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Article

Multivariate Analysis of Metal Contamination in Street Dusts of Istanbul D-100 Highway

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Metais são encontrados na poeira de rua, principalmente, em grandes cidades como Istambul, contribuindo assim para aumentar a poluição ambiental significativamente. Com esse propósito, cinqüenta e seis amostras de poeira de rua de Istambul foram recolhidas e analisadas quanto à contaminação por metais. O estudo foi realizado entre dezembro de 2003 e abril de 2004 e as concentrações médias de Pb, Zn, Ni, Cd e Cu, determinadas por absorção atômica em forno de grafite, foram 368,3, 431,2, 27,1, 0,3 e 191,1 µg g^{-1}, respectivamente. A concentração de metais nas amostras de poeira foi bem mais elevada do que na amostra de controle. Foram calculadas correlações para as diferentes concentrações de metal. Análises estatísticas multivariadas (componente principal e análise de clusters) foram aplicadas à matriz de dados para determinar os resultados analíticos e identificar a possível origem dos metais na poeira. Os resultados indicaram que Pb, Zn, Cd, Ni e Cu originam-se principalmente a partir de fontes antropogénicas.

Metals are found in street dust especially in big cities, like Istanbul. This is a significant contribution to the environmental pollution. For this purpose, fifty six samples of Istanbul street dust were collected for metal contamination analysis in the period of December 2003 to April 2004. The mean concentration of Pb, Zn, Ni, Cd and Cu determined by graphite furnace atomic absorption spectrometry were found to be 368.3, 431.2, 27.1, 0.3 and 191.1 µg g^{-1} respectively. Metal values in street dust samples were several times higher than the control. Correlations among the different metal concentrations were calculated. Multivariate statistical analyses (principal component analysis - PCA and cluster analysis - CA) were applied to the data matrix to determine the analytical results and to identify the possible origin of metals in these dusts. The results indicate that Pb, Zn, Cd, Ni and Cu are mainly originated from anthropogenic sources.

Keywords: trace metals, Istanbul, street dust, road transport, PCA

Introduction

Metal ions at trace levels play an important factor affecting human health. The vehicle traffic, industry and weathered materials are the main factors that influence the levels of trace elements in dust samples in big cities of the world. Numerous studies have been performed on the metal pollution due to the transportation activities; however a few have been studied in Istanbul. Istanbul is the biggest city of Turkey with a population around 12 million in 2007, which corresponds to 14.8% of country's total population. Furthermore, neighbor cities surrounding Istanbul are quite populated and they have enormous industrial and commercial activities which create dense import, export and trade events. The selected part of the city holds mainly residential areas, as well as numerous commercial and industrial zones are included within the boundaries. Transportation network is not well planned and major highways that are mainly responsible for the pollution is either too close to critical facilities or sometimes completely inside the urban areas.

Contaminated dust may threaten health since it is easily remobilized by wind from the roadside to air, cars and residences, and easily comes into contact with humans by inhalation and skin contact. In addition, highway dust can be easily carried by the storm water runoff which results in massive transport of contamination to environmentally critical places such as water reservoirs, rivers and seas. Lead (Pb) is one of the hazardous metals among the others for habitat.

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The main Pb source of pollution is from the leaded gasoline which includes tetraethyl or tetramethyl lead used to increase octane rate of the fuel. Roadside soils have been shown to contain high amounts of Pb which is mainly originated from petroleum combustion. Tyre abrasion and corrosion of roadside safety fences contribute to most of the zinc (Zn) pollution present within the roadside soils[1]. Wearing of the brake linings and other leakages, abrasions and spills from the vehicles are the major sources of pollution for other metals, especially for copper.

Many studies of street dust have focused on elemental concentrations and source identification.[2-5] Although there are some studies of metals contamination of street dusts in Istanbul,[6-8] there is no study related to multivariate statistical approach to describe the origin of metals in street dust.

Principal component analysis (PCA), cluster analysis (CA) and to some extent the correlation analysis for soil studied and their results have been used to establish some models to predict the origin of pollutants and for classifying both samples and pollutants.[9-11]

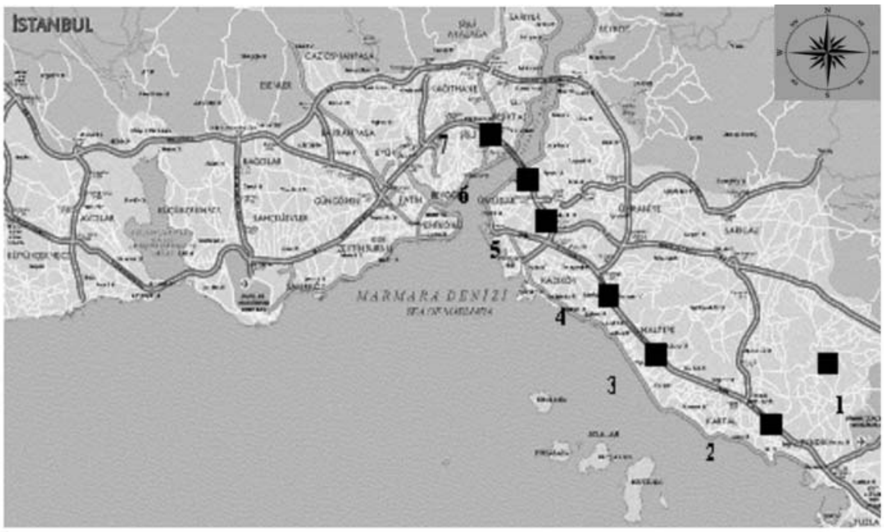
The aim of this study was firstly to determine the average concentrations of five metals (Pb, Zn, Ni, Cd and Cu) in street dusts sampled in seven different selected stations in Istanbul; secondly, to define their natural or anthropogenic origin by PCA and CA; thirdly, to calculate the degree of anthropogenic influence on metal contamination in urban dusts and finally, to generate information for the level of traffic related to metal pollutants in the Asian side of Istanbul.

Experimental

Study area and street dust sampling

Pendik-Levent vicinities in D-100 highway were selected as the study areas. Because D-100 highway is one of the heaviest traffic existing roads in Istanbul (Figure 1). Total length of the selected route is approximately 40 km. The D-100 highway, which connects Europe to Asia and plays a major role in intercontinental transportation, makes the situation worse since most of the activities in the country are achieved by D-100 highway. The estimated motor vehicles are over 2 million in Istanbul.

Consequently, this study presents selected seven different stations on the highway to determine metal concentrations in street dust samples between December 2003–April 2004 were shown in Figure 1. Aydos Mountain (station 1) was



Station Numbers	Sampling Stations	Geographical Coordinates	Vehicle Numbers/h
1	Control point (Aydos Mountain)	40°55`51.22``N 29°13`48.65``E	0
2	Pendik (D-100 highway bus station)	40°53`18.30``N 29°14`18.42``E	608
3	Maltepe (D-100 highway bus station)	40°56`10.67``N 29°08`19.06``E	1489
4	Bostancı (D-100 highway bus station)	40°57`55.10``N 29°06`18.83``E	3021
5	Altunizade (D-100highway bus station)	41°01`20.40``N 29°02`43.54``E	3922
6	Bosphorus bridge (D-100 highway bus station)	41°02`11.13``N 29°02`17.13``E	5218
7	Levent (D-100 highway bus station)	41°04`01.77``N 29°00`48.31``E	6054

Figure 1. The study area.

selected as a control point due to its zero traffic volume. Other stations were Pendik (2), Maltepe (3), Bostancı (4) and Altunizade (5), which are located on the Asian side, The Bosphorus bridge (6), and the last station was Levent (7) which is found on the European side. The sampling stations are near to critical places such as densely used bus stop stations under the footbridges on highways. The dust samples were taken from road pavements in each sampling points.

Analytical procedure

Approximately 5 g of the dust sample was collected from each point by gently sweeping an area of about 1 m^2 at the bus stations for twice a month and samples were put into polyethylene bags. Street dust samples were dried at 100 ^oC for two hours and sieved through a 100 mesh sieve

In order to achieve homogeneity of the sample, and to isolate impurities that may be available within the dust. Samples were properly labeled, placed in plastic containers and analyzed as soon as possible.

In this study USEPA (Method 3050B)[12] was used for sample digestion. 1.0 g of street dust sample was taken and added 10 mL 32% m/m HNO_3 and refluxed for 10 min. Allowed to sample cool, added 5 mL of concentrated HNO_3 and refluxed for 30 min. Sample was cooled again and added 2 mL of water and 3 mL of 30% m/m H_2O_2. Then, the volume was reduced approximately 5 mL heating at 95 ± 5 ^oC without boiling for two hours, diluted to 100 mL with double distilled water. A Shimadzu model 6800 graphite furnace atomic absorption spectrometer, with a deuterium lamp for continuous background correction, was used for Pb, Zn, Ni, Cd and Cu determination and the wavelengths applied were 283.3, 213.9, 232.0, 228.8 and 324.8 nm, respectively.[13]

Statistics

Mean, standard deviation, minimum and maximum concentration, Pearson's correlation coefficient were used for statistical analysis. Calculated coefficient of variation (CV), which is the standard deviation ratio to the mean, was applied to determine the degree of distinct distribution of different metal concentrations, and to point out statistically significance of the selected element in the studied areas. In addition, correlation coefficients were also calculated to determine relationships among different metals. All statistical analyses were performed using Statistica 6.0.

PCA enables a reduction in data and description of a given multidimensional system by means of a small number of new variables.

PCA with Varimax normalized rotation was applied to data set. The Varimax rotation is the most commonly used rotational strategy and maximizes the sum of these variances for all the factors. The aim of rotational algorithms is to become clear pattern of loadings, that is, factors that are clearly marked by high loadings for some variables and low loadings for others. In this respect, loadings > 0.71 are typically regarded as excellent and < 0.32 very poor.[14]

CA was applied to data set using the Ward's method combined with 1-Pearson r for clustering of the metals. Ward's method is distinct from all the other methods because an analysis of variance approach is used to evaluate the distances between clusters. The objective of cluster analysis is to group objects into clusters such that objects within one cluster share more in common with one another than they do with the objects of other clusters. CA was also applied to evaluate similarity of sampling stations with respect to metal concentrations in street dust. Euclidian distance was calculated as measures of similarity and the Single linkage was used to link clusters.

Results and Discussion

Metal concentrations

The descriptive determination of the metal concentrations of street dust are given in Table 1. Metal concentrations in street dust of Istanbul are much higher than USEPA[15] values, except Ni, when we compared them with the acceptable limits for soil.[16]

Table 1. Metal concentrations of street dusts in Istanbul (μg g^{-1})

Element	Control samples	Range	Mean	SD	CV	Reference value(*)
Pb	37.2-41.6	165-1170	368.32	364.61	0.99	10
Zn	110-115.6	325-546	431.26	79.56	0.18	50
Ni	16-18.8	21-35	27.16	6.34	0.23	40
Cd	0.08-0.12	0.21-0.7	0.34	0.17	0.49	0.06
Cu	46.5-56.1	136-257	191.10	40.88	0.21	30

*USEPA, Mclean, JE., Bledsoe, BE., October. Behavior of metals in soils, Office of Solid waste and emergency response. 1992 EPA/540/S-92/018.

Sezgin *et al.*[6] studied the area over the most loaded highway in European district of Istanbul. The mean concentrations of Pb, Cd, Ni, Zn and Cu were 211.88 µg g^{-1}, 1.91 µg g^{-1}, 31.52 µg g^{-1}, 520.81 µg g^{-1} and 208.49 µg g^{-1} respectively. In our study, although it seemed that Cd level was much lower, Pb level was much higher and the rest of the measured metals (Ni, Cu, Zn) were slightly lower than Sezgin *et al.*[6] results. The results of this study also were compared with others similar cities of the world (Table 2).

Table 2. Global studies of individual metal concentrations, ranges of concentrations, comparisons between urban dusts (µg g^{-1}) [16]

City	Metal				
	Cd	Cu	Ni	Pb	Zn
New York	8	355	Nd	2582.5	1811
London	6250	61-323	32-74	413-2241	Nd
Hong Kong	Nd	92-392	Nd	208-755	574-2397
Madrid	Nd	188	44	192.7	476
Amman	2.5-3.4	69-117	27-32.8	219-373	Nd
Oslo	1.4	123	41	180	412
Bahrain	72	Nd	126 697	152	
Lancaster	3.6	75	Nd	1090	260
Seoul	3	101	Nd	245	296
Taejon, Korea	Nd	47-57	Nd	60-52	172-214
Hamilton	4.1	129	Nd	214	645
Jordan	Nd	1.8-84.9	1.7-6.5	2.1-314.1	15.4-136.9
Istanbul	0.21-0.7	136-257	21-35	165-1170	325-546

Nd: Not detected.

Pearson's correlation coefficient matrix for five metals (Pb, Zn, Ni, Cd and Cu) was shown in Table 3. In this table, Pb-Zn-Ni and Cd-Cu groups have significant positive correlations. For the first group; the correlation coefficients of Pb with Zn and Ni are 0.630 and 0.495 respectively, also Zn and Ni have a positive correlation (0.430). For the second group; the correlation coefficient for Cd and Cu is 0.628. High correlations were found between metal concentrations and number of vehicles (Table 4).

Table 3. Pearson's correlation matrix between the concentrations of metals

Metal	Pb	Zn	Ni	Cd	Cu
Pb	1				
Zn	0.630	1			
Ni	0.495	0.430	1		
Cd	-0.378	0.052	-0.523	1	
Cu	0.012	0.266	-0.276	0.628	1

$p < 0.01$ (2-tailed).

Table 4. Correlation coefficients between vehicle numbers and metal concentrations

	Correlation coefficient (r)				
	Cu	Ni	Zn	Pb	Cd
Numbers of vehicle	0.906	0.901	0.884	0.726	0.693

Multivariate analysis results

The number of significant factors, initial Eigenvalues, the percent of variance and cumulative percent were explained by using a Varimax rotation with Kaiser normalization for the street dust samples are tabulated in Table 5.

Table 5. Rotated component matrix for data of Istanbul street dusts

Element	Component	
	1	2
Cd	**0.88**	- 0.24
Cu	**0.87**	0.17
Pb	- 0.15	**0.94**
Zn	0.26	**0.88**
Ni	- 0.50	**0.68**
Initial Eigenvalue	2.32	1.68
Percent of Variance	46.37	33.64
Cumulative percent	46.37	80.01

PCA loadings > 0.4 are shown in bold.

The PCA produces two factors explaining approximately 80% of the total variance in the data. The first factor comprised Cd and Cu with respective loadings of 0.88 and 0.87 and explains 46.37% of the variance. The second factor extracted explained 33.64% of the variance, and it was made up of Pb and Zn with respective loadings of Ni which was found to be with a negative loading in factor 1 and high positive loading in factor 2. The loadings were –0.503 and 0.679 for factor 1 and factor 2, respectively.

It is evident from the rotated component matrix in Table 5 that all the five metals analyzed were explained by two factors. The first factor spanning the greater amount of variance (46.37%) includes Cd, Cu and Ni. This factor could be industrial, traffic, geological structure and from the automobile tyres. The negative loading for Ni might indicate that Ni is controlled by a different geochemical mechanism or it has a different source in this region. The concentrations of Pb, Zn and Ni appear in the second factor may be related to primarily, the vehicle emissions associated to the high traffic volume for Pb and secondarily for oil leakage also contributed to the concentration of these metals in street dust. The second factor groups were Pb and Zn. This association may suggest that the source of these metals is also anthropogenic in the studied area.

The results of CA are shown in the dendograms (Figure 2). Cluster diagram shows two main clusters. Cluster 1 contains Cd and Cu, Cluster 2 contains Ni, Pb and Zn.

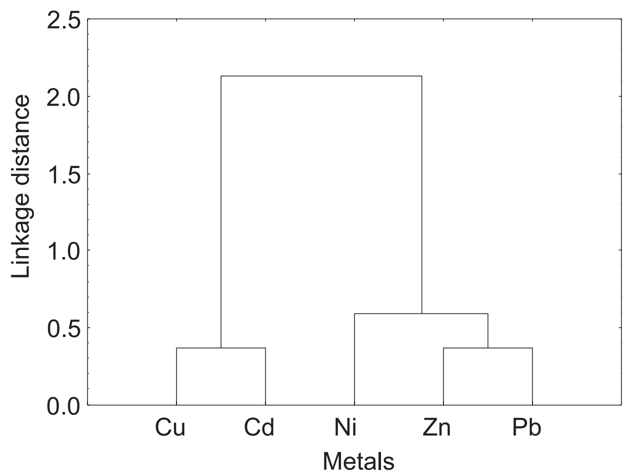


Figure 2. Dendogram resulting from the Ward's method of hierarchical cluster analysis for the 6 variables (in 48 samples). Similarities have been calculated from 1-Pearson-r.

Source identification

Compared with background values of USEPA soils, Pb, Zn, Cd, Ni and Cu, which involves these elements coming from anthropogenic sources, have extremely elevated concentrations in street dust of Istanbul. For Pb, the highest value of CV (0.99) was attributed to the high concentration measured at station 7.

There is a high Pearson correlation coefficient between Cd and Cu. PCA and CA analyses are consistent with each other when considering a strong correlation between Pb and Zn**.** Beside this**,** Ni grouped together with Pb and Zn in both PCA and CA. Ni positively contributes to the second principal component and negatively contributes to first principal component in PCA. Hence, Ni forms a third cluster close to the Pb and Zn cluster in CA.

The initial cluster analysis of the sampling stations based on their metal content (not shown here) indicated a strong separation of station 7 from the rest due to its extremely high levels of Pb.

This situation may mask the grouping of the other stations. Therefore, the data associated with station 7 were removed and the CA was performed on the remaining data from the 6 stations. The dendogram (Figure 3) shows how stations are clearly divided into three areas with different characteristics with respect to the measured concentrations of metals. Thus, it might be seen that the station 1 (control station), and stations 2 and 3, and the stations 4, 5 and 6 are grouped separately. The dendograms show that the stations close to each other are grouped together.

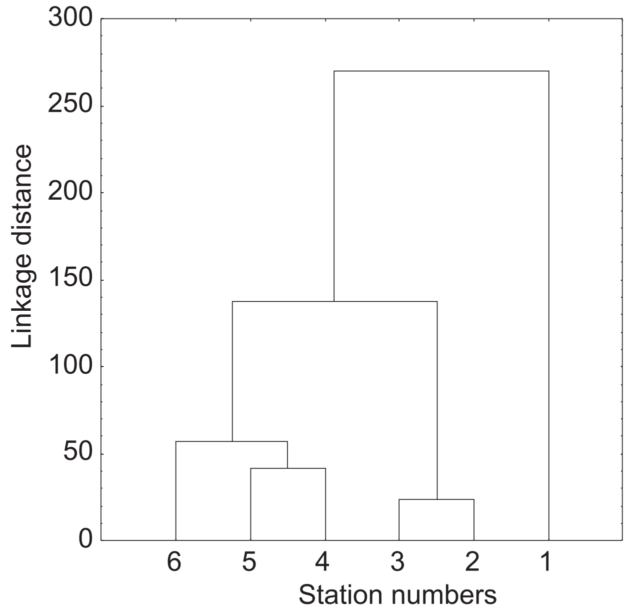


Figure 3. Cluster analysis of the sampling stations based on their metal concentrations in street dust (Single linkage, Euclidian Distance).

Conclusions

Because of having higher metal concentrations than the standard values for Pb, Zn, Cd and Cu, our studies indicate that there is metal pollution at the sampling points.

All statistical analyses including principal component analysis, cluster analysis and Pearson's correlation analysis provided information on the source of metals. When concentrations of studied metals were compared with USEPA values in soil, these elements were originated from anthropogenic sources such as traffic, industry and weathered materials.

Results of combined multivariate statistical analyses and the distribution patterns of the pollutant metals suggested that the vehicle traffic represents the most important pollutant source for the studied urban environment. Multivariate techniques of statistical analysis seem to provide an important tool for a better understanding of the complex dynamics of pollutants. Significant relationships were also supported by the results of statistical methods such as PCA and CA.

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