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Investigation of Trace Metal Accumulation Along Roadside Soil Using Aqua Regia As Extraction Media

Yol Kenarlarındaki Toprakta Eser Metal Birikiminin Kral Suyu Ekstraksiyonu İle İncelenmesi

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SUMMARY

A simple procedure using aqua regia for the extraction of lead, cadmium, zinc and nickel from the soil was optimized. The recoveries are 94 % for lead, 95 % for cadmium, 81 % for zinc and 86 % for nickel for the soil-type investigated.

Samples of roadside soil were collected along the highway E-5 at various locations and at both sides between Ankara and Gölbaşı and at two circles, one being in the center of the city.

Lead, cadmium, zinc and nickel content of the samples were determined by flame atomic absorption spectrometry. Lead concentration-was the highest among four metals (ranged from 77 ppm to 226 ppm). Zinc and nickel concentrations of the soil were close to lead concentration but wore lower than that. Cadmium concentration was the lowest (ranged from 1 ppm to 6 ppm).

ÖZET

Kurşun, kadmiyum, çinko ve nikelin topraktan kral suyu ile ekstraksiyonuna dayanan basit bir yöntem optimize edilmiştir. İncelenen

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toprak cinsinde % geriye kazanım kurşun için % 94, kadmiyum için % 95, çinko için % 81 ve nikel için % 86 dır.

Numuneler, E-5 karayolunun Ankara- Gölbaşı güzergahı üzerindeki değişik noktalarda, yolun her iki tarafından ve biri şehrin içinde bulunan iki kavşaktan toplanmıştır. Numunelerde bulunan kurşun, kadmiyum, çinko ve nikel alevli atomik absorpsiyon spektrometrisi ile tayin edilmiştir. Dört metal arasında topraktaki konsantrasyonu en yüksek olan kurşundur (77-226 ppm). Çinko ve nikel konsantrasyonları kurşun konsantrasyonuna yakın olmakla birlikte daha düşüktür. Konsantrasyonu en düşük olan metal ise kadmiyumdur (1-6 ppm).

Key Words: Soil analysis; lead, cadmium, zinc and nickel determination: atomic absorption spectrophotometry.

Among the nondegradable pollutants, heavy metal contamination of environment was widely studied because of the potential hazards to human health. Industrial processes and fossil fuel combustion has led to substantial increase of the metals in the atmosphere, especially near urban areas and roadsides (1,2). Lead is probably the most widespread contaminant, in the global environment. It is added to gasoline as tetraethyl lead (TEL) against knocking. It was shown that 70 % of lead exhausted as particle from motor vehicles and 85 % of the total particulate emission is deposited by the roadside (3).

Zinc and cadmium, as an impurity, come from lubricating motor oils, tires and galvanized parts of vehicles. Nickel emission also results from nickel added to gasoline and by atmospheiic abrasion of nickel containing parts of automobiles (4).

A number of studies on the heavy metal content of soil along the road including lead, cadmium, zinc and nickel and its relationship to traffic volume have been reported (5-9).

In this work, the lead, cadmium, zinc and nickel contents of roadside soil along E-5, intercity highway, binding central Ankara to Konya through Gölbaşı were determined by atomic absorption spectrometry. A simple extraction method was investigated and the relationship between the metal contents and traffic density was studied.

EXPERIMENTAL

Materials and Methods

Apparatus: Varian Techtron 1200, Flame atomic absorption spectrophotometer.

Reagents: Stock solutions containing 1000 μg metal/ml were prepared by using analytical reagent grade (BDH) $Pb(NO_3)_2$, $3\ CdSO_4 \cdot 8H_2O$, $NiSO_4 \cdot 7H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$.

Working solutions were prepared by diluting of suitable aliquots of stock solutions with distilled water. They were prepared freshly everyday and kept in polyethylene bottles.

Aqua regia was prepared by mixing three volumes of concentrated hydrochloric acid and one of nitric acid.

Sampling sites and collection of soil samples: Six sites and two junctions were selected along E—5 Highway between central Ankara and Gölbaşı along 30 km as shown in Figure 1. Tandoğan square is in the center of Ankara which is opened to highway through Çiftlik junction.

Annual average daily traffic (AADT) along the highway was 7475 vehicles in 1986. The average traffic density between Tandoğan square and Çiftlik junction was 1306 vehicles/hour in the morning and 2385 vehicles/hour in the evening rush-hours (10). The highway runs in a north-south direction and consists of four lanes divided by a median boundary.

Surface soil (0-3 cm) samples collected from the two sides of the highway and from the median boundary according to Jackson (11).

Soil collections were made in September 1986 and in September 1987. The weather was dry and temperature was 25°C during the sampling dates.

Sample treatment: Samples were allowed to air dry for a week (12). Then each sample was ground thoroughly in a mortar and passed through a 1 mm-sieve. Subsamples were then taken by the coning and quartering method. For collection and treatment wooden and/or plastic material were used.

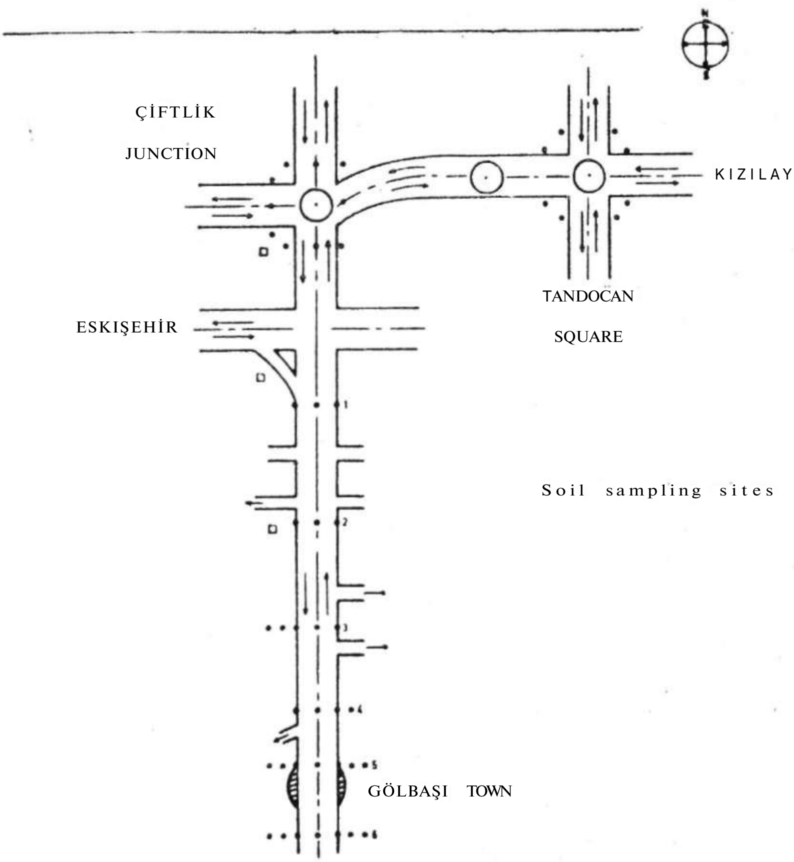

Figure 1. Sampling sites at the junctions and E-5 Highway. Sampling sites are shown by dost.

Analysis: The effect of acid volume and heating period on the digestion of the metals from the soil were investigated (7). The following procedure was applied as the most suitable method: 0.500 g of soil samples were accurately weighed into 50 ml pyrex conical flasks and digested with 5.0 ml aqua regia on a water-bath for 15 minutes. The stoppers were kept closed during the procedure. After digestion the samples were allowed to cool to room temperature and filtered through Whatman No. 42 filter papers and made up to 50 ml with distilled water.

Samples spiked with 50-200 $\mu g.g^{-1}$ lead, zinc and nickel and 1-2 $\mu g.g^{-1}$ cadmium were analysed to check for matrix interference.

Blank was prepared by diluting 5.0 ml aqua regia to 50.0 ml with distilled water. It is treated as mentioned above for the sample solutions.

For the measurements of lead, cadmium, zinc and nickel by atomic absorption spectrophotometry, air-acetylene flame was used. Analyses were performed at wavelengths 217.0 nm (for lead), 228.8 nm (for cadmium), 213.9 nm (for zinc) and 232.0 nm (for nickel).

RESULTS AND DISCUSSION

Table 1 indicates that 5 ml aqua regia and a heating period of 15 min. (Working Condition Nr.9) is sufficient for digestion of lead, cadmium, zinc and nickel from the soil. Although in different working conditions higher results might be obtained for the metals, the differences are not significant at the 95 % confidence level.

The recoveries for the extractable amounts of metals added to the soil are 94 % for lead, 95 % for cadmium, 81 % for zinc and 86 % for

Table 1. The effects of acid volume and heating period on the digestion of metals from the soil.

CONDITIONS of DIGESTION			METAL CONTENT (ppm) $\bar{x} \pm (t\ s/\sqrt{N})$**			
No.	Volume of aqua regia added (ml)	Heating period (mm)	Lead	Cadmium	Zinc	Nickel
1	15	30	278 ± 18	3.8 ± 0.5	139 ± 17	42.2 ± 1.3
2	15	20	289 ± 27	4.0 ± 0.2	139 ± 25	44.3 ± 6.6
3	15	15	285 ± 9	4.0 ± 0.7	123 ± 35	39.6 ± 3.9
4	10	30	296 ± 44	3.8 ± 0.2	154 ± 49	42.7 ± 2.6
5	10	20	293 ± 53	3.9 ± 0.2	135 ± 8	41.7 ± 1.3
6	10	15	278 ± 18	3.8 ± 0.2	142 ± 58	38.5 ± 2.6
7	5	30	285 ± 27	3.9 ± 0.2	142 ± 28	41.7 ± 2.6
8	5	20	285 ± 35	3.9 ± 0.2	134 ± 7	42.2 ± 2.6
9*	5	15	296 ± 35	4.0 ± 0.3	145 ± 11	41.7 ± 2.6
10	5	10	300 ± 62	4.0 ± 0.2	125 ± 9	37.5 ± 1.3
11	5	—a	228 ± 18	3.7 ± 0.2	112 ± 11	32.2 ± 1.3

Note 1. -a, allowed at room temperature for 15 minutes. 2.*, working conditions chosen for following experiments. 3 . **, t= 2.78 (p=0.05). 4. The concentrations are the arithmetic mean of three experiments. 5. The determinations were carried out on portions of the same soil sample.

nickel, respectively. But before accepting these values, the method should be applied to another soil types as well.

Soil usually contains high levels of silicates, in the crystal lattice of which trace amounts of metal salts could be trapped. Somer and Aydm (9) stated that if the sample is heated immediately after adding the acid, a gel of silicic acid is formed which my slow down the acid diffusion and consequently metal salts extraction. The formation of this gel can be prevented by allowing the sample to stand overnight in acid at room temperature. Our observations confirmed that gel formation did not affect the extraction of metal salts significantly and is in accordance with Berrow and Stein (13).

The arithmetic mean concentration of lead, cadmium, zinc and nickel in the roadside soil investigated were shown in Table 2.

Surface soil lead levels ranged from 76 to 314 $\mu g.g^{-1}$ (ppm) at Tandogan square and from 102 to 298 ppm at the highway in 1986. Lead content of soil of Tandogan square was the highest. This was attributable to higher traffic volume at Tandoğan Square than the highway traffic. Our results indicates that lead level ofroadside soil in the highway is not as high as that in some U.S.A. highways (4,5,8), and in Istanbul (7). This can be expected as the traffic is not as dense in the highway as those mentioned. But the lead content of soil was found far higher than the initial lead level of the soil (16 ppm according to Swaine (14)).

Cadmium levels of soil near the highway was found higher (mean 4.1 ppm) than the Tandogan square in the central Ankara (mean 3.5 ppm). Although the difference was not found significant, our results were far higher than many other studies (4,6,7). Zinc and nickel contents of the roadside soil were found at the same order but somewhat lower than lead.

No significant correlation between any pairs of lead, cadmium, zinc and nickel were found (coefficient of correlation were ranged from 0.033 to 0250 in 1986 and from 0.002 to 0.230 in 1987). Only in 1986, a correlation was found between lead and zinc at one side of E-5 highway (coefficient of correlation is 0.433, $p < 0.005$). Our results confirms with the findings of some authors (4) but differs from some authors(6).

Table 2. Arithmetic mean concentrations of lead, cadmium, zinc and nickel in roadside soil in two circles and 6 selected sites in E-5 highway.

Sampling Site		1986 September Mean ± Sd (ppm)	1987 September Mean ± Sd (ppm)
LEAD			
Tandoğan Sq.	Mean (n:7)	165 ± 89	173 ± 101
	Range	76 + 314	99 — 338
Çiftlik June.	Mean (n:14)	152 ± 56	162 ± 67
	Range	102 — 298	94 — 326
E-5 Higliway	Mean (n:18)	108 ± 36	152 ± 42
	Range	29 — 177	77 — 226
ZINC			
Tandoğan Sq.	Mean (n:7)	184 ± 35	166 ± 20
	Range	141 — 263	144 — 199
Çiftlik June.	Mean (n:14)	124 ± 26	120 ± 21
	Range	53 — 166	85 —T66
E-5 Highway	Mean (n:18)	84 ± 48	108 ± 45
	Range	37 — 161	46 — 206
CADMIUM			
Tandoğan Sq.	Mean (n:7)	3.5±1.2	3.4 ± 1.0
	Range	2.7 ± 6.2	1.8 — 5.4
Çiftlik June.	Mean (n:14)	2.9 ± 0.8	3.3 ± 1.2
	Range	1.9 ± 4.3	1.5 ± 5.1
E-5 Highway	Mean (n:18)	4.1 ± 1.5	4.4 ± 1.2
	Range	1.0 — 6.4	2.4 — 5.8
NICKEL			
Tandoğan Sq.	Mean (n:7)	127 ± 70	132 ± 84
	Range	67 — 249	64 — 284
Çiftlik June.	Mean (n:14)	90 ± 15	88 ± 18
	Range	65 — 125	68 — 122
E-5 Highway	Mean (n:18)	78 ± 23	78 ± 26
	Range	39 — 118	20 — 117

Although metal levels in the roadside soil in 1987 were found somewhat higher than in 1986, the difference was not significant by Whitney U-test.

As conclusion; lead, cadmium, zinc and nickel contents of soils adjacent to the highway and cityroads were found far higher than the ground level of those metals. Further studies are needed in Turkey to monitor trace metal accumulation on roadsides and find out the relationship between trace metal concentrations and traffic, road construction type, meteorological conditions, time and other factors.

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