



Spatial distribution and analysis of heavy metal pollution in urban roadside dusts from Sanandaj, Iran

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Original Article

Abstract

Industrial activities and high traffic density are the most important heavy metal pollution sources in urban areas. Roadside dust created by atmospheric deposition can be one of the best indicators for heavy metal contamination levels. The present study reports the spatial distribution patterns and degree of heavy metal pollution (Cd, Cr, Ni, Pb, Zn, and As) in 50 roadside dust samples from urban areas of Sanandaj, Iran. For this purpose, sampling points were selected on different roads including primary roads, high roads, and main roads. The geographic coordinates of sampling points were recorded by the Global Positioning System (GPS). The geoaccumulation index (I_{geo}) and integrated pollution index (IPI) were used to present the heavy metal contamination levels. The results obtained by the geoaccumulation index suggest that the roadside dust samples were moderately contaminated with Ni and Cr, moderately to heavily contaminated with Pb and Cd, and heavily to extremely contaminated with As and Zn. The assessment of the data shows that 92% of all roadside dust samples had moderate pollution levels with an IPI of higher than 2, indicating that roadside dust in Sanandaj County has moderately been polluted by anthropogenic emissions. In order to compare the heavy metal concentrations in different parts of Sanandaj County, each heavy metal contamination was interpolated in a geographical information system (GIS). Heavy metal distribution maps showed the different hotspots of each pollutant that indicated high traffic density and industrial centers as the important factors affecting their concentrations in Sanandaj County.

KEYWORDS: Heavy Metals, Urban Roadside Dust, Special Distribution, Geographical Information System

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Introduction

Today, industrialization of communities and rapid urbanization is a worldwide phenomenon. According to the literature, over half of the world's population now lives in urban areas.¹ Moreover, industrial and economic activities are more concentrated in urban areas, and cities have become the geographic focus of resource consumption and chemical emissions.^{2,3} Therefore, urban areas encounter many

environmental problems. Environmental pollutants, which accumulate in the form of roadside dust through atmospheric deposition, are often used as indicators of pollution in urban areas.^{4,5} Roadside dust is a complex mixture of particles derived from different natural and anthropogenic sources which have been found to contain several pollutants including heavy metals from exhaust and non-exhaust processes.⁶ According to numerous studies, roadside dust may act as a temporary storage of metals from a variety of sources and may also act as a source of metals contributing to atmospheric or water source pollutions through resuspension.^{7,8} The

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suspension of a portion of this dust in the ambient atmosphere is caused by transportation and wind. Larger particles with diameters of 500-1000 μm tend to settle on the ground surface while those below 100 μm can become suspended.⁹ Heavy metals are among the most important environmental pollutants. Exposure to heavy metal emissions on roadways (including direct ingestion, respiratory uptake, and skin absorption) has been implicated as detrimental to human health and associated with effects of bioaccumulation.¹⁰⁻¹³ Due to the higher uptake of heavy metals by children's body system, which is because of the higher sensitivity of their hemoglobin, children are more readily prone to the health hazards of these pollutants, as compared with adults.^{2,14} For example, there is substantial evidence that a high Pb level in the environment could affect blood Pb level, intelligence, and behavior of children.⁴ Cd, Pb, Zn, Ni, Cr, and As are reasonable indicators of contamination in urban roadside dust because they have anthropogenic sources.¹⁵⁻¹⁸ In roadside dust of urban areas, anthropogenic sources of heavy metals consist of traffic emission (including vehicle exhaust particles, tire and brake lining wear particles, and weathered street asphalt particles), industrial emission (including power plants, metallurgical industries, auto repairs, chemical plants, and etcetera), domestic emission, building and pavement erosion, atmospheric deposition, and etcetera.^{11,16,19-21} Wei et al. reported that a direct relationship was observed between spatial distribution pattern of Pb, Zn, and Cr and traffic density in Urumqi, NW, China.¹⁶ On the other hand, Ni showed similar distribution in relation with industrial areas and Cd was mostly accumulated in old towns, near factory sites and industrial parks.¹⁶ Today, due to industrialization and rapid urbanization, air pollution has become a major environmental issue in many developing countries, including Iran. However, no studies have, thus far, reported the level and distribution of heavy metals in urban areas of

Iran. Therefore, the objective of the present study is the determination of spatial distribution patterns and contamination levels of heavy metals in Sanandaj, Iran. For this purpose, 50 samples of roadside dust were collected from different roads and concentrations of Cd, Cr, Ni, Pb, Zn, and As were determined. In addition, 5 deep soil samples (> 50 cm depth) were collected from areas at a distance of more than 100 m from the roads and used as background value. Then, the contamination level of these metals was assessed using the integrated pollution index (IPI) and geoaccumulation index (I_{geo}). Finally, spatial distribution patterns of these metals in Sanandaj were obtained.

Materials and Methods

The study sites, consisting of road surfaces, were selected in Sanandaj, the capital of Kurdistan Province. Sanandaj with approximately 2,906 km^2 area is the 23rd largest city of Iran and is located in the West of Iran with a population of over 370,000. The urban area of Sanandaj in all directions is surrounded by Zagros Mountains. The city is 1,4501,538 m above sea level with average annual rainfall of 500 mm and a cold semi-arid climate. Environmental pollution in the urban area of Sanandaj may be due to exhaust emissions from natural particulate matter, vehicles, domestic heating, industrial discharging. A major environmental problem in Sanandaj is dust storms created in the deserts of Syria, Iraq, and Saudi Arabia.²² According to the World Health Organization (WHO), the annual outdoor average of PM_{10} in Sanandaj was 254 $\mu\text{g}\cdot\text{m}^{-3}$ in 2011, which ranked it as the third most polluted city in the world.²³ The city has been undergoing rapid urbanization in the past decade with most of the industrial parks and automobile service businesses located around its urban area.

During April 2014, 50 samples of roadside dust were collected from different roads (including primary roads, high roads, and main

roads) within the city of Sanandaj. The samples were collected in order to investigate the spatial distribution and contamination levels of heavy metals in these areas. The sampling points are shown in figure 1. At each sampling point, 3 roadside dust samples were taken (with a minimum distance of 100 m), and then, mixed thoroughly to obtain a representative bulk sample. The central point position of the 3 subsamples was recorded by a Global Positioning System (GPS) instrument. The roadside dust samples were mainly collected by sweeping an area of about 1 m² of road surface of each sampling site. Sample dusts, which were collected and gathered into coded plastic bags using a clean dustpan and a brush, weighed 100–150 g. From areas at a distance of more than 100 m from the roads (Figure 1), 5 deep soil samples (> 50 cm depth) were collected to be used as background values.¹⁸ Finally, the roadside dust and deep soil samples were transferred to the laboratory for analytical characterization. The weather condition was stable during the sampling period and there had been no rainfall during the two weeks prior to sampling.

Analytical grade of nitric acid (90%) and hydrogen peroxide solution (30 wt.% in H₂O) were purchased from Aldrich and used without further purification. Deionized distilled water was used in the preparation of analysis solutions. The roadside dust samples were dried thoroughly and then sieved through a < 0.5 mm sieve. Sieved dust samples were digested with HNO₃ and H₂O₂ using the 3050B methods suggested by the United States Environmental Protection Agency (USEPA).²⁴ The digested samples were centrifuged, and then deionized water was added to the supernatant to make 25 ml of the analysis solutions. Finally, the concentrations of the heavy metals, including As, Cd, Pb, Ni, Cr, and Zn, in the digestion solution were analyzed using a graphite furnace atomic absorption spectrometer (GFAAS) (Phoenix-986, China).

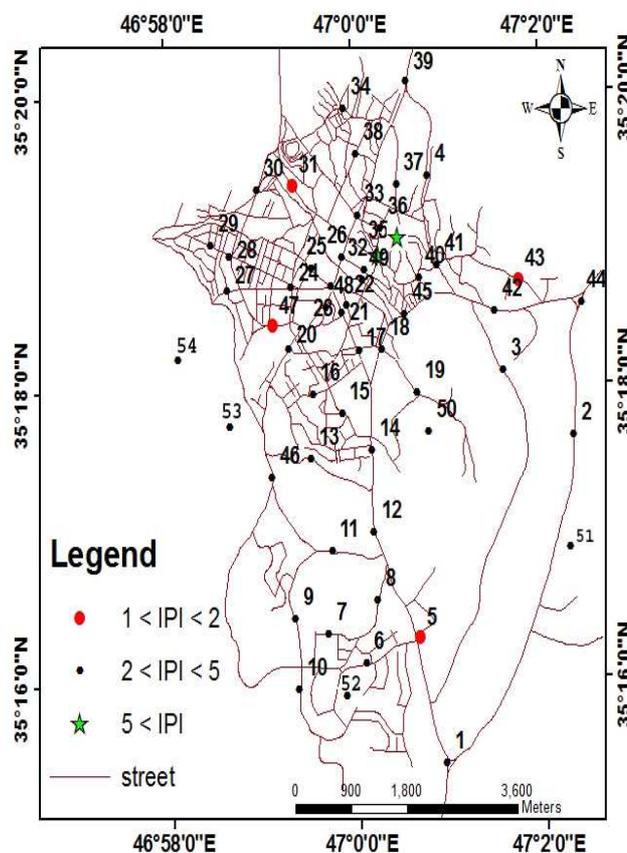


Figure 1. Sampling points (1-50 sampling points and 51-55 control points) and spatial distribution of the integrated pollution index (IPI) in the studied area

The contamination levels of heavy metals in urban roadside dust were assessed using the I_{geo} introduced by Muller.²⁵ The I_{geo} was computed using the following equation:²⁶

$$I_{geo} = \log_2 \left(1.5 \times \frac{C_n}{B_n} \right) \quad (1)$$

where C_n is the measured concentration of the elements in the environment, B_n is the geochemical background value in soil (average value of 5 control points in the present study). The constant 1.5 allows us to analyze natural fluctuations in the content of a given substance in the environment and to detect very small anthropogenic influences.¹⁶ The I_{geo} was calculated and categorized for each element according to Muller's classification (Table 1).

Table 1. Classification of the geoaccumulation index (I_{geo})

Class	I_{geo} value	Sample quality
0	$0 \leq I_{geo}$	Practically uncontaminated
1	$I_{geo} \leq 1 < 0$	Uncontaminated to moderately contaminated
2	$I_{geo} \leq 2 < 1$	Moderately contaminated
3	$I_{geo} \leq 3 < 2$	Moderately to heavily contaminated
4	$I_{geo} \leq 4 < 3$	Heavily contaminated
5	$I_{geo} \leq 5 < 4$	Heavily to extremely contaminated
6	$I_{geo} \geq 5$	Extremely contaminated

I_{geo} : Geoaccumulation index

The contamination levels of the heavy metals in dust samples of Sanandaj were further evaluated by calculating the pollution index (PI) and the IPI of the selected metals. The PI of each element was defined as the ratio of the metal concentration in the roadside dust samples (C_n) to the background concentration of the corresponding metal (B_n), calculated by the following formula:

$$PI = C_n / B_n \quad (2)$$

The IPI is defined as the mean value of the PI of an element^{16,27,28}. In this study, The PI and IPI classifications are presented in table 2.

Table 2. Classification of pollution index (PI) and integrated pollution index (IPI)

Class	PI value	IPI value	Pollution level
1	$1 \geq PI$	$1 < IPI \leq 2$	Low
2	$1 < PI \leq 3$	$2 < IPI \leq 5$	Moderate
3	$PI > 3$	$IPI > 5$	High

PI: Pollution index; IPI: Integrated pollution index

SPSS software for Windows (version 16, SPSS Inc., Chicago, IL, USA) was used to analyze the normality of data, using the Kolmogorov-Smirnov test, and to determine the Pearson correlation coefficients between the heavy metal concentrations in the study area. All GPS recorded sample points were geocoded with the universal transverse mercator (UTM) projection (Datum WGS-1984, zone 38). The sample points were

added to geographical information system (GIS) environment (Arc GIS version 9.3), using DNR Garmin (version 5.4, Minnesota Department of Natural Resources, USA), and then, placed on a layer of Sanandaj city road (Figure 1). The heavy metals of the samples were interpolated to Sanandaj area using the inverse distance weighted (IDW) algorithm in GIS environment (Figure 2).

Results and Discussion

Statistical analysis and normality test

The descriptive statistical parameters of dust heavy metals are presented in table 3. The results indicated that Cr, Ni, and As had passed the normality test of Kolmogorov-Smirnov ($P > 0.05$) with an exception of the other variables including Pb, Zn, and Cd. The minimum and maximum concentrations, and the mean values and standard deviations for each heavy metal are also presented in table 3. In addition, the background values of the metals in Sanandaj deep soil (> 50 cm) that is the average value of the 5 control points were also calculated. The results show that the mean concentrations of Cd (112.83 mg.k^{-1}), Cr (1.80 mg.k^{-1}), Ni (2.76 mg.k^{-1}), Pb (9.8 mg.k^{-1}), and particularly Zn (410.99 mg.k^{-1}) as well as As (11.31 mg.k^{-1}) were higher than their background values. These results suggest that the studied elements in Sanandaj roadside dust were influenced by anthropogenic pollution sources. The coefficient variation (C.V.) values of heavy metals in the study ranged from 0.26 to 0.70 indicating moderate variations. The highest C.V. of the 6 heavy metals belonged to Cd (0.70), suggesting that Cd has the greatest variation among the roadside dust samples. Thus, it would have the highest possibility of being influenced by point-anthropogenic sources such as industrial emission. This is in agreement with the previous study.¹⁶ On the other hand, the lowest C.V. belonged to Pb (0.26), suggesting that Pb has a weak variation and its content would have the highest possibility of being influenced by non-point anthropogenic sources such as traffic emissions.

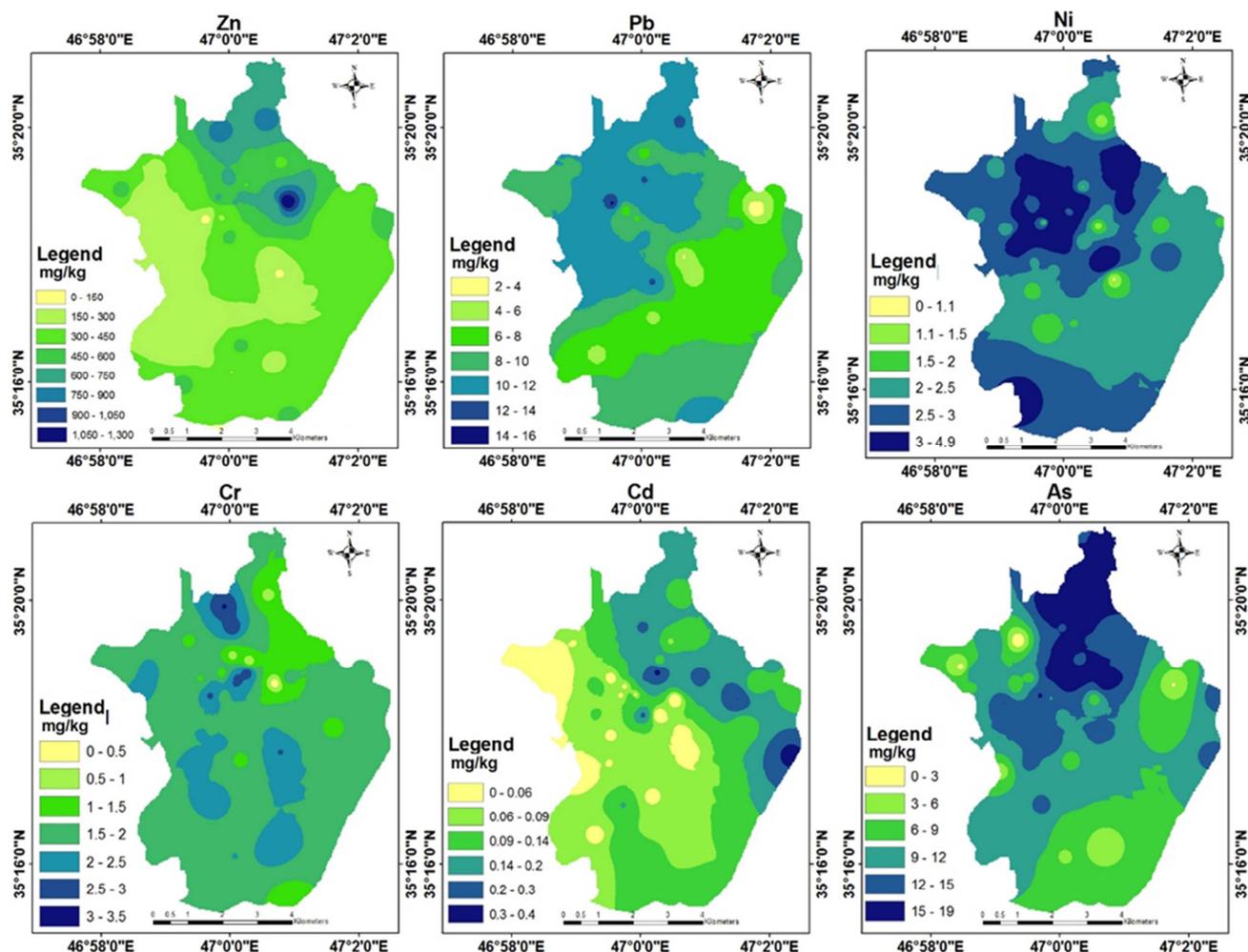


Figure 2. The spatial distribution maps of 6 heavy metal contents

Table 3. Descriptive statistics parameters and tests of normality for roadside dust heavy metals

Heavy metals	$B_n^{\dagger\dagger}$	Concentration (mg.kg^{-1})			SD*	C.V**	$(K-S)^\dagger$ ($P > 0.05$)	Distribution
		Min.	Mean	Max.				
Cd	105.00	23.88	112.83	333.78	79.18	0.70	0.003	Abnormal
Cr	1.23	0.23	1.80	3.03	0.59	0.33	0.200	Normal
Zn	100.54	130.58	410.99	1259.68	213.24	0.52	0.007	Abnormal
Ni	1.56	1.06	2.76	4.05	0.89	0.32	0.200	Normal
Pb	4.39	2.71	9.48	12.24	2.45	0.26	0.025	Abnormal
As	1.51	0.74	11.31	18.85	4.49	0.40	0.118	Normal

CV: Coefficient variation; SD; Standard deviation

* Standard deviation; ** Coefficient of variation; † Kolmogorov–Smirnov normality test; †† Background values.

Correlation between roadside dust heavy metals

Correlation measures the linear relationship between variables. The Pearson correlation coefficients and their significance levels between all of the variables are presented in table 4.

Strong positive correlations were observed between Cd, and As and Zn, indicating that they were closely related to each other. A significant correlation was also observed between Zn, Pb, and As.

Contamination assessment by I_{geo}

The maximum, minimum, and mean values of I_{geo} for each element are shown in table 5. Based on the I_{geo} data and Muller's classifications listed in table 1, the mean I_{geo} value for Cd was in the range of class 1, which indicates that roadside dust in Sanandaj was uncontaminated to moderately contaminate with Cd. The mean I_{geo} values for Cr, Ni, and Pb were in the range of class 2, which indicates that roadside dust was moderately contaminated with the mentioned heavy metals. The element of Zn, according to I_{geo} classification, was in the range of class 3, which shows that roadside dust was moderately to heavily contaminate with Zn. The highest I_{geo} mean value in Sanandaj roadside dust was observed for As that was in the range of class 4, which indicates heavy contamination. The maximum I_{geo} value for each element (Table 5) also showed that roadside dust was moderately contaminated with Ni and Cr, moderately to heavily contaminated with Pb and Cd, and heavily to extremely contaminated with As and Zn. These results may suggest that As, Zn, Pb, and Cd, in roadside dust, are most significantly impacted by anthropogenic pollution sources.

Contamination assessment by IPI

The PIs of the considered heavy metals in urban roadside dust were calculated according to the background value (B_n) of each metal (Table 5). The mean PI values for Cd (1.07), Cr (1.46), Ni (1.77), and Pb (2.16) were in the range of class 2, indicating a moderate pollution level. However, Ni from sampling site 21 and Cd from sampling sites 2 and 35 were highly polluted. On the other hand, the mean PI values for Zn (4.09) and As (7.47) were classified as high pollution levels (class 3), indicating the presence of problematic Zn and As pollution of roadside dust in Sanandaj. The IPIs of all the analyzed dust samples varied from 1.59 to 5.05. Figure 1 represents the spatial distributions of IPIs in Sanandaj.

The assessment of the data shows that 92% of all roadside dust samples had moderate pollution levels with an IPI of higher than 2, indicating that the roadside dust quality of Sanandaj is moderately polluted by anthropogenic emissions. In addition, heavy metal concentrations would have the highest possibility of being influenced by non-point anthropogenic sources such as traffic emissions (including vehicle exhaust particles, tire and brake lining wear particles, and weathered street asphalt particles).¹¹

Table 4. Pearson correlation coefficients of Sanandaj roadside dust heavy metals

Heavy metals	As	Cd	Cr	Ni	Pb	Zn
As	1					
Cd	0.363**	1				
Cr	0.197	0.053	1			
Ni	0.206	0.173	0.027	1		
Pb	0.186	0.187	-0.204	0.006	1	
Zn	0.358*	0.536**	-0.273	0.205	0.376**	1

* Correlation significance in the level of 0.05; ** Correlation significance in the level 0.01

Table 5. Geoaccumulation index (I_{geo}) and pollution index (PI) of urban roadside dust in Sanandaj

Heavy metals	Background values	I _{geo}			PI		Max.
		Min.	Mean	Max.	Min.	Mean	
Cd	105.00	-1.55	0.37	2.25	0.23	1.07	3.18
Cr	1.23	-1.86	1.02	1.88	0.18	1.46	2.46
Zn	100.54	0.96	2.45	4.23	1.30	4.09	12.53
Ni	1.56	0.04	1.33	1.96	0.68	1.77	3.11
Pb	4.39	-0.11	1.63	2.06	0.62	2.16	2.79
As	1.51	-0.44	3.30	4.22	0.49	7.47	12.46

I_{geo}: Geoaccumulation index; PI: Pollution index

Moreover, some of the dust samples with high pollution levels (IPI of higher than 4) such as sampling sites 26, 32, 35, and 38 were in crowded areas influenced by high traffic density. Sampling sites 34, 40, and 41, with high pollution levels, were affected by industrial emissions such as auto repairs and car washes. Finally, sampling sites with low pollution levels (IPI of lower than 2) were estimated for about 8% of all samples, located in new urban areas and the countryside.

Spatial distribution of heavy metals

The spatial distribution of heavy metal concentrations is an effective visual method to evaluate the possible sources of enrichment and to identify hotspots with high metal concentrations.^{16,29} In the present study, the spatial distribution patterns of the considered elements were analyzed by GIS methods. The maps of Zn, Cr, Pb, Cd, Ni, and As concentrations in the entire urban area of Sanandaj are presented in figure 2. It was observed that the spatial distributions of Pb and Zn have similar patterns, they had relatively less spatial variability, and the scope of pollution for Zn was relatively small. Their hotspots were mainly associated with main roads at the North and Northwest edge of the city, where high traffic density was identified. The features suggest the existence of these metals in roadside dust is probably due to vehicular emission. From the map of As and Ni spatial distribution, the highest concentration area was located in the Northern and central part of the city. For these elements, they had relatively high spatial variability. Furthermore, 2 different hotspots were identified, i.e., in the Eastern part of the city for As, and in the Southern part of the study area for Ni. The most contaminated roadside dust samples by As and Ni are in the proximity of the local industrial park and streets with high traffic flows. The distribution pattern of Cd concentration presented relatively high spatial variability. One of the hotspots was located in the city center close to the old urban area that

was mainly a commerce center. Other hotspots for Cd were located in the Eastern part of the city. In the studied region, anthropogenic emission sources of Cd in the roadside dust may be attributed to industrial activities and application of organic manures as well as phosphate fertilizer in farming practices. Several studies reported that activities, such as smelting, waste disposal, waste water irrigation, and phosphate fertilizer application resulted in the emission of significant quantities of Cd into the environment.^{16,30-33} The spatial distribution pattern of Cr concentration was different from those of the metals mentioned above, and Cr presented moderate variability. The hotspots were located in the center and Northwest of the study area close to the old residential area. Cr and As were used to preserve wooden instruments like door, window, sofa, and cabinets.

Conclusion

Heavy metals created by human activity are among the main factors affecting the human health in residential areas. In this paper, roadside dust was analyzed to determine the effect of traffic density and industrial centers on heavy metal concentrations in an urban area. using a GFAAS, 50 samples of roadside dust collected from Sanandaj were analyzed for Cd, Cr, Ni, Pb, Zn, and As. The concentrations of these elements were generally higher than their background values. I_{geo} showed that most of the heavy metals including As, Zn, Pb, and Cd have high or moderate level concentrations. The highest PI index was observed for Zn (4.09) and As (7.47) that indicate hazardous levels of Zn and As pollution in Sanandaj. Surface maps of heavy metals, drawn in GIS environment helped show similar patterns of heavy metal distributions which indicted the same sources. Surface maps also helped identify the different sources of heavy metals by presenting the individual distribution of metals like Cd which may be attributed to industrial activities,

application of organic manures, and phosphate fertilizers in farming practices. From the results of this study, we conclude that GIS is an excellent tool for studying the variables which can affect the concentration of heavy metals in urban areas.

Conflict of Interests

Authors have no conflict of interests.

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