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SUMMARY

The metal pollutants' accumulation caused by the traffic in Adana-Turkey was investigated. The samples were collected from two sides of the road in Adana during the period of March to June 2003. The metal contents of the samples were determined by flame atomic absorption spectrometry (AAS). The mean concentration levels of Pb, Ni, Cd, Cu, and Zn were found to be 183, 58, 3.3, 76 and 53 $\mu\text{g/g}$, respectively. A significant correlation between the number of vehicle and the metal contents of the soil samples was found.

KEYWORDS:

Pollution, heavy metals, trace metals, soil, traffic, Adana.

INTRODUCTION

Among the non-degradable pollutants, heavy metal contamination of the environment was widely studied due to its potential hazards to human health. Orescanin et al. [1] have reported that the main source of heavy metals in plants was absorption from soil, and that higher Pb values determined in soil samples taken near the road were attributable to gasoline combustion. Industrial processes and fossil fuel combustion have contributed to a substantial increase of metals in the atmosphere, especially near urban areas and roadsides [2]. Street dusts are important environmental materials in which the levels of heavy metal ions can be monitored. Since the 1970s the possible health implications of chronic lead exposure have been discussed [3]. One potential source for human Pb intake is the inhalation of particulate matter from automobile exhaust [4-7]. Lead is the most widespread contaminant in the global environment. It is added to gasoline as tetraethyl lead to prevent knocking. Zinc and cadmium impurities come from lubricating motor oils, tires and galvanized parts of vehicles. Nickel emission also results from nickel added to gasoline and by atmospheric abrasion of nickel containing parts of automobiles [8]. A number of

studies on the heavy metal content of street dust samples including lead, cadmium, zinc and nickel and its relationship to traffic volume have been reported [4-7, 9-11].

Adana, with population of ~1.9 million in 2000, is one of the important cities of the ancient Kilikya region (South Anatolia - 37.0° N 35.3° E) and was established at an easily passable point of the Seyhan River. The city, which is famous for its orange and lemon gardens, is located in the largest touristic region of Turkey, but also a large industrial region with 207 factories. The population of the city is over two million in summer. Moist, hot summers and mild winters characterize the weather conditions of Adana. Temperatures range between 6 and 34 °C, average values being 33 °C during summer and 7°C during winter season.

Chemical analyses of soil samples find important application in environmental and geochemical exploration studies. Most of the studies have been performed using wet chemical methods for analyzing such samples [12-14]. This is mainly due to the better detection limits obtainable from instrumental methods like AAS, used in the present study and AES for a large number of elements.

In this work, road soil samples were taken from nine locations around the city of Adana. For each location, the numbers of vehicles driven on the road were counted. For each soil sample, the concentrations of lead, nickel, cadmium, copper, and zinc were obtained by AAS. The environmental pollution levels of heavy metals in soil were determined and compared with the data from other cities. The relationships between the traffic density and heavy metal concentration were calculated.

MATERIAL AND METHODS

Reagents

Analytical reagent-grade chemicals were employed for the preparation of all solutions. Standard solutions (1000 mg/L) of the Pb, Ni, Cd, Cu, and Zn metal ions were prepared by dissolution of the pure metals or their salts. For each element, six standard solutions of different concentra-

tions in the linear range were prepared in 2M HNO₃, the optimum linear concentration range for the measurement [4, 7]. Working solutions were prepared by diluting suitable aliquots of stock solutions with distilled water. They were prepared freshly everyday and kept in polyethylene bottles.

Sampling

Nine locations were chosen among the low- and high-density traffic roads in Adana from which a number of soil samples were collected over a period of March to June 2003. Sampling was performed according to detailed guidelines mentioned by Arslan [10]. Samples consisted of soil dust collected from both sides of a 10-15 m length of the road. They were dried at 60°C and sieved through a 170-mesh sieve. Samples were then taken by the coning and quartering methods.

Preparation of samples

The soil samples were dried at 110 °C for 3 h, ground to pass through a 200-mesh sieve and homogenized for analysis. One g aliquots of soil samples were digested with 15 mL concentrated hydrochloric acid and 5 mL of concentrated nitric acid at room temperature, and then heated to 95 °C. After the evolution of NO₂ fumes had ceased, the mixture was evaporated to near dryness on a sandbath and mixed with 20 mL solution containing 1% (v/v) HCl and 1% (v/v) HNO₃. The resulting mixture was filtered through a gouche filter and the insoluble fraction of silicates was determined. A clear solution was used for an FAAS measurement after dilution to 50 mL [10].

Measuring conditions

All the samples were analyzed with a Perkin Elmer Model 3110 Flame Atomic Absorption spectrophotometer. Atomization was performed by an acetylene/air flame with a flow rate of 2.5 L/h for acetylene and 6 L/h for air. Two types of sources from Cathedon and Perkin-Elmer were used to excite the elements.

Statistical Analysis

The data were subjected to a statistical analysis and correlation matrices were produced to examine the inter-relationships between the metal concentrations and also correlations between the number of vehicles and the metal concentrations. Student's t-test was applied to estimate the significance of the values.

RESULTS AND DISCUSSION

Before starting the sample analysis, the accuracy and precision of the digestion procedure were tested to determine recovery of the metal ions. The procedure given in the experimental section was applied to a sample collected from Train Station Junc. to determine recoveries of the metal ions. The sample was analyzed both with and

without spiking with a standard containing a known mixture of the examined metals of different amounts. The results are shown in Table 1. No appreciable losses of Pb, Ni, Cd, Cu, and Zn were found during the digestion. Recovery values were $\geq 96\%$. A preliminary test involving seven replicate digestions on one soil sample for these metals produced relative standard deviations of 5-10%. The concentrations of Pb, Ni, Cd, Cu, and Zn in the dust samples and the number of vehicles and cars in the 07.00-19.00 h period at the respective stations are given in Table 2.

Kabasakal Hill was selected as a control for the experiment as there is no traffic volume. If the heavy metal concentrations in the roadside soil dusts are compared with the metal contents in location 1, it is seen that the metal concentrations of the dusts are systematically higher than the control samples. These data suggest traffic volume have a strong influence on the metal pollution of the roadside soil dusts.

The Pb concentrations from the nine locations, 260 $\mu\text{g/g}$, 56 $\mu\text{g/g}$ and 183 $\mu\text{g/g}$, are the maximum, minimum and mean values for the city of Adana, respectively (Table 2). The lead content of soil of Baraj Street station was the highest and is directly correlated to higher traffic density at this location. The factors responsible for Pb enrichment of roadside soils are probably similar to those for major urban areas. The median range for lead in city center dust samples around the world is 100-568 $\mu\text{g/g}$ [15-16, 7]. New automobiles should burn only unleaded fuel, but leaded gasoline still contains alkyllead products, albeit in decreasing quantities. With up to 80% of atmospheric Pb still derived from auto exhaust, it should come as no surprise that the roadside environment is Pb enriched despite this city's relatively low traffic volume. It is noted that the lead concentration increases with increasing traffic volume as shown by the significant correlation between lead concentrations and traffic intensity (Table 3). This is in agreement with the results obtained for various cities [7, 17, 18].

The median range found for zinc in street dust samples in a prior study is 15-25 $\mu\text{g/g}$ [19]. In another study, Narin et al. [6] have reported that an average dust zinc concentration in Nigde is in the range of 73-103 $\mu\text{g/g}$. The zinc concentration was found to be in the range of 43-79 $\mu\text{g/g}$ in this study. As seen in Table 3, a reasonable correlation between zinc concentration and the total number of vehicles is found with a correlation coefficient calculated to be $r = 0.836$. The reason for high zinc concentration in samples, relative to average zinc concentrations around the world, can be explained by the use of zinc in lubricating oil, tires, accumulator, and in the carburetor. These results are in agreement with those of Arslan [10].

The mean, minimum and maximum values of Cu in the dust samples from Adana, Turkey, are found to be 76 $\mu\text{g/g}$, 50 $\mu\text{g/g}$, and 88 $\mu\text{g/g}$, respectively. The mean Cu concentration in dust worldwide is 100-300 $\mu\text{g/g}$. The source of Cu from traffic has been reported to be coming from corrosion of metallic parts of vehicles. The results found in

TABLE 1
Analytical performance of digestion.

Metal	Recovery, %	Relative standard deviation, (s/x)*
Pb	99	0.055
Ni	96	0.049
Cd	98	0.101
Zn	98	0.081
Cu	96	0.078

*N = 7

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

Location	No. of cars 07.00-19.00h	No. of vehicles 07.00-19.00h	Concentration. $x \pm t^*s/\sqrt{N}$. $\mu\text{g/g}$				
			Pb	Ni	Cd	Zn	Cu
1. Kabasakal Hill	0	0	56.4 \pm 2.9	26.3 \pm 4.5	1.63 \pm 0.10	15.1 \pm 1.5	49.8 \pm 1.6
2. 5-Ocak Square	12135	19780	202.4 \pm 7.2	60.8 \pm 1.2	3.10 \pm 0.20	52.0 \pm 2.9	76.4 \pm 5.4
3. Belediye Square	18961	24651	147.2 \pm 8.4	65.5 \pm 5.9	3.68 \pm 0.39	55.7 \pm 2.3	70.4 \pm 3.8
4. University Road	12875	16930	166.2 \pm 4.3	67.4 \pm 2.7	3.17 \pm 0.24	54.1 \pm 3.8	76.8 \pm 4.8
5. Turgut Özal Street	18354	26306	181.0 \pm 10.3	65.5 \pm 3.4	2.91 \pm 0.22	68.4 \pm 2.8	70.6 \pm 3.1
6. Baraj Street (Hosp. Junc.)	22516	30191	260.0 \pm 9.1	57.5 \pm 2.2	3.42 \pm 0.28	78.8 \pm 1.9	82.2 \pm 5.5
7. M. Kemal Street	18360	23801	227.8 \pm 13.1	50.7 \pm 2.7	3.44 \pm 0.35	43.7 \pm 1.6	88.2 \pm 6.6
8. Gazi Paşa Street	20293	26115	225.8 \pm 8.1	71.1 \pm 2.2	4.45 \pm 0.29	43.2 \pm 4.7	85.2 \pm 3.7
9. Train Station Junc.	18816	22505	167.0 \pm 4.7	59.3 \pm 5.3	3.40 \pm 0.25	47.6 \pm 4.6	86.0 \pm 4.1
10. T.C. Beriker street	19670	27822	193.8 \pm 11.1	59.7 \pm 1.6	4.20 \pm 0.21	74.0 \pm 6.1	78.2 \pm 2.9

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

TABLE 3
Coefficient correlation data between vehicle types and metal concentrations.

Vehicle types	Correlation coefficient, r				
	Pb	Ni	Cd	Zn	Cu
Cars	0.817	0.743	0.836	0.762	0.809
All vehicles	0.850	0.762	0.819	0.836	0.769

TABLE 4
Coefficient correlation data between metal concentrations (r = 95%).

	Pb	Ni	Cd	Zn	Cu
Pb	1.000				
Ni	0.600	1.000			
Cd	0.699	0.761	1.000		
Zn	0.664	0.625	0.532	1.000	
Cu	0.855	0.629	0.770	0.459	1.000

this study for dust samples are in agreement with the results found for soil samples by Narin et al. [6], Kartal et al. [4] and Arslan [7] and lower than world average values.

The mean Cd concentration in soil world-wide is 0.5-4.0 µg/g [11]. The contents of Cd in the dust samples are in the range of 1.6 (No. of vehicle/h = 0) to 4.5 (No. of vehicle/h = 2176) µg/g. Street dust Cd concentrations of Adana are higher than the world-wide average concentration. The reason for the higher Cd concentration in dust would be as a result the use of Cd in accumulators in motor vehicles or in carburetors; however, Cd concentrations are in agreement with the results obtained for various other cities [4, 6, 7].

The median range of nickel in street dust samples has been reported by Fergusson and Kim [11] as 50-100 µg/g. The concentration of nickel in the dust samples from Adana was measured to be in the range of 26-71 µg/g (mean = 58 µg/g). A clear correlation between the number of cars and the nickel contents was found. It indicates that nickel pollution also originates from traffic. The source of nickel in street dust has been attributed to corrosion from cars [11, 19].

It is seen that the metal concentrations of dusts are higher than the control station of location 1. This also indicates that traffic volume has a strong influence on the metal pollution of roadside soil dusts. There is a good correlation between the number of cars and the metal contents (Table 3). According to statistical calculations, at the 95% confidence level, the correlations both between the investigated metal contents and the number of cars or total number of vehicles and between the heavy metal concentrations are significant (Tables 3 and 4). Our present correlation data have shown good agreement with the results found by Tatsumi et al. [20]. As is expected, the best correlations are observed with the Pb concentrations, due to leaded petrol commonly used in cars.

CONCLUSIONS

Heavy metal pollution is a problem for cities. It has been found that the concentration of Pb in roadside soils is generally less than that found in major urban areas. Declining consumption of Pb based gasoline and the lower overall traffic volume in Adana probably contributes to this trend. Lead levels in roadside soils are positively correlated with increasing traffic. Pronounced changes in soil Pb levels are affected neither by prevailing wind direction nor automobile idling behaviour.

These data suggest the use of both electricity and alternative fuels, LPG (liquid petroleum gas) and CNG (compressed natural gas), to run vehicles may decrease heavy metal pollution in urban areas. In addition, with further demands on transport and lowering of permitted emission, automotive manufacturers and suppliers will continue to reduce emission from engines by cleaner

combustion and by optimized catalyst systems. It is clear that traffic plays the dominant role in metal pollution, but Adana values are within acceptable limits.

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REFERENCES

- [1] Orescanin, V., Katunar, A., Kutle, A. and Valkovic, V. (2003) Heavy Metals in Soil, Grape, and Wine. *Journal of Trace and Microprobe Techniques*, 21(1), 171-180.
- [2] Ardakani, A.F. (1980) Ecotoxicol. Contamination of Environment with heavy metal emitted from automobiles. *Environ. Safety*, 44, 45-62.
- [3] Mahaffey, K.R., Annest, J.L., Roberts J. and Murphy R.S. (1982) National estimates of blood lead levels: United States 1976-1980: association with selected demographic and socio-economic factors. *New England J. Medicine*, 307, 573-579.
- [4] Kartal, S., Elci, L. and Dogan, M. (1992) Investigation of lead, nickel, cadmium and zinc pollution of traffic in Kayseri. *Fresenius Environ. Bull.*, 1, 28-33.
- [5] Narin, I. and Soylak, M. (1999) Monitoring trace metal levels in Nigde, Turkey: nickel, copper, manganese, cadmium and cobalt contents of the street dust samples. *Trace Elements and Electrolytes*, 16(2), 99-103.
- [6] Narin, I., Soylak, M. and Dogan, M. (1997) Traffic pollution in Nigde-Türkiye: Investigation of trace element contents of soil samples. *Fresenius Environ. Bull.*, 6, 749-752.
- [7] Arslan, H. (2001) Heavy metals in street dust in Bursa, Turkey. *Journal of Trace and Microprobe Techniques*, 19(3), 439-445.
- [8] Lagerwerff, J.V. and Specht, A.W. (1970) Contamination of roadside soil and vegetation with cadmium, nickel, lead and zinc. *Environ. Sci. Technol.*, 4(7), 583-586.
- [9] Thornton, I. (1988) Metal Contents of Soil and Dusts. *Sci. Total Environ.*, 75, 21-39.
- [10] Arslan, H. (2001) Investigation of heavy metal pollution of traffic in Kemalpaşa-Turkey. *Fresenius Environ. Bull.*, 10, 405-408.
- [11] Fergusson, J.E. and Kim, N.D. (1991) Trace Elements in Street and House Dusts: Sources and Speciation. *Sci. Total Environ.*, 100, 125-150.
- [12] Tokalioglu S. and Kartal, S. (2002) Atomic absorption spectrometric determination of heavy metal contents of soils around different highways in turkey and statistical interpretation of the data. *Journal of Trace and Microprobe Techniques*, 20(4), 127-140.

- [13] Hussain, S.T., Tahir, H., Saleem, M. and Afzal, M. (2000) Trace Metal Pollution Assessment of Sediments and Liquid Westes from Textile Industries of Pakistan. *Journal of Trace and Microprobe Techniques*, 18 (1), 99–106.
- [14] Soylak, M. and Turkoglu, O. (1999) Trace Metal Accumulation by Traffic in an Agricultural Soil Near a Motorway in Kayseri, Turkey. *Journal of Trace and Microprobe Techniques*, 17 (2), 209–217.
- [15] Somer, G. and Aydin, H. (1985) Determination of Lead in Roadside Soil Using Anodic Stripping Voltammetry. *Analyst*, 110, 631-633.
- [16] Warren, R.S. and Birch, P. (1987) Heavy Metal Levels in Atmospheric Particles, Roadside Dust and Soil Along a Major Urban Highway. *Sci. Total Environ.*, 59, 253-256.
- [17] Bereket, G. and Yücel, E. (1990) Monitoring of Heavy Metal Pollution of Traffic Origin in Eskisehir. *Tr. J. of Chem.*, 14, 266-271.
- [18] Yalcın, N., Aydın, A.O. and Sevinc, V. (1989) Tarım alanlarında motorlu arac trafiğinin actığı Pb ve Zn birikimi. *Doğa TU Müh. ve Cev. D.*, 13, 429-434.
- [19] Akhter, M.S. and Madany, I.M. (1993) Heavy Metals in Street and House Dust in Bahrain. *Water Air Soil Poll.*, 66, 111-119.
- [20] Tatsumi, Y., Yoka, K. and Ikedo, A. (1983) Effect of soil pollution by heavy metals on annual plants in Sakai City. *Jap. J. Ecol.*, 33, 293-303.

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