HEAVY-METAL CONTENT OF ROADSIDE SOIL IN MERSIN, TURKEY

Hakan Arslan and A. Murat Gizir

Department of Chemistry, Faculty of Arts and Sciences, Mersin University, 33343 Mersin, Turkey

SUMMARY

Lead, nickel, cadmium, copper, and zinc were determined in roadside soil samples collected from different locations in Mersin metropolis. The samples were digested with a 3/1 mixture of conc. hydrochloric/ nitric acid. The metal content was determined by flame atomic absorption spectrometry. The method of analysis was evaluated using Soil-7, a certified reference material (International Atomic Energy Agency, IAEA). For each location, the numbers of vehicles driven on the road were counted. Results showed that the soil contained significant levels of metals, when compared to control values. The mean values for Pb, Ni, Cd, Cu, and Zn in street soil were 183, 120, 3.4, 55 and 20 $\mu g\ g^{-1}$, respectively. A significant correlation was found between the number of vehicles and the metal contents in soil samples. These values suggested that motor vehicles form a major source of these metals in the soil. The concentrations of heavy metals in the samples were also compared with those reported by scientists in various countries.

KEYWORDS:
Heavy metals, Mersin, pollution, soil, traffic.

INTRODUCTION

In urbanized areas, heavy metals originate from many different sources, including vehicle emissions, industrial discharges and other activities [1]. Atmospheric pollution is one of the major sources of heavy metal contamination [2]. Heavy metals can accumulate in the top soil from atmospheric deposition by sedimentation, impaction and interception, and, therefore, top and roadside soils in urban areas are indicators of heavy metal contamination from atmospheric deposition. There is strong evidence that soil is an important pathway causing exposure of people to metals that may reach toxic levels [3]. The toxicity of heavy metals towards humans has been well documented, and because of the relative paucity of data on pollution by these metals from vehicle exhausts, there is clearly a need for further studies [4, 5].

Several studies in the world, for example, have stressed the possibility that contaminated soil, ingested either directly or indirectly as a result of hand-to-mouth activity, may represent a significant pathway of toxic metal intake during early childhood [6].

Although there has been a considerable number of studies on the concentrations of heavy metals in soils, most of them have been carried out in developed countries with long histories of industrialization and, crucially in the case of lead, extensive road building and use of leaded gasoline [1, 7, 8]. But very few studies in this area have been done in developing countries such as Turkey. The data on pollutant metal concentrations and distributions are extremely sparse.

The variations in the levels of lead in roadside soil are frequently attributed to traffic density [9-12]. The levels of nickel, cadmium, copper, and zinc were also reported to correlate with traffic density [10, 11, 13-17]. This contamination of roadside soil is considered to arise mainly from motor vehicle exhaust, such as lead from tetraethyl lead compounds in petrol [10, 18]. Lead, nickel, cadmium, zinc, selenium, antimony and arsenic come from fossil fuel combustion and motor vehicle tire wear [18, 19]. Nickel emission also results from nickel added in gasoline and atmospheric abrasion of nickel-containing parts of automobiles [20].

Mersin, a seaside city, is located in the southern part of Anatolia (36.0° N, 34.0° E). It is one of the large industrial regions in Turkey with an area of 15,853 km^2 and a population of ~1.7 million in 2000. The climate in Mersin is moist-hot in summers and mild in winters. Temperatures range between 9 and 33 °C, the average values being 30 °C during summer and 12 °C during winter season. The city is famous for its orange and lemon fields and also one of the largest tourist attractions in Turkey.

The health of children and elderly people is likely to be affected by exposure to an environment with high metal concentrations. Therefore, it is necessary to establish the levels of heavy metals in the cities. In this study, the concentrations of lead, cadmium, zinc, copper and nickel in Mersin

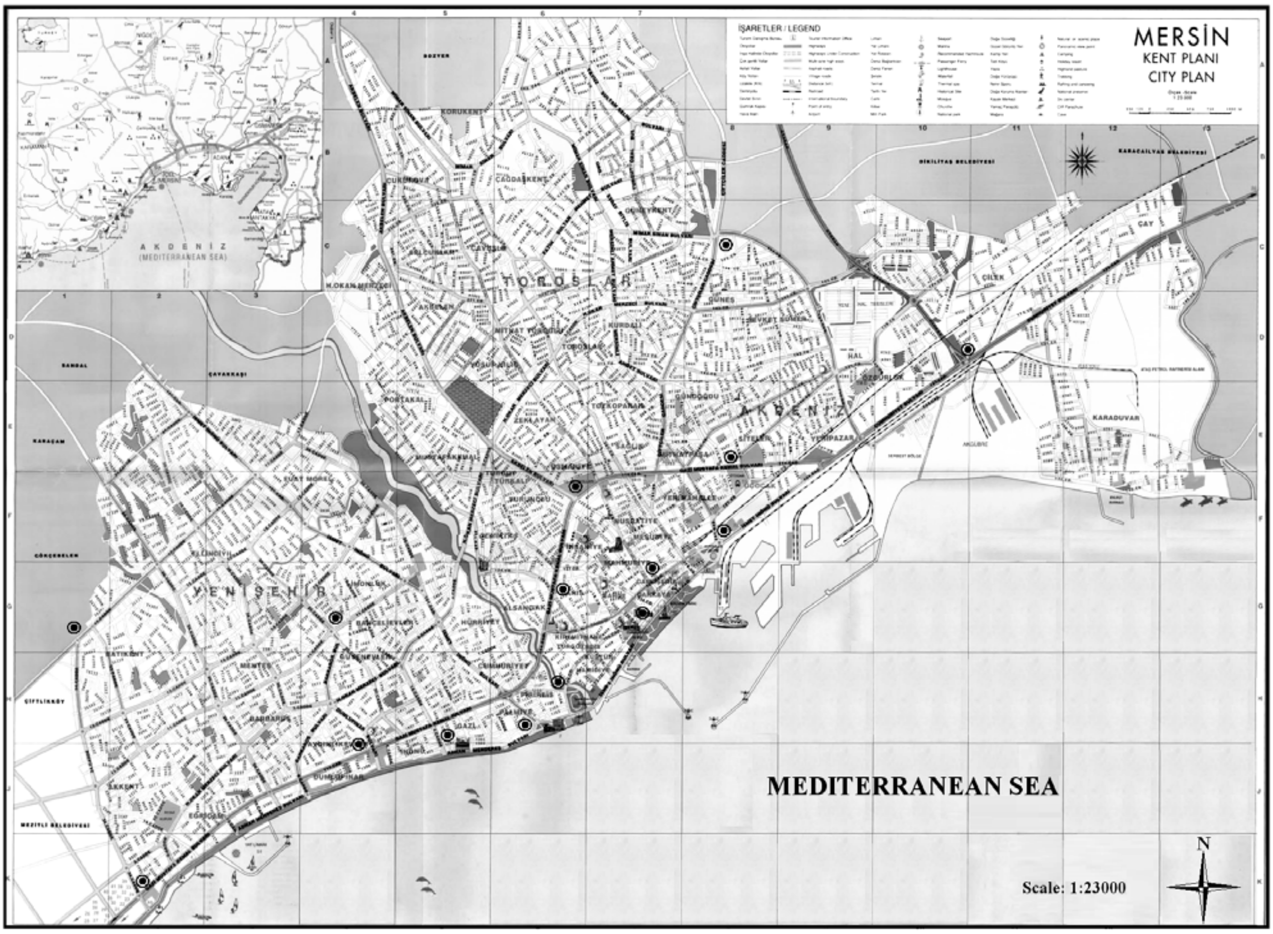

FIGURE 1 - Location map of the study area (Mersin city).

soil samples have been analyzed by AAS, and relationship between heavy metal contents and traffic densities were established.

MATERIAL AND METHODS

Reagents

Analytical reagent-grade chemicals were employed for the preparation of all solutions. Standard solutions (1000 mg/L) of Pb, Ni, Cd, Cu, and Zn were prepared by dissolving respective pure metals or their salts. For each element, six standard solutions of different concentrations in linear ranges were prepared in 2M HNO_3 [12]. Working solutions were prepared by diluting suitable aliquots of stock solutions with distilled water. They were prepared freshly every day, and kept in polyethylene bottles.

Sampling

Street dust samples were collected from 14 sites, to include low and high-density traffic roads in Mersin during the period of March to June 2003 (Figure 1). The samples consisted of soil dust collected from both road sides, about 10-15 m in length, using a brush and plastic dustpan. They were dried at 60 °C and sieved through a 170-mesh (90 microns) sieve. Representative samples were then withdrawn by coning and quartering, and were stored in clean self-sealing bags [12].

Analytical techniques

The soil samples were dried at 110 °C for 3 hrs, then ground to pass through a 200-mesh sieve, and homogenized for analysis. 1.0 g of soil samples were digested with 15 ml conc. hydrochloric acid and 5 ml conc. nitric acid at room temperature, and heated to 95 °C. After the evolution of NO_2 fumes had ceased, the mixture was evaporated to dryness on a sand-bath and mixed with 20 ml solution containing 1% (v/v) HCl and 1% (v/v) HNO_3. Finally, this mixture was filtered and the resulting clear solution used for FAAS measurement, after being diluted to 50 ml [15].

The accuracy and precision of digestion procedure were checked using a standard reference material (IAEA Soil-7, International Atomic Energy Agency). The results shown in Table 1 indicate good agreement among experimental and certified values. In addition, the procedure was applied to a sample collected from Istiklal Street Station. The sample was analyzed both with and without a spiked standard containing a mixture of the relevant metals in different amounts. The recovery rates for Pb, Ni, Cd, Cu, and Zn in Istiklal Street Station were found to be 99%, 97%, 98%, 96%, and 97%, respectively, during the digestion. A preliminary test involving seven replicate digestions on one soil sample for these metals produced relative standard deviations of about 6-12%.

TABLE 1
Observed and certified heavy metal values (mg/kg) for IAEA Soil-7.

Element	Measured values	Certified values
Pb	66.7±0.05	55-71
Ni	25.9±0.06	21-37
Cd	1.8±0.04	1.1-2.7
Cu	10.1±0.08	9-13
Zn	99.7±0.07	101-113

Apparatus

All the samples were analyzed with a Perkin Elmer FAA spectrophotometer, Model 3110. Atomization was performed by acetylene/air flame with a flow rate of 2.5 L/hr for acetylene and 6 L/hr for air. Two types of sources from Cathedon and Perkin-Elmer were employed to excite the elements.

Statistical Analysis

The data were analyzed statistically. Correlation matrices were produced to examine the interrelationships among metal concentrations, but also the correlations between vehicle numbers and metal concentrations. Student's t-test was employed to estimate the significance of these values.

RESULTS AND DISCUSSION

The concentrations of Pb, Ni, Cd, Cu, and Zn in street dusts samples are listed in Table 2, together with the 24-hrs numbers of vehicles and cars at the respective stations. Roadside dusts can indicate the short-term contamination released from vehicle exhaust emission and vehicle components. Ciftlikkoy station with its zero traffic volume was selected as control. In general, Istiklal Street dust data show higher concentrations of five metals studied, compared to those from Ciftlikkoy Station soils. This shows that traffic volume has a strong influence on the metal pollution of the roadside soil dusts.

TABLE 2 - Heavy metal concentrations in surface soil of different traffic volume locations in Mersin (March-June 2003).

Location	Concentration. x±t*s/√N. µg/g					No. of cars 24 hrs	No. of vehicles 24 hrs
	Pb	Ni	Cd	Zn	Cu		
Adnan Menderes Boulevard- (Hilton)	330.1±15.9	286.1±14.3	165.7±8.2	165.7±10.6	162.8±9.4	77521	104112
Mersin University Road	144.5±7.5	147.5±6.5	130.5±6.7	102.2±5.3	133.7±4.1	66816	110448
Pozcu Center Road	3.75±0.23	4.06±0.44	4.08±0.41	3.17±0.21	3.17±0.29	50832	92784
Ataturk Park Square	27.4±3.3	26.5±3.1	28.9±4.2	16.6±3.7	14.5±1.7	88605	119984
Football Stadium Junc.	64.6±3.3	73.9±4.8	61.7±3.2	46.9±3.7	48.8±4.1	27604	38925
Train Station Street	174.9±12.1	138.4±8.8	125.3±5.9	156.6±9.7	240.1±12.9	6880	95856
Harbour Gate Road	116.5±4.7	124.6±4.2	111.9±5.7	121.7±5.3	149.2±6.8	51845	94369
Motorway Road	3.40±0.39	3.42±0.38	4.26±0.52	3.42±0.30	3.82±0.36	53996	98064
Mersin Oteli Junc.	15.7±1.2	13.1±2.0	24.7±2.5	19.1±2.6	21.6±3.5	18478	24912
G.M.K Boulevard -(Turizm Ok.)	49.8±3.4	41.1±5.4	75.1±6.1	54.7±5.4	47.0±4.3	59809	107472
Central Bus Station Road	245.2±13.8	134.8±6.5	56.4±5.3	347.9±14.8	19.9±2.1	27888	32368
Cetinkaya Road	99.5±4.3	109.9±3.9	117.2±5.1	132.7±5.8	61.7±3.5	81552	123648
Mugdat Cami Road (GMK)	3.42±0.28	2.92±0.17	2.91±0.21	3.98±0.37	1.63±0.12	62160	73685
Istiklal Street	26.2±2.7	15.3±2.6	13.7±2.8	27.8±2.3	11.9±1.1	82749	113136
Ciftlikkoy (Mersin University)	76.4±5.7	38.1±4.5	38.1±3.1	79.4±6.9	29.3±4.5	0	0

*: Uncertainty at 95% confidence level (N=6).

The 14 urban street dust samples had metal concentrations in the range of 20-348 µg/g for Pb, 1.6-4.3 µg/g for Cd, 12-29 µg/g for Zn, 29-79 µg/g for Cu, and 62-149 µg/g for Ni, with mean values of 183, 3.4, 20, 55 and 120 µg/g, respectively.

The Mersin Pb levels were compared with values of other cities. In Lancaster [1, 21], 1090-2500 µg/g were reported for urban road samples, a range of 172-9660 µg/g and a geometric mean of 1354 µg/g was found in London [22], a range of 14-2200 µg/g found in Auckland [19], a range of 82-450 µg/g and an average of 168 µg/g found in Nigde [23], a range of 13-375 µg/g found in Kemalpasa [9], a mean of 1762 µg/g found in Riyad [24], a mean of 970 µg/g found in Manchester [8], a mean of 697 µg/g found in Bahrain [25], and a mean of 444 µg/g found in Pittsburgh [7]. Lower mean Pb levels of 89, 139, 180, 181, and 210 µg/g have been reported for Des Moines, Lake Charles, Hong Kong, Birmingham, and Bursa [7, 9, 26, 27]. The dominant source of Pb in urban street dusts is the emission of aerosol particles from gasoline vehicles [15]. High lead concentrations are not always found in developing cities, e.g. data reported for Merida city in Venezuela and Nigde city in Turkey (Pb concentrations of 65 and 168 µg/g, respectively) [23, 28]. Lead content in soil of Cetinkaya Road Station in Mersin was the highest one and is attributed to higher traffic density there. The factors responsible for Pb enrichment in roadside soils are similar to those of major urban areas. New automobiles should burn only unleaded fuel, but leaded gasoline still contains alkyllead compounds, albeit in decreasing quantities. With up to 80% of atmospheric Pb still being derived from auto exhaust, it should come as no surprise that roadside environments were Pb-enriched, despite relatively low traffic volume in this city. It is noted that the lead concentration increases with traffic volume, as shown by a significant correlation between lead concentrations and traffic intensity (Figure 2 and Table 3). This is in agreement with the results obtained for other cities [6, 8, 10-13, 23, 29, 30].

In Mersin, a mean level of 3.4 µg Cd/g soil was found, whereas mean values of 2.8 and 5.2 µg/g in Lancaster [21], a range of <1-28 µg/g with a geometric mean of 4.2 µg/g in London [22], a range of 1.1-5.8 µg/g in Kemalpasa [9], a geometric mean of 3.61 µg/g in Hong Kong [27], 0.89 µg/g in Des Moines [7], 0.7 µg/g in Birmingham [26], 2.1 µg/g in Nigde [13], 3.1 µg/g in Bursa [15], 2.5 µg/g in Riyad [24], and 0.36 µg/g in Lake Charles [7] were reported. The mean Cd concentration in soil worldwide is 0.5-4.0 µg/g [17]. Street dust Cd concentrations of Mersin were higher than the worldwide average concentration. It is noted that Cd increases with increasing traffic volume, as evident from the significant correlation between lead concentrations and traffic intensity (Table 3). The reason for the highest Cd concentration in dust would be its use in accumulators of motor vehicles and carburettors. The same trend in dust Cd concentrations has been obtained for various cities [9, 11, 14].

The mean concentration of Zn in Mersin was found to be 20 µg/g. Zn values for other cities in various countries are as follows: a range of 64-480 µg/ in Auckland [19], a range of 27-108 µg/g in Kemalpasa [9], a range of 121-5150 µg/g and a geometric mean of 513 µg/g in London [22], a geometric mean of 1170 µg/g in Hong Kong [27], a mean of 152 µg/g in Bahrain [25], a mean of 443 µg/g in Riyad [24], a mean of 57 µg/g in Bursa [15], and a mean of 205 µg/g in Birmingham [26]. As can be seen in Table 3, a reasonable correlation between zinc amount and the total number of vehicles was found with a correlation ratio of r = 0.646. High zinc concentrations in samples can be explained by its use in lubricating oil, tires, accumulators and carburettors [9, 13, 14, 24, 27]. In addition, a significant correlation was found between Pb and Zn contents in soil samples (Figure 3).

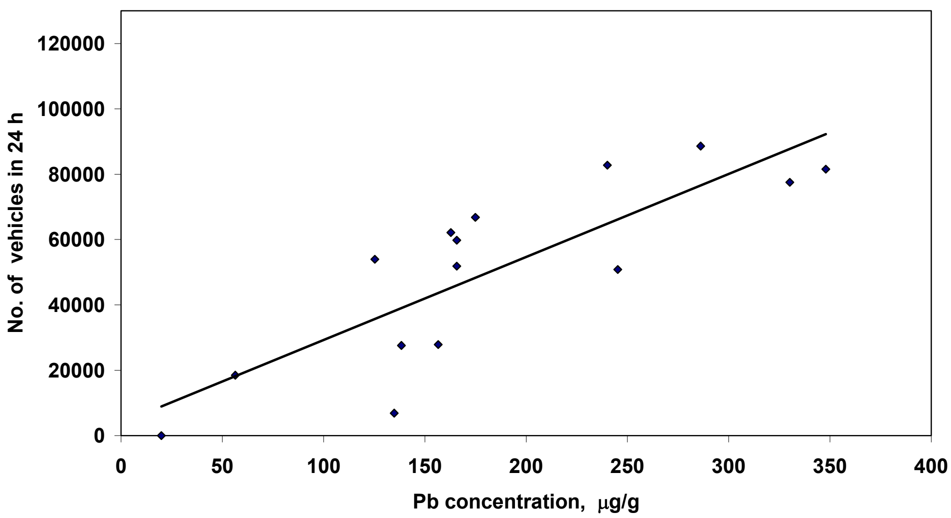

FIGURE 2 - The relationship between the Pb concentrations and number of vehicles in soil samples.

TABLE 3 - Coefficient correlation data (N=6).

	Pb	Ni	Cu	Cd	Zn
Pb	1.000				
Ni	0.671	1.000			
Cu	0.732	0.405	1.000		
Cd	0.665	0.765	0.779	1.000	
Zn	0.750	0.484	0.891	0.774	1.000
Cars	0.827	0.710	0.669	0.736	0.653
All vehicles	0.758	0.546	0.630	0.712	0.646

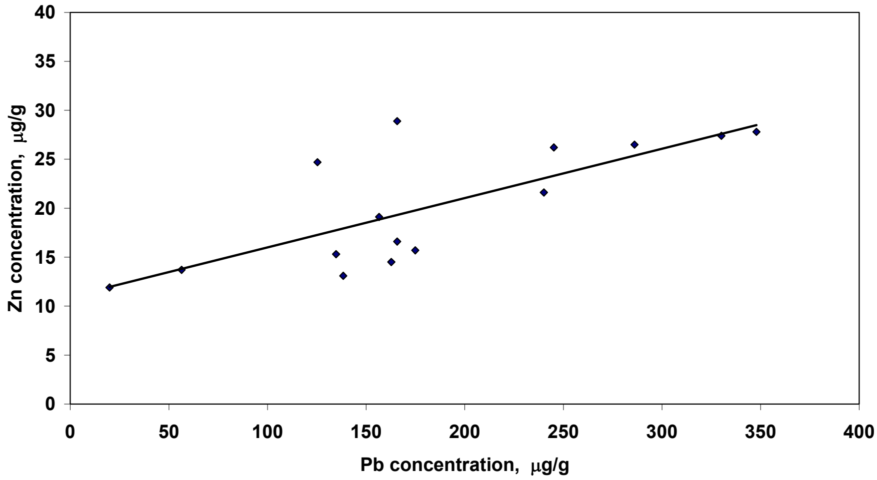

FIGURE 3 - The relationship between Pb and Zn concentrations in soil samples.

The mean Cu concentration in dust world-wide is 100-300 µg/g [17]. The mean, minimum and maximum values of Cu in the dust samples from Mersin were found to be 55 µg/g, 29 µg/g, and 79 µg/g, respectively. The comparative Cu levels are as follows: a mean of 94 µg/g reported for urban road samples in Riyad [24], a geometric mean of 126 µg/g found in Hong Kong [27], a mean of 44 µg/g in Nigde [13], and a range of 12-200 µg/g in Auckland [19]. The source of Cu from traffic has been reported to be the corrosion of metallic vehicle parts. The Cu dust sample results in this study are in agreement with those found for soil samples by Narin et al. [14], Kartal et al. [11] and Arslan [9].

The mean concentration of Ni in Mersin was 120 µg/g. The relevant comparative values obtained in other cities are 8-105 µg/g in Auckland [19], 30-145 µg/g in Kemalpasa [9], a mean of 44 µg/g in Riyadh [24], a mean of 67 µg/g in Bursa [15], and a mean of 52 µg/g in Nigde [13]. The range of the median of nickel in street dust samples has been reported by Fergusson and Kim [17] to be 50-100 µg/g, whereas in the dust samples from Mersin 62-149 µg/g were analyzed. This shows that Ni pollution is not only of traffic origin. Soil is a complex system and its constituents are constantly undergoing changes due to weather conditions, geographic location and human activities, such as traffic, industrial and agricultural ones. The source of nickel in street dust has been reported to be corrosion of cars [9, 17, 25]. The clear correlation between the number of cars and the nickel contents support this idea.

CONCLUSIONS

Most authors had pointed out that all these metals are used in parts of motor vehicles that are subject to wear, and that vehicles are a source of metals in the street environments. Metal concentrations in Mersin roadside dusts are found to be significantly higher than the control. This indicates that traffic volume in Mersin metropolis, a large urban center with high population and traffic density, has a strong influence on metal pollution of its roadside soil dusts. A comparison of Pb, Ni, Cd, Cu, and Zn in Mersin street dust samples with the corresponding levels of cities in other countries clearly evidenced that they are lower. There is a good correlation between the number of cars and the metal contents. Regarding the statistical calculations, at 95% confidence level, the correlations between both the investigated metal contents and the number of cars with heavy metal concentrations are significant. The heavy metal levels in roadside soils are positively correlated with increase in traffic. It is clear that traffic plays the dominant role in metal pollution, but values found in Mersin are within the acceptable limits. These data suggest the use of both electricity and alternative fuels would decrease heavy metal pollution in urban areas. In addition, with further demands on transport and lowering permitted emission, automotive manufacturers and suppliers will continue to reduce emission from engines by cleaner combustion and optimized catalyst systems.

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CORRESPONDING AUTHOR

Hakan Arslan
Department of Chemistry
Faculty of Arts and Sciences
Mersin University
33343 Mersin
Turkey

e-mail: arslanh@mersin.edu.tr

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