Assessment of Heavy Metal Levels in Street Dust Samples from Denizli, Turkey, and Analysis by Flame Atomic Absorption Spectrometry

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ABSTRACT

In this study, toxic heavy metal contamination in dust samples obtained from different streets in Denizli, Turkey, was monitored. The areas selected include heavy, moderate, and normal traffic flow, building construction sites and other industrial activities near roads, car parks, school gardens, health centers, and hospitals. The metals were determined by flame atomic absorption spectrometry. The concentration ranges were Cu at 20.4–147.4 µg g^{-1}, Cr at 9.9–75.0 µg g^{-1}, Ni at 22.8–86.2 µg g^{-1}, Pb at 14.4–145.3 µg g^{-1}, and Mn at 52.3–158.3 µg g^{-1}. The Cd content for all dust samples was below 0.1 µg g^{-1}. According to the geoaccumulation index (I_{geo}) classification, Cr and Mn were present at the lower level ($0<I_{geo}\leq1$), and Pb, Cu, and Ni at moderate level ($1<I_{geo}\leq2$). This is the fist time that the concentrations and the effect of heavy metals on the environment, in particular, in street dust of Denizli, Turkey, have been investigated.

INTRODUCTıON

Soil, sediments, and dust originate primarily from the earth's crust. However, street dust is also a consequence of the interaction of solid, liquid, gaseous materials and heavy metals produced from sources such as traffic, industry, building construction, heating, solid waste incineration, and other man-made activities, which cause contamination and affect human health. Roadways and automobiles are considered to be one of the largest sources of heavy metals in solid matter (1-5). Heavy metal pollution in environmental samples has been increasing for a long time (6-9) and is due to human activities as well as atmospheric events (1, 10-12).

Street dust samples are an important and easily obtainable source for monitoring environmental pollution (13-16). Traffic in particular is a source of emission of heavy metals such as Pb, Ni, Cd, Zn, Mn, Cu, Co, and Cr (15, 17-20). These types of metals are non-degradable and hazardous to human health. A number of studies have been carried out for the determination of trace metals in urban street dust (21-27) in order to obtain the level of heavy metal pollution in certain areas.

In general, when heavy metals are inhaled from street dust and also attach to the skin, they can affect the nervous, blood-forming, cardiovascular, renal, and reproductive systems. Street dust is also mobilized from wind and moving cars. In addition, dust is carried by storm water runoff and contaminates reservoirs, rivers, and the sea. Some trace metals such as Cu and Zn are harmless at low levels, but Pb, As, Hg, and Cd are toxic even at extremely low concentrations (28-34). Thus, the determination of metals in environmental samples such as dust, plants, soil, and surface waters is highly important to assess environmental pollution and to avoid jeopardizing human health (35).

Denizli is in the Aegean part of Turkey and lies at 354 m above sea level. The highest mountain in the province and in Western Anatolia is Mount Honaz (2571 m). Though located in the Aegean region, Denizli is not totally affected by the Aegean climate. It is partially dry, but the average humidity is 70% in the winter months, while in the summer it is 50%. It is an agricultural city with some textile industry. According to the census taken in the year 2000, the city has a population of 850,000.

To our knowledge, a study for heavy metal levels in street dust samples from Denizli, Turkey, has not before been reported. We investigated the level of metals in street dust samples from different areas of the city using flame atomic absorption spectrometry (FAAS). The correlation between metal concentration in the samples and the geoaccumulation indices was also investigated. Information about the traffic patterns was obtained from the Traffic Department in Denizli.

EXPERIMENTAL

Instrumentation

For this study, a PerkinElmer® AAnalyst™ 700 flame atomic absorption spectrometer (PerkinElmer, Inc., Shelton, CT, USA) was used, equipped with a stainless steel nebulizer, deuterium background correction, and hollow cathode lamps (HCL). All measurements were carried out in an air/acetylene flame. The instrumental operating parameters and linear ranges are listed in Table I.

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Reagents and Standard Solutions

All reagents were of analytical reagent grade unless otherwise stated. Milli-Q® double deionized water (Millipore Corporation, USA, 18.2 MΩ•cm^{-1} resistivity) was used for all dilutions. HNO_3 and HCl were of Suprapur® quality (E. Merck, Darmstadt, Germany). All plastic and glassware was cleaned by soaking in dilute HNO_3 (1+9) and rinsing with distilled water prior to use. The stock solutions (1000 mg L^{-1}) of the analyte elements were prepared from appropriate amounts of their nitrate salts in 1% HNO_3 and then further diluted daily prior to use.

Sampling

A total of 59 street dust samples were obtained from areas around hospitals and health centers, school gardens, as well as from areas with heavy, moderate, and normal traffic flow in the Denizli city center. Sample collection was done by sweeping an area of 2 m^2 and transferring the sweepings into a polyethylene container. The samples were then passed through a 30-mesh sieve, dried at 110 °C in NUVE dry-heat sterilizers (NUVE FN 055, Ankara, Turkey) for 20 hours. The control samples were collected from two hills on the outskirts of Denizli.

Sample Preparation

Each of the 59 samples was digested in triplicate (N=3). A 0.5-g amount of dust sample was weighed and transferred to a Pyrex® tube, and 10 mL of *aqua regia* was added. The sample was transferred to a heating block for 6 hours to complete the digestion. The residue was filtered through a 0.45–µm pore size micro filtration system (Millipore Corporation, USA). A 1-g amount of the filtrate combined with the leachate was diluted to 25 mL with deionized water, and the metal levels were determined by flame atomic absorption spectrometry (FAAS). Blank digestions were also carried out.

Accuracy and Precision

In order to validate the method for accuracy and precision, a certified reference material NIST CRM 8704 Buffalo River Sediment (National Institute of Standards and Technology, Gaithersburg, MD, USA) was used. The certified concentrations of the studied heavy metals in CRM 8704 Buffalo River Sediment were 2.94 mg kg^{-1}, 121.9 mg kg^{-1}, 544.0 mg kg^{-1}, 42.9 mg kg^{-1} and 150.0 mg kg^{-1} for Cd, Cr, Mn, Ni and Pb, respectively. The digestion procedure given above was also applied to the CRM 8704 Buffalo River Sediment to determine the recoveries of the analytes and the results are listed in Table II. The samples were analyzed both with and without spiked standards containing a mixture of different amounts of the examined metals. The results in Table II indicate that in the digestion procedure the recovery of the metal ions was generally 95%. A preliminary test involving six replicate digestions of one dust sample for Cr, Pb, Cu, Ni, Mn, and Cd produced relative standard deviations of about 1.1–6.5%.

RESULTS AND DISCUSSION

Analyte elements were chosen as representative metals whose levels in the environment represent a reliable index of hazardous environmental pollution. The minimum and maximum concentrations of the metals found in the street dust samples are listed in Table III. The concentration range of the different metals was as follows: Cu at 20.4–147.4 µg g^{-1}, Cr at 9.9–75.0 µg g^{-1}, Ni at 22.8–86.2 µg g^{-1}, Pb at 14.4–145.3 µg g^{-1}, and Mn at 52.3–158.3 µg g^{-1}. The Cd content for all dust samples was found to be below 0.1 µg g^{-1}. High traffic areas had the highest heavy metal levels (Figure 1), while the lowest values of the analytes were found in school gardens, except for lead and copper. Concentrations of Cu and

TABLE I
Instrumental and Operating Conditions Using the AAnalyst 700 FAAS and Linear Ranges for Cu, Cd, Ni, Pb, Cr, and Mn

-	Parameters			
Elements	Wavelength (nm)	Slit Width (nm)	Lamp Current (mA)	Linear Range (µg mL^{-1})
Cu	324.8	0.7	30	0.5 - 4.0
Cd	228.8	0.7	4	0.1 – 2.0
Ni	232.0	0.2	30	0.5 – 4.0
Pb	283.3	0.7	10	2.0 – 16.0
Cr	357.9	0.7	30	1.0 – 6.0
Mn	279.5	0.2	25	0.5 – 4.0

TABLE II
Analytical Performance of Sample Digestion Procedure of Samples (N=6)

	Sediment (CRM 8704)		Street Dust From Heavy Traffic	
Elements	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Cr	95	2.5	98	2.5
Pb	98	2.9	102	1.7
Cu	96	6.0	97	5.7
Ni	101	6.5	101	1.1
Mn	99	1.2	101	1.5
Cd	104	1.7	103	3.6

RSD (%): relative standard deviation.

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Pb exhibited a similar pattern. An increased concentration for Cu and Pb was observed at locations with high traffic and, to some extent, in the industrial areas. The concentrations of the analytes in all analyzed samples were higher than those in the control samples. The concentrations of the heavy metals in the control samples were as follows: Cu at 12.4 ± 0.7 µg g^{-1}, Cr at 3.1 ± 0.2 µg g^{-1}, Ni at 10.7 ± 0.7 µg g^{-1}, Pb at 8.7 ± 0.5 µg g^{-1}, and Mn at 21.4 ± 1.7 µg g^{-1}.

The levels of the different analytes in the street dust samples reported for various cities around the world are listed in Table IV. It was found that the chromium levels around Denizli were generally lower than in cities such as Bahrain, Xi'an, Kayseri (1, 3, 36, 37). The Pb concentrations varied greatly from city to city and were from 1.03 to 697 µg g^{-1}. The concentration of Cu varied from 38 to 467 µg g^{-1}, Ni from 10 to 128 µg g^{-1}. Interestingly, the Ni concentrations found in this work were lower than the values found by Tuzen in Tokat, Turkey (7). Table IV shows that the highest concentration of Ni was found in Tokat city. It was a positive sign that the levels of Mn and Cd in the investigated areas of Denizli were generally lower than those found in other cities around the world.

The mean levels of the investigated analyte ions are depicted in Figure 1. The maximum allowable concentrations (MAC) as per the Official Gazette of the Republic of Turkey in soil samples are as follows: 50 µg g^{-1} for Pb, 1 µg g^{-1} for Cd, 100 µg g^{-1} for Cr, 50 µg g^{-1} for Cu, and 30 µg g^{-1} for Ni (38). Thus, the findings of this study show that the Pb and Ni levels exceeded the MAC levels in heavy, moderate, and low traffic areas and around the hospitals, while Cu exceeded in heavy and moderate traffic areas.

TABLE III
Descriptive Statistics for Concentrations of Trace Metals in Dust Samples From Denizli, Turkey (µg g^{-1})

Elements	Minimum Value	Maximum Value	Arithmetic Mean	Standard Deviation	Soil Background Conc.
Cr	9.9	75.0	49.7	24.5	50
Pb	14.4	145.3	69.2	47.1	26
Cu	20.4	147.4	63.0	47.2	26
Ni	22.8	86.2	44.4	25.0	18.5
Mn	52.3	158.3	131.0	40.7	490
Cd	<0.1	<0.1	–	–	0.41–0.57

TABLE IV
Mean Concentration of Heavy Metals (µg g^{-1}) in Street Dust in Cities Worldwide

City	Cr	Pb	Cu	Ni	Mn	Cd	Ref.
Bahrain	144	697	-	-	-	72	(1)
Amman, Jordan	-	236	177	88	-	1.7	(6)
Tokat, Turkey	41	266	38	128	415	5.4	(7)
Luanda, Angola	26	315	42	10	258	1.1	(8)
Istanbul, Turkey	-	105–556	49–234	33	-	2.3	(18)
Sivas, Turkey	-	197	84	68	-	2.6	(19)
Birmingham, UK	-	48	467	-	-	1.6	(34)
Kayseri, Turkey	72.8	166	66.7	57	274	10.1	(36)
Xi'an, P.R. China	167	231	94.9	-	687	-	(37)
Islamabad, Pakistan	-	104	52	23	-	5.0	(39)
London, UK	-	1.03	155	-	-	3.5	(40)
Manchester, UK	-	265	113	-	-	-	(41)
Denizli, Turkey	75.0	145	147	86.2	158	<0.1	This work

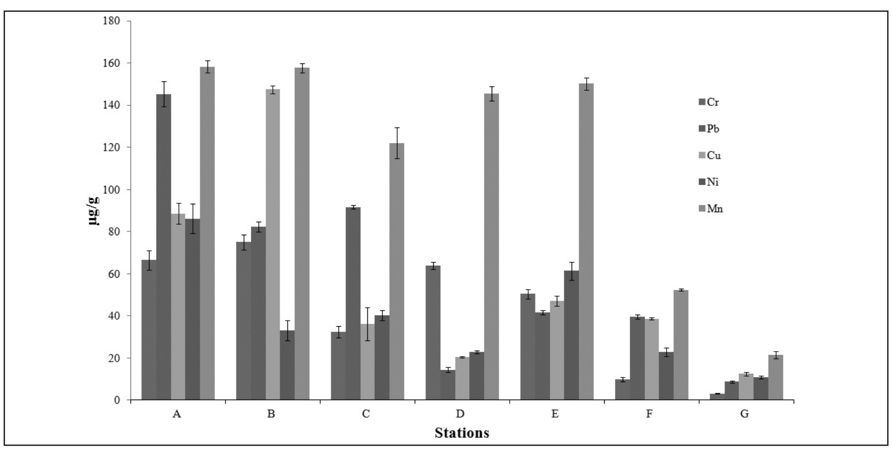

Fig.1. The mean level of trace heavy metals in street dust samples from Denizli city center: A: Heavy traffic (N:10), B: Moderate traffic (N:10), C: Low traffic (N:9), D: Car parks (N:10), E: Health and hospital, centers (N:10), F: School gardens (N:10), G: Control sample (N:3).

Figure 1 also shows that samples A, B, and C are Pb-contaminated, A and B are Cu-contaminated, and A and E are Ni-contaminated. All were collected at high-level polluted areas, thus all exceeded the MAC. The mean level of the investigated ions in the control sample collected from one park, which has no traffic, is depicted in Figure 1. The concentrations of the analytes in all analyzed samples werefound to be higher than those in the control sample.

Relation Between Metal Concentrations

In order to establish the inter-element relationship in road dust samples, the Pearson correlation coefficients were calculated. The correlations of the metals in the street dust samples of Denizli are given in Table V. All metals have a positive correlation. The maximum correlation value was 0.928, which is between Mn and Cr. The lowest value of the correlation coefficient was between Ni and Cu at 0.238. A moderate correlation coefficient was found between Cu and Pb (0.533) and between Cu and Cr (0.585). This may imply that Cu and Pb have somewhat similar sources, i.e., due to vehicular and industrial activities. The origin of Cu and Cr is also related to heavy traffic, which must come from exhaust fumes, engines, wear and tear of tires, leakage of oil from vehicles, and corrosion of batteries and metallic parts. The Ni-Cu (0.238) and Pb-Cr (0.279) pairs were weakly correlated at the 95% confidence level.

Assessment of Metal Pollution in Street Dust

The results of this study were subjected to analysis using the Geoaccumulation Index (I_{geo}), a formula introduced by G. Muller (42). The geoaccumulation index helps to assess the metal contamination levels in urban soils, urban road dust, street dust, and agricultural soil by comparing current and pre-industrial concentrations (43). The geoaccumulation index is calculated as follows:

$$I_{geo} = \log_2 (C_n/1.5B_n) \qquad \text{Eq. 1}$$

where C_n is the measured concentration of the element in street dust, B_n is the geochemical background value (Table III). The I_{geo} values for the analytes in street dust samples from Denizli are shown in Figure 2. The I_{geo} represents the following: free of contamination ($I_{geo} \leq 0$); low contamination ($0 < I_{geo} \leq 1$); moderately contaminated ($1 < I_{geo} \leq 2$); moderate to high contaminated ($2 < I_{geo} \leq 3$); high level contamination ($3 < I_{geo} \leq 4$); high to extremely high level contamination ($4 < I_{geo} \leq 5$), and extremely high level contamination ($I_{geo} \leq 5$) (43). Cr and Mn were found at lower levels, but moderate Pb, Cu, and Ni contamination was found in all samples. Cd was not found at contaminant levels. The plots in Figure 2 represent the contamination levels for all elements studied.

CONCLUSION

The present work studied the heavy metals concentrations in street dust of Denizli, Turkey. The highest metal values were found in heavy traffic sites, while the lowest concentrations of the metals were found in school gardens, hospitals, and health centers. The concentration ranges were Cu at 20.4–147.4 µg g^{-1}, Cr at 9.9–75.0 µg g^{-1}, Ni at 22.8–86.2 µg g^{-1}, Pb at 14.4–145.3 µg g^{-1}, and Mn at 52.3–158.3 µg g^{-1}. The Cd content for all dust samples was below 0.1 µg g^{-1}. The mean concentrations of the studied metals follow the order of: $C_{Mn} > C_{Cu} > C_{Pb} > C_{Ni} > C_{Cr} > C_{Cd}$. The concentration of Mn in the dust of Denizli is comparatively high (average value is 131.0 µg g^{-1}), since the main origin of Mn is from the geological material from middle Anatolia in addition to traffic. The trend of an increase in industrialization and traffic in Denizli center indicates the need for pollution control of the local environment. Furthermore, this study could help other researchers for comprehensive

TABLE V
Pearson's Correlation Matrix Between the Concentration of Trace Metals in Dust Samples (r=95%)

Elements	Cr	Pb	Cu	Ni	Mn
Cr	1				
Pb	0.279	1			
Cu	0.585	0.533	1		
Ni	0.345	0.731	0.238	1	
Mn	0.928	0.337	0.434	0.509	1

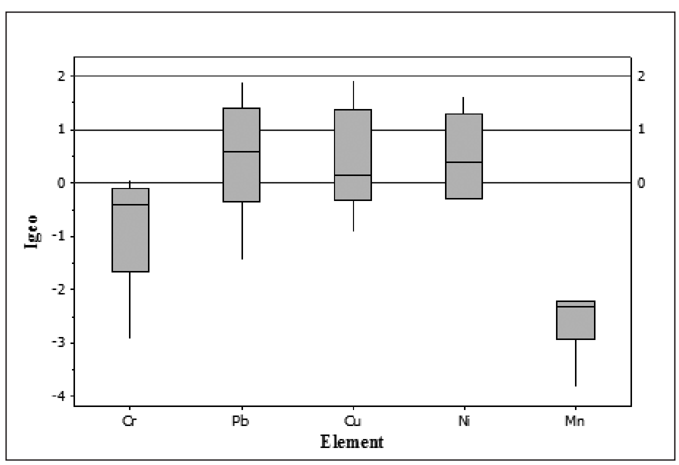

Fig.2. Box plot for the metal values of I_{Geo} in Denizli, Turkey.

assessment of environmental quality, better city planning, and sustainable management of urban resources in all big cities in all countries.

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