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Spatial Distribution of Heavy Metal Contamination in Road Dust Samples from an Urban Environment in Samsun, Türkiye

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Abstract
Road dust is an environmental pollution indicator created by human activities for urban land use. This study aimed to determine the spatial distribution pattern and degree of trace metals in road dust samples collected from 5 different areas in Samsun city center. The trace metals of Mn, Co, Cd, Cr, Cu, Ni, Pb, and Zn are the most examined contaminants in road dust because their hot-spot areas were mainly associated with high traffic density. Factors governing potential contamination index range values of Co, Cr, and Ni were 0.34–0.62, 0.23–0.78, and 0.24–0.48 as the lowest contamination. However, potential contamination index values of Cu, Pb, and Zn in the main road site were 1.80, 2.32, and 2.84 suggesting that relatively high values were uncontaminated to moderately. Pollution assessment methods were applied to toxic metals and revealed that Samsun city had been affected as uncontaminated to moderately contaminated by anthropogenic emission of heavy metals.

Keywords Air pollution · Digital mapping · Ecological risk index · LULC, Urban modeling

Urban areas face a severe threat in terms of environmental health with the effect of many internal and external complex dynamics (Isinkaralar and Varol 2023). Heavy metal (HM) pollution, which arises from the accumulation of human activities, is a problem that reduces the quality of urban life and negatively affects public health (Kelly and Fussell 2019). Road dust causes to accumulate on soil, airborne particulates, soot, fumes, and construction building by meteorological activities because of contains high levels of air pollutants such as HMs (Ambade et al. 2022). Furthermore, fine particle dust on road surfaces contributes to various sizes of particulate matter through the air flow in cities by accelerating the speed of vehicles in traffic and atmospheric convection (Gupta and Elumalai 2019; Jonidi Jafari et al. 2021). In settlements of this scale, the daily amount of dust and air pollutants may be more significant than the annual amount in rural areas or smaller cities (Fang et al. 2021; Men et al. 2021; Yeom 2021). Therefore, HMs associated with road dust have become a severe issue in the urban environment in cities (Lin and Zhu 2018).

Toxic elements cause severe contamination in many large cities and can persistently accumulate through various pathways (Chenery et al. 2020; Isinkaralar 2022a, b). They may show undesirable levels in the ecosystem and the human. Thus, the source and amount of HMs reported that fuel combustion from traffic is the principal factor in many cities' leading HM emissions (Ghariani et al. 2010; Kováčik et al. 2016). It also contributes to the roadside greenbelts for energy generation and heating purposes in houses, urban sludge application, mining and smelting operations, agricultural soils, and sewage irrigation (Krupnova et al. 2020; Qin et al. 2021). Road dust is the source and sink of HMs allowed to move away into roads, agricultural soils, recreational areas, urban parks, and clean water beds with atmospheric conditions have a significant impact on dust concentrations; the highest concentrations are usually recorded at weak advection, lack of precipitation and temperature drop; in rural areas, the primary source of particulate matter (PM_{10}) is the soil (agricultural activities, erosion) and households (combustion of fuel in home furnaces) and transport (Jia et al. 2021; Mach et al. 2022).

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Also, dust particles can easily pass from the food chain to humans and threaten human health, such as distribution, dispersion, dust ingestion, inhalation, and absorption through the skin (Shabanda et al. 2019; Anwar et al. 2020).

For this reason, determining the contamination level and risks attracted much attention to precisely preserve human health while delivering the novelty insight into monitoring sources and emission amounts of HMs. The objective of this study was to evaluate the pollution assessment and the spatial distribution patterns using the Geographic Information System (GIS) by determining the trace metal concentrations in road dust collected from various locations of Samsun city in June 2022. Therefore, this study contains a critical index analysis of the environmental impact. Also, it has revealed the current status and possible future directions for research in urban air quality.

Materials and Methods

Samsun city (41°16′49.4″N 36°20′04.1″E) locates in the Black Sea Region in the North Center of Türkiye. The study area is situated at the country's northern border, and its population was more than 1.3 million in June 2022, with most of the population centered in urbanized areas. It is centered in urbanized areas heavily polluted by commercial areas and industries such as automobile, machine, tire, rubber, cement, chemical, and other manufacturers. In recent decades, the number of vehicles has increased sharply with the rapidly developing economy in Samsun, which was significantly influenced. Thus, hot-spot locations have accumulated anthropogenic trace metals, which five different areas are defined in Table 1.

Table 1 Sites number according to locations

Sites ID	Locations	Description
S1	Residential area	Moderate traffic volume, heating residents
S2	Industrial area	Industrial activities of various scales
S3	Main road	Heavy traffic volume
S4	City center	High traffic volume, commercial activity
S5	Forest area	Away from emissions in the city

A total of 125 road dust samples, each piece occurs five areas, were collected to analyze spatial distribution and contamination level in Fig. 1.

Each sample was taken more than portions of 300 g via a polyethylene brush, and a broom was used to collect the samples at the side of the road (Wang et al. 2009; Men et al. 2018). The samples were air-dried at 45°C for two weeks and s and sieved through a 1000 µm mesh sieve (AS200 Basic, Retsch, Germany) to separate large particles such as debris, hair, and leaves. The further procedure was inserted into polyethylene bags, which were stored at 4°C until analysis. After that, dry mass samples of 0.5 ± 0.01 g were mixed with an aqueous solution of 7.5 mL of HNO_3, 5 mL H_2O_2 and 5 mL HCl was mixed within more 20 min and hold 2 h at 95 ± 5°C for acid digestion. They were mixed and filtered via 0.45 µm filters and were digested in a microwave at 280 PSI and 180ºC for 20 min using US EPA Method 3052 (USEPA 1995). Then, the element concentrations were read at the appropriate wavelengths in the inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectro Blue, Germany). The study elements' concentrations were determined after multiplying the obtained values with the dilution factor, and all chemicals-reagents used were of analytical grade.

The enrichment factor (EF) and geo-accumulation index (*I*geo) are indicators that are used to evaluate deposition HMs on surface soil as the intensity of anthropogenic contaminant (Olawoyin et al. 2018). Two main parameters were used to assess the pollution level of urban dust pollution status derived from road dust by Jahandari (2020), which are *I*geo with Eq. 1 by Müller (1969) and enrichment ratio (ER) with Eq. 2 by Wei and Yang (2010).

$$I_{geo} = \log_2 \left(C_n / KB_n \right) \tag{1}$$

C_n represents dust samples' concentration, and B_n reflects upper continental crust concentration by Rudnick & Gao (2003). The *K* value is a constant coefficient, and its value is 1.5, which means balancing the effect of natural change. According to *I*geo values, explain pollution case as follows (i) *I*geo values < 0 for no pollution, (ii) between 0 and 1 for low, (iii) between 1 and 2 for moderate, (iv) between 2 and 3 for above medium, (v) between 3 and 4 for high; (vi) between 4 and 5 for above high, and (vii) > 5 for extreme. The EFs are used to determine pollution levels and assess the degree of human impact on the dust. It was studied based on a reference element measured as a non-pollution area. Also, it is used to identify anthropogenic contributions, which metals come from human activity or crustal elements by Yongming et al. (2006).

$$EF = \left(\frac{Cx_{sample}}{Cref_{Sample}} \right) / \left(\frac{Bx_{crust}}{Bref_{crust}} \right) \tag{2}$$

C_x is the element concentration that examines the environment, and C_{ref} is the element concentration of the reference environment (Lu et al. 2009). Fe was used as the reference element in B_x content, and B_{ref} was used for crust concentrations in sampling sites. The EF value could be determined that the element enrichment was of crustal

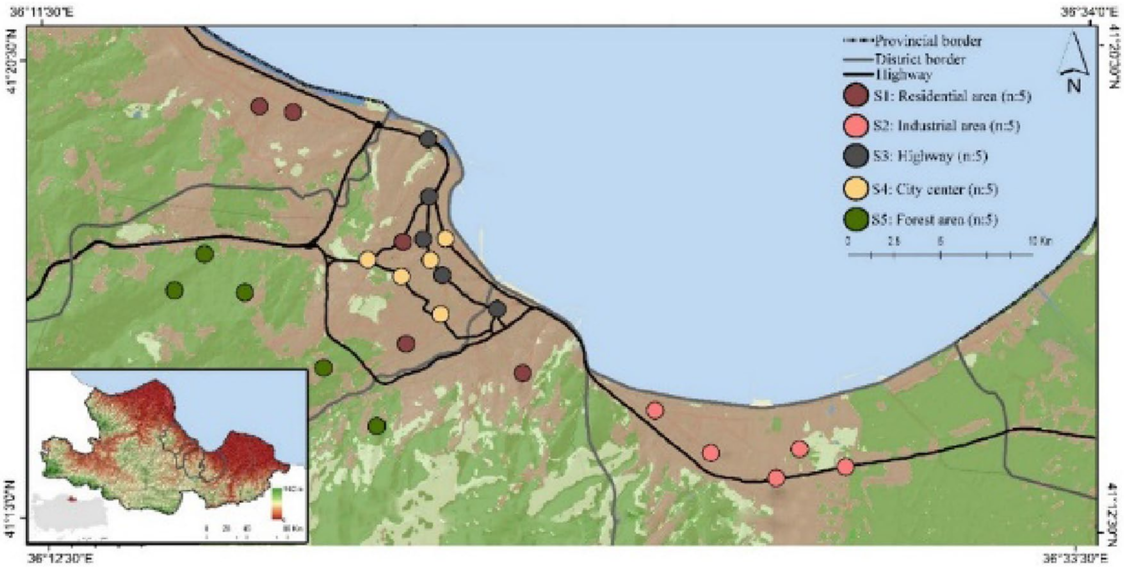

Fig. 1 Sampling sites in Samsun city

origin as follows (i) values < 2 for the deficiency to be minimal, (ii) between 2 and 5 for moderate, (iii) between 5 and 20 for significant, (iv) between 20 and 40 for highly (Lu et al. 2009). However, the EF value can differ depending on the composition, which does not necessarily remain static from one location to another due to variable fraction (Joshi et al. 2009).

To further assess the HMs in road dust, the potential contamination index (C_p) is used to define contamination status by Dauvalter and Rognerud (2001). The possible contamination index could be calculated following Eq. 3 (Tomlinson et al. 1980).

$$C_p = HM_{max}/HM_{Ba} \tag{3}$$

Where HM_{max} is the maximum HM concentration in sediment, and HM_{Ba} is the average same metal value at a sampling site. The crustal abundance data were used background by Krauskopf and Bird (1967).

Samsun city center was mapped to examine their spatial distribution to reveal their relationship with the land throughout the city. Concentrations measured by HM species were spatially analyzed using ArcGIS 10.4 software via the inverse distance weighting method (IDW) in the 3D analyst extension tool. IDW works on averaging the values of sample data points in the neighborhood of each rendering cell. It applies the interpolation process by accepting the weight as higher depending on the proximity. Thus, a relationship can be established with the current land use and land cover (LULC). Strict quality control/quality assurance (QC/QA) procedures were carried out using BCR-701 certified reference material to prevent and minimize possible errors during the experiment with analytical precision (Bisht et al. 2022). The QA/QC difference of the studied metals is between 0.7 and 5.3. Gloves and several collecting apparatuses, such as brushes and dustpans made of polyethylene, were used to avoid contamination. Also, all-glass materials were cleaned with pure water and nitric acid before experiments. The calibrations curve was drawn and measured before the analysis, which detection limits of Cd, Cr, Cu, Mn, Ni, Pb, and Zn were 0.03, 0.04, 0.02, 0.047, 0.04, 0.06, and 0.04 µg/kg as three duplicates. Each sample measured a relative standard deviation that was below 2%. The data were evaluated for *F* value, error rate, and thus the difference of the factors by SPSS software packaged (SPSS Inc., Version 22.0.0, Chicago, IL) for Windows at the 95% confidence level by applying variance analysis (ANOVA) to the data. Duncan's Multiple Range Test was used to identify which model was closer to the actual data with statistically significant differences at the 95% confidence level. The obtained results were interpreted after simplifying and tabulating.

Results and Discussion

The HM concentrations are presented that the highest value of Co was obtained in the forest site with 10.7 mg/kg. The lowest value was obtained in the industry with 5.9 mg/kg. It can be said that Co concentration is in a narrower range compared to other elements. It is noteworthy that the difference between the lowest and highest Mn values in different regions is higher than the mean values.

Table 2 Duncan test results for HMs content between road dust (mg/kg) according to locations

Location	Elements							
	Mn	Co	Cd	Cr	Cu	Ni	Pb	Zn
S1	523.8 ± 215 c	7.7 ± 1.8 b	3.8 ± 1.2 a	20.7 ± 11.9 a	4.7 ± 2.1 a	11.6 ± 9.7 a	16.2 ± 5.7 a	19.9 ± 6.1 a
S2	326.9 ± 136.2 ab	5.9 ± 1.3 a	2.5 ± 0.2 a	71.8 ± 72.8 b	3.1 ± 0.5 a	22.4 ± 18.3 b	18.1 ± 15.3 a	23.2 ± 11.9 a
S3	242.7 ± 81.3 a	8.7 ± 1.8 b	3.9 ± 0.6 b	21.3 ± 9.6 a	50.4 ± 44.2 b	12.6 ± 7.6 a	39.5 ± 13.2 b	190.4 ± 80.9 b
S4	411.6 ± 250.8 bc	9.0 ± 3.1 b	3.8 ± 1 b	27.8 ± 14.5 a	8.0 ± 2.2 a	13.3 ± 6.3 a	19.5 ± 4.6 a	39.2 ± 10.6 a
S5	388.2 ± 121.2 bc	10.7 ± 1.5 c	4.5 ± 0.5 c	19.6 ± 8.4 a	5.1 ± 1 a	11.4 ± 2.5 a	18.6 ± 2.9 a	30.4 ± 4.4 a
F value	5.134 ***	10.222***	11.967***	6.314***	15.642***	2.896*	14.744***	57.685***

*shows *SC* $p < 0.05$ and *** *SC* $p < 0.001$ level, lowercase letters state vertical direction for each variable

There is a slightly more than two-fold difference between the lowest mean value of 242.7 mg/kg and the highest mean value (523.8 mg/kg), while, for example, the lowest mean value of 214.8 mg/kg obtained in the center and the highest. More than four times the difference between the value (931.8 mg/kg). It is seen that the Cd concentration is still in a relatively narrow range in all locations, and the differences between the lowest and highest values are about two times. While the Cr concentration is up to 48.2 mg/kg in other places, it is seen that it reaches 211.4 mg/kg in industry. According to these results, it can be said that industrial facilities are an essential source of Cr pollution. While the highest average Cu concentration was 8.0 mg/kg, the average Cu concentration on the road was 50.4 mg/kg. Again, the highest Cu concentration obtained in other places was only 10.6 mg/kg, while the highest Cu concentration obtained on the road was 105.7 mg/kg. The lowest average Ni value was obtained in the forest (11.4 mg/kg), while the highest average value was obtained in the industry (22.4 mg/kg). While the Ni concentration, which varies between 11.4 mg/kg and 13.3 mg/kg on average in other places, is 22.4 mg/kg in industry and up to 30.2 mg/kg in other areas, it is 56.9 mg/kg in industry. The level was determined. According to these results, it can be said that the industry is an essential source of Ni pollution. It has been determined that the Pb concentration, up to 28.3 mg/kg in the neighborhood, center, and forest, reaches 47.8 mg/kg in industry and 54.2 mg/kg on the road. When the Zn values are examined, it is seen that the Zn concentration, which reaches up to 52.6 mg/kg in other places, varies between 80.3 mg/kg and 269.2 mg/kg on the road. According to these results, it can be said that traffic is an essential source of Pb and Zn pollution. The lowest mean value of Pb concentration in the road dust subject to the study was obtained in the neighborhood at 16.2 mg/kg. In contrast, the highest mean value was obtained in the area and received route at 39.5 mg/kg. As a result of the Duncan test, the values obtained in the neighborhood, industry, center, and forest were in the first group, while the values obtained on the road were in the second group. The change in Zn concentration was collected in 2 groups. The value obtained on the road (190.4 mg/kg) was approximately 9.5 times the value obtained in the neighborhood (19.9 mg/kg). Table 2 shows the analysis of variance and Duncan test results regarding the change of all metals on a regional basis when the table shows the lowest, highest, and standard deviation values. The difference in HM concentration that is examined, the evolution of all HM concentrations on a regional basis, is statistically significant at the 99.9% confidence level. As a result of the Duncan test, the data were collected in 3 groups and determined a significant correlation (*SC*). The values obtained in industry and road were in the first group, the values obtained in the neighborhood were in the second group, and the values obtained in the center and forest were in the last group.

Table 3 demonstrates the correlation matrix results demonstrating that Pb and Zn are accumulated brought to traffic-related pollution. The correlation analysis also shows *SC* as follows: (i) between Co, Cd, and Fe, (ii) between Cd and Co, (iii) between Ni and Cr, and (iv) between Pb and Zn in the road dust ($p < 0.01$). So, from the above discussion, most trace elements of road dust, even if it seems correlated. However, it is quite high in cases where it is not related. From this, it could be said that their source was almost the same, which may be derived from the ship-breaking activity (Siddiquee et al. 2012).

The EF was calculated for each HM in road dust relative to the background value in the upper crust. Fe was the most abundant metal in all the samples. The EF of Cu, Co, Cr, Ni, Zn, and Cd ranges are 0.78–165.21, 3.29–37.69, 3.38-100.56, 4.19–52.98, 6.92–175,84, and 97.25–296.6. Their average is 22.29, 21.25, 15.34, 13.28, 39.59, and 179.92, respectively. The average EF values above ten showed that Cu, Co, Cr, Ni, Zn, and Cd in several zones in Samsun mainly originate from anthropogenic sources. The increasing trend of average EF values is as follows: Ni < Cr < Co < Cu < Zn < Pb < Cd.

Table 3 Correlation matrix results of trace elements of road dust samples

	Al	Mn	Fe	Co	Cd	Cr	Cu	Ni	Pb	Zn
Al	1									
Mn	0.478**	1								
Fe	0.653**	0.613**	1							
Co	0.508**	0.601**	0.892**	1						
Cd	0.825**	0.525**	0.892**	0.828**	1					
Cr	−0.434**	0.13	−0.267*	−0.112	−0.396**	1				
Cu	−0.207	−0.297**	−0.096	0.148	0.144	−0.117	1			
Ni	−0.437**	0.137	−0.171	0.029	−0.337**	0.883**	−0.119	1		
Pb	−0.014	0.037	0.093	0.386**	0.314**	0.304**	0.772**	0.272*	1	
Zn	−0.199	−0.275*	−0.033	0.221	0.188	−0.055	0.887**	0.019	0.834**	1

* *SC* $p<0.05$ level (two tailed); ** *SC* $p<0.01$ level (two tailed)

Table 4 The results of *I*geo classes of HMs

Elements	*I*geo Location					Potential contamination indexes				
	S1	S2	S3	S4	S5	S1	S2	S3	S4	S5
Co	0	0	0	0	0	0.45	0.34	0.50	0.52	0.62
Cd	2	1	2	2	2	4.22	2.78	4.33	4.22	5.01
Cr	0	0	0	0	0	0.23	0.78	0.23	0.30	0.21
Cu	0	0	0	0	0	0.17	0.11	1.80	0.29	0.18
Ni	0	0	0	0	0	0.25	0.48	0.27	0.28	0.24
Pb	0	0	1	1	0	0.95	1.06	2.32	1.15	1.09
Zn	0	0	1	0	0	0.30	0.35	2.84	0.59	0.45

The *I*geo values by Abrahim and Parker (2008) and the potential contamination index are given to support the classification for each location in Table 4.

The *I*geo values for Cd in all sites fell in class 2 except S2 because of is moderately contaminated. The *I*geo values of Co, Cu, Cr, and Ni metals fell in class 0 as uncontaminated. However, Pb, and Zn metals present moderately to strongly contaminated due to class 1 in S3. Also, S4 indicated that it comes relatively strongly contaminated with Pb in class 1. This analysis exhibited that the road dust of several locations was low contamination to some contamination with the Cu, Co, Cr, Ni, Zn, and Cd according to *I*geo values. Potential contamination indices showed that all samples of Cd at all locations (2.78–5.01) indicated very moderate pollution due to the most extensive contamination. The potential contamination index range values of Co, Cr, and Ni were 0.34–0.62, 0.23–0.78, and 0.24–0.48 as the lowest contamination. However, the potential of S3 contamination index values of Cu, Pb, and Zn were 1.80, 2.32, and 2.84, with relatively high values and medium pollution. According to these results, it can be said that vehicles are one of the most critical sources of Cu pollution.

Figure 2 shows that the spatial distribution of metal amounts is beneficial to determine the probable sources of enrichment and define hot-spot areas with quantitative properties. Distribution patterns of the analyzed elements in the whole urban area of Samsun.

The relationship of HMs with the existing LULC in the Samsun city center was analyzed based on the spatial distribution maps. The primary source of Cu, Pb, and Zn pollution is emissions from fossil fuels for urban transportation. While the spatial distribution of these HMs exhibited similar behavior, the highest score was achieved in Zn metal and the lowest score in Pb metal. Co and Cd's are low in the industrial area of the city. It has been determined that it is high in the forest area outside the city and can be found from natural origin. Cr and Ni are not located in the city's commercial center and main axis. While it is located in the eastern part of the city, in the area where the industrial facilities are located, the distribution of Cr has a more intense score depending on the production type of the current industrial activity. Mn values are higher in residential areas close to the city walls.

The concentrations of heavy metals in the urban road dust of Samsun city and assessed the contamination levels using GIS for the spatial distribution. Several researchers have presented that the high accumulation level of Cu and Zn can cause by brake abrasions (Gietl et al. 2010; Duong and Lee 2011; Khademi et al. 2020) computed metals including Cd, Cr, and Cu (eight particle size fractions) in street dust in Murcia. They reported metal concentration and their

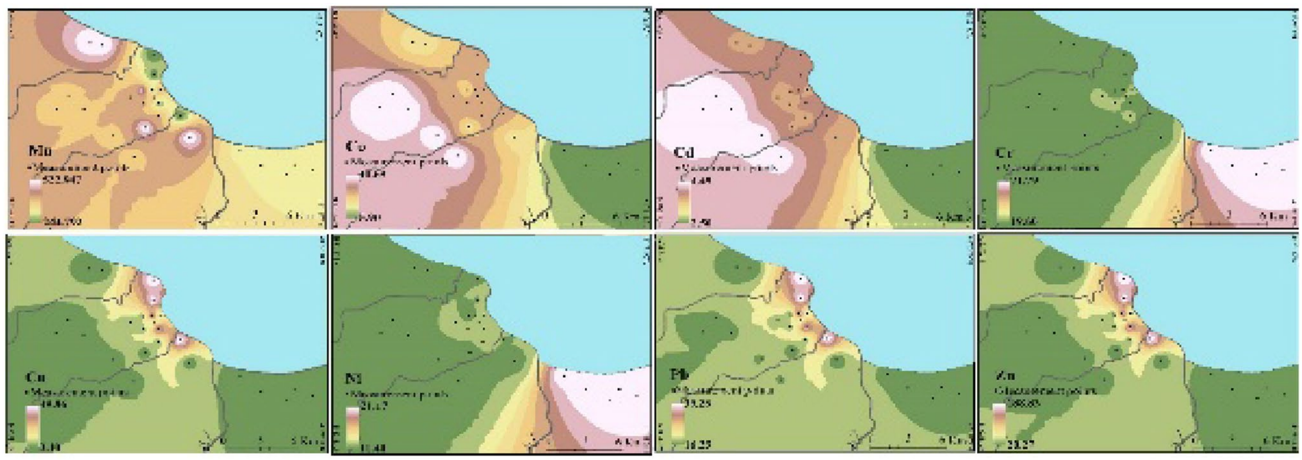

Fig. 2 Spatial distribution of the HMs concentrations in the studied area

distribution depends on the population density of some groups. Recent studies have reported that were similar to the results of our study about HMs in the street dust caused by traffic and industrial activities (Bartholomew et al. 2020; Aguilera et al. 2021; Esfandiari and Hakimzadeh 2022) investigated HMs in tree leaves in Yazd–Ardakan Plain, Iran. They showed that rapid industrialization and transportation could cause emitted HMs (mg/kg) from low to high (Cd < Co < Ni < Pb < Cu < Zn < Cr < Mn). Their study used pollution assessment methods to classify toxic metals from motor vehicles and their pieces. Similarly, they researched HM pollution in the street dust in Khorasan-Razavi, Iran, by Soleymani et al. (2022). They reported an average concentration of several metals, although they represented a carcinogenic risk to children and adults for Cr (96.18 mg/kg), Co (14.86 mg/kg), and Ni (73.25 mg/kg). Mehta et al. (2022) performed an HM deposition solid waste landfill site in Ahmedabad, India. They carried out 11 metals in particular matters. The mean concentration was obtained as follows Fe > Al > Cu > Cr > Co > Hg > Cd > Zn > Pb > Ni > As. This study showed possible sources of toxic metals in the urban environment as mining industries, vehicular emissions, fossil fuel combustion, and road dust. According to these studies, the HM concentration in road dust is considerably higher than in reference regions (Alsbou and Al-Khashman 2018; Zgłobicki et al. 2019; Dytłow and Górka-Kostrubiec 2021). In addition, studies showing the effects of toxic metals in road dust on public health are available in the literature (Long et al. 2021; Kafle et al. 2022; Malunguja et al. 2022). Even though our study was carried out in a specific region with intense traffic activities, the findings could also procure convenient policy advice for areas with similar contaminations worldwide. The complicated source-exposure risk analysis methods also could be updated and used in HM and organic pollutants co-contaminated studies.

Currently, researchers investigated the harmful effects of urban road dust in several areas without broadly considering the source (Khalid et al. 2018; Liu et al. 2018; Tan et al. 2018). Tran et al. (2022) analyzed seven HMs and identified the probable sources in Ngan Son, Vietnam. They determined health risk assessment and pollution indices by EF, the pollution index (PI) and potential ecological risk (RI). The EF values in the samples close to the ore deposits were relatively high (EF: 88.3 for Pb, EF: Cd for 34.9, EF: 27.2 for As, EF: 14.9 for Zn). The equation for calculating EF has already been well-mentioned in many previous studies (Shafie et al. 2013; Barbieri 2016; Kowalska et al. 2018). Wang et al. (2021) observed six toxic HMs (Cr, Cu, Mn, Ni, Pb, and Zn) contaminated in Nantong, China. They ranged from 19.4 mg/kg to 1089.7 mg/kg in the ground dust samples. In this study, the average concentrations of Co, Cr, Cd Ni, and Pb were higher, although Al, Cu, and Zn were lower than other average concentrations (Kabata-Pendias 2011; Soltani et al. 2015). Regarding the spatial distribution of the HM, it is a versatile tool that has been successfully applied in contaminated areas. In sum, the HM concentrations can be used to present within urban road dust pollution for quantitatively describing the geospatial characteristics of possible source types.

The widespread existence of HMs in road dust reveals they originate from various anthropogenic sources such as heating, transportation, and industrial activities. *I*geo showed that the contamination levels ranged from no pollution to moderate contamination with Cd and Pb. In addition, the data obtained were compared with the data in the literature, and it was found that it was on average in general and below for some metals. The Cu (from 6.2 to 94.6 mg/g), Pb (from 26.3 to 52.7 mg/g) and Zn (from 109.5 to 271.3 mg/g) showed positive correlations due to wear and corrosion of vehicles and fuel combustion. In parallel with this, based on the degrees of the population, industrialization and traffic, GIS-based map formation is a valuable, functional, and easy-to-handle tool for contamination levels in the urban area. Based on this, sustainable urbanism goals can be defined, and it can guide the site selection criteria and construction conditions of urban land use. Nevertheless, expanding public transportation will prevent environmental pollution by reducing the rate of individual vehicle use. It is seen that the current situation can be improved by disseminating alternative energy sources instead of coal-based energy production used in heating houses and activities in industries. In addition, it is vital to take precautions because the particles formed due to increasing urban transformation activities contain toxic metals. In addition, this study reveals that to follow the current situation. The research should be extended to the prospective, urban scale solid monitoring methods and used effectively in the spatial decision-making and planning processes. This study will lead and appraise other urban road dust studies and heighten awareness of the associated health risks of road dust.

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Declarations

Conflict of interest The authors declare that they have no competinginterests.

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