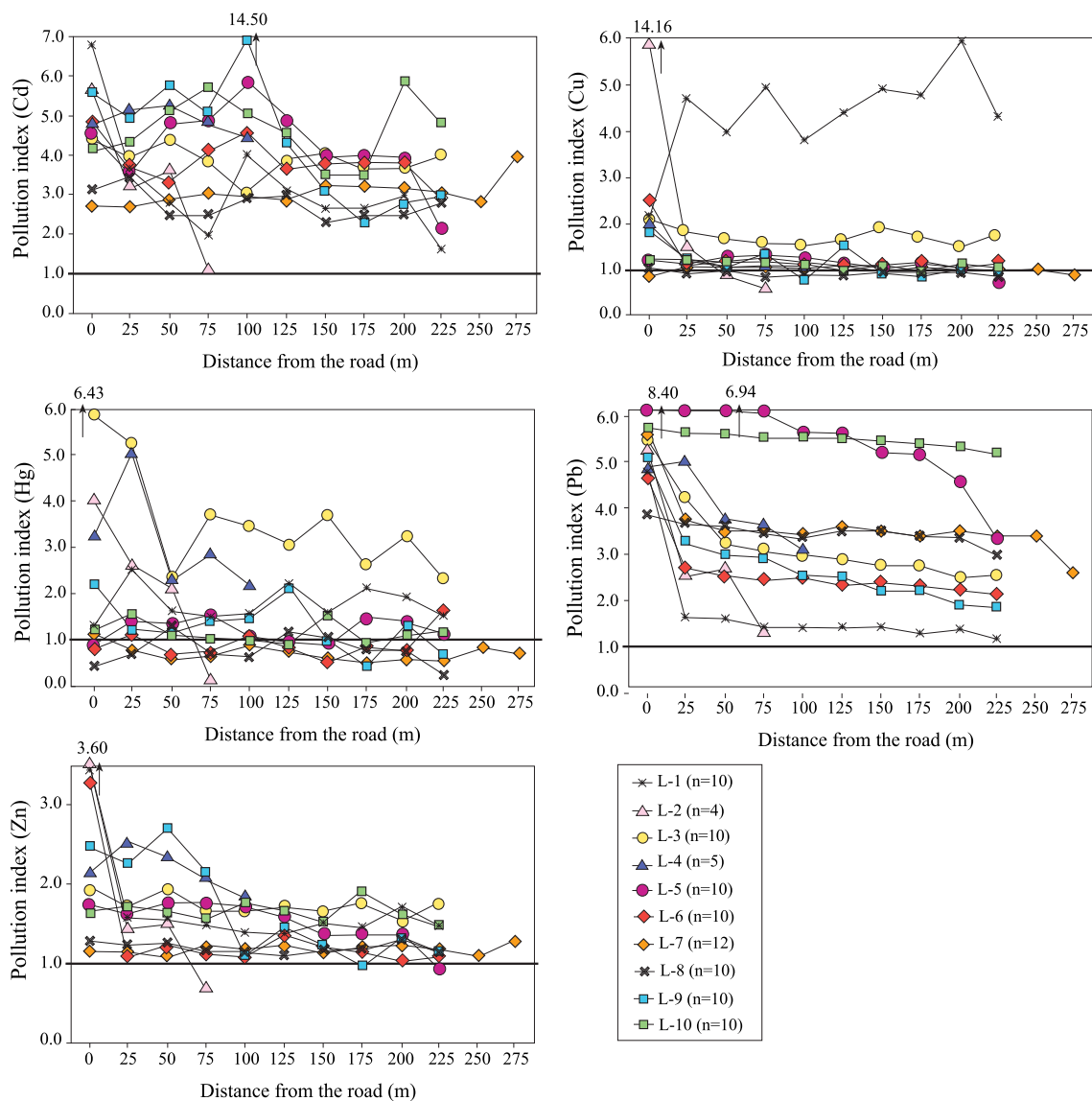


Fig. 7 Distribution of pollution index values with respect to distance to the road

for Pb, 5.0–19.3 for Cd, 5.8–13.3 for Co, and 5.5–22.6 for Ni. Arsenic is moderately enriched at location 7 and it shows significant to very high enrichment at other locations.

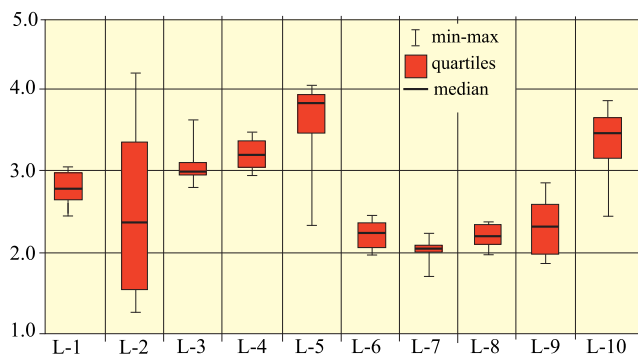


Fig. 8 Box-plot of IPI for sampling locations

Chromium is moderately enriched at L-2, L-7, and L-8 and it shows significant enrichment at other locations.

Copper shows minimal enrichment at L-8 and moderate to significant enrichment at other locations. The average enrichment value of Mn is between 3 and 5.2 and all locations are represented by moderate Mn enrichment. The highest enrichment value (32.73) was obtained for As at location 2 (Table 7).

Pollution index values were calculated for studied elements and minimum, maximum, and average PI values are given in Table 8. In addition, in Fig. 7, metal pollution indexes (PIs) of Pb, Cd, Zn, Hg, and Cu elements are graphically illustrated which are notably decreased away from the road indicating traffic-related pollution.

Pollution index values of Pb at all locations are greater than 1. PI values of Pb at locations 4, 5, 8, and 10 are > 3 indicating very high pollution. The highest PI value was from L-5 (8.40).

Pb pollution is moderate to very high at locations 3, 6, and 7 and low, moderate, and high at other locations. These high PI values show that Pb main source is directly associated with emissions from vehicle exhaust using leaded gasoline.

The highest PI value in soil samples was for Cd from location 9 and this value, 14.50, is indicative of very high Cd pollution. Pollution index values computed for Cd are  $> 1$  at all locations and PI values are considerably decreased with increasing distance to the road.

Pollution index values computed for Zn indicate pollution except for 3 locations. There are significant decreases in Zn pollution index values with increasing distance to the road. Pollution index values for Cu and Hg show signs of pollution at some locations and PI values are  $< 1$  at some others. However, in graphics of these elements, PI values are shown to significantly decrease with increasing distance to the road.

The source of Cu, Zn, and Cd in roadside soils was indicated by research as tire abrasion, the corrosion of some parts of vehicles and tires and engine oil, and the corrosion of metal coatings, rocker arms, crank shafts, and rings (Akhter and Madany 1993; Christoforidis and Stamatis 2009; Duong and Kyu Lee 2011; Markus and McBratney 1996).

In IPI calculations, the highest values were obtained from L-2 (4.38) and L-5 (4.29). Soils collected from L-2 are affected and polluted by both road and automotive industry nearby. L-5 is located between D-90 highway and O-33 motorway. Consequently, soils at these locations are affected by both roads. IPI values of locations based on average IPI values are in the decreasing order of  $L-5 > L-10 > L-4 > L-3 > L-1 > L-2 > L-9 > L-8 > L-6 > L-7$  and respective values from these locations are 3.73, 3.53, 3.36, 3.13, 2.83, 2.62, 2.38, 2.31, 2.30, and 2.15 (Fig. 8). Among the soil samples, only three of them are represented by moderate pollution and others show very high pollution. In other words, 3.3% of samples are moderately polluted whereas 96.7% indicate very high pollution. This might point out that soils along the roadside are intensely affected by heavy metals that arose from the traffic. In addition to traffic-related pollution, intense industrial activities in the region also give rise to pollution of soils. In other words, soils in the city of Bursa are affected and mainly polluted by heavy metals as a result of anthropogenic activities such as traffic.

## Conclusions

In this study, traffic-related metal pollution was investigated along D-90 highway and O-33 motorway extending at the north of Bursa which is one of the largest metropolitans in Turkey. With the application of various statistical methods, elements of anthropogenic and lithologic origin were determined in soils sampled in the study area. Results of correlation, cluster, and principal component analyses reveal that

elements form three different groups. Two of these three groups are Pb–Cd–As and Zn–Hg–Cu, indicating anthropogenic source (traffic and industrial). Concentrations of Pb, Zn, and Cd elements are negatively correlated with distance to the road showing significant decrease in concentrations away from the road. It is clear that these elements are originated from traffic load. On the other hand, As, Cu, and Hg elements are associated with industrial activities around the study area. Mn, Cr, Co, and Ni from the 3rd group are lithogenic.

Arsenic, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn concentrations in soils sampled along the highway and motorway were evaluated using enrichment factor, pollution index, and integrated polluted index methods. Enrichment factor ratios showed a considerable variation in element concentrations among the locations. The highest EF values were obtained for As at L-2, L-3, L-4, L-5, and L-19 and for Ni at L-5. The pollution index showed that the lead contents of roadside soils decrease with increasing distance from the motorway. Likewise, Pollution Index values for cadmium and zinc are decreased away from the road. Evaluation of PI values shows that concentrations of Pb, Cd, Cu, Hg, and Zn elements notably vary and decreased in distal parts of the road. According to IPI values, there are moderate to very high pollution in soil samples from the study area. As a result, it is concluded that soils along the Bursa D-90 highway and O-33 motorway are intensely affected by the traffic and seriously polluted by the heavy metals. In addition to traffic-related pollution, intense industrial activity and resultant pollution are also remarkable. Since metals are transported from polluted soils to via roots of plants along the roads, the locations of agricultural sites should be reconsidered and, if necessary, they should be moved in distal parts of the roads.

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