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ACCUMULATION OF SOME METALS IN ROADSIDE SOILS OF ESKISEHIR

ESKİŞEHİR'İN YOL KENARI TOPRAKLARINDA BAZI METALLERİN BİRİKİMİ

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Roadside soils show considerable metal contamination due to both direct deposition of vehicle-derived metals and to relocation of the metals deposited on the road surface.

In this prospective analytical study, accumulation of some metals including Pb, Cd, Zn, Ni, Cr, Mn in roadside soils sampled from 10 different trafic-dense roads and from 5 control places far from the traffic were determined in Eskişehir. Soil samples were taken from 0-15 cm and 15-30 cm depths in March 31, April 23, May 5, July 7. The elements in the samples were extracted for the solution phase. Pb, Cd, Zn, Ni, Cr, Mn elements in the solutions were analyzed by an atomic absorption spectrophotometer. All the statistical analyses were based on paired t and student t tests.

In general, the metal concentrations of subject soils were significantly higher than the controls, where as the washed samples were lower than the non-washed samples. However, there was no significant difference between the samples of subject soils at the depth of 0-5 cm and 15-30 cm and the same results were obtained for the controls for both the non-washed and washed samples. By comparison of the results from March to July, Pb and Cd concentrations of the samples were decreasing while Zn, Ni, Mn and Cr concentrations were increasing. It was also observed that, the samples taken from the deeper layers, of the soil had lower concentrations of Pb, Cd and Mn than the upper layers while Zn, Ni and Cr concentrations were increasing from the upper to deeper layers. Compared to the literature, the mean Cr and Mn concentrations were in the normal range, while Zn, Ni, Cd and Pb concentrations were high.

In conclusion, it can be stated that there is a great high risk of these metals for both the atmospheric pollution and therefore for soil pollution. Probability exists for exposure of human populations to heavy metals that have been accumulated in the landscape of the modern urban-industrial environment.

Yol kenarındaki topraklar, hem motorlu araçlardan kaynaklanan metallerin doğrudan birikmesi, hem de yol yüzeyinde biriken metallerin yer değiştirmesi yüzünden önemli ölçüde metalik kirlenme gösterir.

Bu prospektif analitik çalışmada, Eskişehir ilinde trafiği yoğun olan 10 farklı bölgeden ve trafikten uzakta bulunan 5 kontrol bölgesinden alınan toprak örneklernide Pb, Cd, Zn, Ni, Cr ve Mn birikimi incelendi. Toprak örnekleri 31 Mart, 23 Nisan, 5 Mayıs ve 7 Temmuz 1997 tarihlerinde 0-15 cm ve 15-30 cm derinlikten alındı. Örnekler ekstraksiyon yoluyla solüsyon fazına hazırlandı. Bu solüsyon içindeki Pb, Cd, Zn, Ni, Cr ve Mn elementleri atomik absorpsiyon spektrofotometresi ile analiz edildi. İstatistiksel analizlerde eşleştirilmiş t testi ve student t testleri kullanıldı.

Genelde çalışma bölgelerinden alınan toprak örnekleri kontrol bölgelerinden alınanlardan daha yüksek, yıkanmış örnekler yıkanmamışlara oranla daha az metal konsantrasyonu göstermekteydi. 0-5 cm ve 15-30 cm derinlikten alınan çalışma bölgesi toprak örnekleri arasında metal konsantrasyonu bakımından anlamlı bir farklılık bulunamazken, hem yıkanmış hem de yıkanmamış kontrol bölgesi örnekleri için de aynı sonuçlar elde edildi. Mart ayı ile Temmuz ayı sonuçları karşılaştırıldığında, örneklerdeki Pb ve Cd konsantrasyonları artarken, Zn, Ni, Mn ve Cr konsantrasyonları azalmaktaydı. Toprağın derin kısımlarından alınan örneklerde yüzeyden alınanlara kıyasla daha düşük Pb, Cd ve Mn konsantrasyonu tesbit edilirken, Zn, Ni, Cr konsantrasyonları yüzeyden derine gidildikçe artmaktaydı.
Literatürle karşılaştırıldığında, ortalama Cr ve Mn konsantrasyonları normal sınırlar içindeyken, Zn, Ni, Cd ve Pb konsantrasyonları daha yüksekti.

Sonuç olarak, ağır metaller yoluyla atmosfer kirliliği ve dolayısıyla toprak kirliliği açısından yüksek bir riskin varlığından bahsedilebilir. Modern endüstriyel kentsel ortamlarda insan topluluklarının ağır metaller etkisinde kalma olasılığı mevcuttur.

Keywords :*Soil; Roadside; Pb; Cd; Cr; Mn; Ni; Zn*

Anahtar kelimeler: *Toprak; Yolkenarı; Pb; Cd; Cr; Mn; Ni; Zn*

Introduction

Environmental toxicology is generally concerned with chemicals in food, water and air. In the broadest sense, however the environment includes our home, community and workplace. Therefore our behaviors greatly influence the micro environment. It is customary to deal with the environment in terms of its specific medium: soil, water, air and living organisms (biota). Toxic metals present in the atmosphere, soil and water have hazardous effects on human life. Heavy metals which pollute the environment have a special importance because of their accumulative feature in living organisms. Soils have complex physical structures and compositions that very greatly. Some are rich in organic material, and others are poor. Some are coarse-grained and porous, others fine grained and impervious. The ionic charge of soil particles influence the movement of chemicals through soils. Some toxic elements occur naturally in the soils.

In addition to the variable composition of the soil from one zone to the other based on the mean values of toxic contamination, primary sources of metal contamination of soils include automobile emissions, decomposition of paints in olderhomes and mining and smelting of metaliferrous ores(1). Human activites have resulted in the deposition of many toxic substances within the soil. Contaminated soils are environmentally important since may pose potential adverse health effects upon ingestion of contaminated plants and soil.

Once a chemical is deposited on soil, it may be carried away by water flowing over the surface or may percolate down through the soil, usually aided by atmospheric and surface water, especially by rain.

One of the sources of emission of toxic metals such as lead, cadmium, zinc, nickel, crom and manganese, is traffic(2). Roadside soils show considerable metallic contamination due to both direct deposition of vehicle-derived metals and to relocation of metals deposited on the road surface(3).

Automobile fuels contain tetra-alkyl lead compound such as octane boosting additives. The largest part of the environmental lead is released by combustion of leaded-gasoline. Cadmium and zinc "released as combustion products" exist as alloys in accumulators of motor vehicles or the carburetors. Zinc also exists in motor oils as corrosion and oxidation protector. Mangan compounds are quite likely to be found as additives in many unleaded gasolines in the market as antiknock agents such as Methylcyclopentadenyl Manganese Tricarbonyl (MMT)(4). Thus, the manganese compounds are also being emitted from automobile exhausts and are currently, and unavodably polluting the air at the ground level. Because of their higher performance on pollution, elimination and economic value, the catalytic converter systems has been widely used. But since nickel particles are inevitably escaping from the converters, these systems exhibit great problems upon the environment(5).

Although in many countries, metal contamination, especially by heavy metal concentrations, of soils is well documented, in our country there is no such detailed documentation except some reports originated from only a few universities or institutes.

The objective of this study, conducted in 1996, was to determine the extend of Pb, Cd, Cr, Mn, Ni and Zn contamination of the main roadside soils of Eskişehir.

Materials and Methods

This prospective analytical study was conducted on roadside soils from the main roads and streets, the subject group being the garden soils and the control group far away from traffic, in Eskişehir. Samples were taken from 10 different regions and the control samples were taken from 5 different regions. The investigation including 2 such groups was conducted in four periods (March 31, April 23, May 5 and July 7). The first group of samples was taken from the surface layer, 0-15 cm depth of the soils and the second from deeper layers, 15-30 cm depth; and all samples were analyzed before and after washing.

All the samples were extracted for the solution phase as described by Que Hee SS and Boyle Jr[6] and analzed for Pb, Cd, Cr, Mn, Ni and Zn by using Hitachi (180-70) Polarized Zeeman Atomic Absorption Spectrophotometer. All the samples were analyzed in triplicates and the mean value was taken as the result.

Statistical analyses were based on paired t tests and t tests for independent samples.

Results

Concentrations of Pb, Cd, Cr, Mn, Ni and Zn in both the roadside soils and within the control areas are presented in the tables numbered as 1-6, respectively.

Discussion

The soil samples taken from traffic-dense areas had higher lead, cadmium, crom and nickel concentrations than those from the controls areas which were far from the traffic.

However, there was no significant difference between the manganese and zinc concentrations with respect to the subject and control areas, although the subject values were slightly higher than those corresponding to the controls (Table 1-6).

Table 1. Concentrations of Pb in the roadside soils and the control areas.

Lead (mg/kg)		Nonwashed surface soil	Washed surface soil	Nonwashed deep soil	Washed deep soil
subject areas n=10	mean	46.69	45.36	46.01	41.03
	sd	14.70	14.58	12.54	11.49
	range	28.57-76.18	27.85-74.68	28.59-64.21	26.37-60.44
contorl areas n=5	mean	11.51	10.49	16.28	8.90
	sd	1.11	1.48	15.69	1.16
	range	10.33-12.91	8.84-12.26	8.59-44.38	7.70-10.72
		t=5.24 $p<0.05$	t=5.24 $p<0.05$	t=3.99 $p<0.05$	t=6.13 $p<0.05$

Table 2. Concentrations of Cd in the roadside soils and the control areas

Cadmium (mg/kg)		Nonwashed surface soil	Washed surface soil	Nonwashed deep soil	Washed deep soil
subject areas n=10	mean	3.24	3.03	3.03	2.76
	sd	0.37	0.32	0.41	0.19
	range	2.88-4.13	2.68-3.77	2.45-4.05	2.43-3.03
contorl areas n=5	mean	1.2	1.01	1.25	1.02
	sd	0.35	0.25	0.41	0.35
	range	0.95-1.81	0.82-1.45	0.89-1.77	0.70-1.45
		t=10.25 $p<0.05$	t=12.24 $p<0.05$	t=8.02 $p<0.05$	t=12.79 $p<0.05$

Table 3. Concentrations of Cr in the roadside soils and the control areas

Crom (mg/kg)		Nonwashed surface soil	Washed surface soil	Nonwashed deep soil	Washed deep soil
subject areas n=10	mean	66.14	64.11	70.29	66.36
	sd	12.55	12.77	13.68	14.71
	range	55.42-97.59	53.73-96.17	57.63-105.46	53.46-103.15
contorl areas n=5	mean	44.65	41.35	46.33	45.06
	sd	6.26	7.89	6.87	7.26
	range	36.43-50.38	31.88-48.42	38.06-54.11	36.43-52.14
		t=3.57 $p<0.05$	t=3.62 $p<0.05$	t=3.64 $p<0.05$	t=3.02 $p<0.05$

Table 4. Concentrations of Mn in the roadside soils and the control areas

Manganese (mg/kg)		Nonwashed surface soil	Washed surface soil	Nonwashed deep soil	Washed deep soil
subject areas n=10	mean	364.27	357.79	354.83	349.01
	sd	45.03	43.23	44.54	44.26
	range	299.42-427.76	294.54-416.92	289.84-416.89	285.83-412.23
contorl areas n=5	mean	328.29	322.57	323.54	317.05
	sd	33.91	34.79	36.15	38.19
	range	312.39-388.93	304.76-384.75	306.30-388.19	297.13-385.08
		t=1.57 p>0.05	t=1.58 p>0.05	t=1.36 p>0.05	t=1.37 p>0.05

Table5. Concentrations of Ni in the roadside soils and the control areas

Nickel (mg/kg)		Nonwashed surface soil	Washed surface soil	Nonwashed deep soil	Washed deep soil
subject areas n=10	mean	176.53	167.81	191.58	183.57
	sd	13.46	16.36	19.40	19.50
	range	159.51-195.32	143.19-192.96	169.71-229.66	157.44-219.51
contorl areas n=5	mean	75.50	72.10	81.64	75.59
	sd	8.85	8.87	10.65	12.23
	range	67.48-89.87	64.08-86.60	69.72-98.25	59.97-93.85
		t=15.08 p<0.05	t=12.05 p<0.05	t=11.68 p<0.05	t=11.21 p<0.05

Table 6. Concentrations of Zn in the roadside soils and the control areas

Zinc (mg/kg)		Nonwashed surface soil	Washed surface soil	Nonwashed deep soil	Washed deep soil
subject areas n=10	mean	62.13	57.61	61.57	56.67
	sd	24.25	22.28	25.74	23.98
	range	43.12-115.29	40.98-108.43	33.71-115.69	29.85-107.34
contorl areas n=5	mean	42.15	39.64	44.54	41.15
	sd	10.22	9.53	11.19	9.07
	range	25.20-51.91	23.68-48.43	25.99-53.62	25.64-48.65
		t=1.74 p>0.05	t=1.70 p>0.05	t=1.39 p>0.05	t=1.38 p>0.05

The amounts of lead, added to gasoline for octane boosting, ranges from 0.4 to 1.1 g/L depending on the laws of the countries. In the USA, for example, it is 130 mg/l, whileas in Switzerland 400 mg/L and in Turkey for gasoline 340 mg/L and for premium gasoline 550 mg/L(7). These additives pollute the air upon combustion, by emithing lead, halojenated compounds, lead oxide, lead oksicarbonate, etc. Therefore, the lead concentration in the air may increase upto 1-10 μg/m^3. Although the solid and liquid fuels can also pollute air depending on their types, their effects are considered secondary in compared to the automobile exhausts(7). High blood Pb concentrations reported during the air pollution episode in Ankara, in 1984 were mainly considered due to the traffic density(8). In this study, lead concentrations in the air were not measured. According to Patat Şaban, however, central parts of the cities and the areas nearby the transit roads are exposed to environmental pollution due to the dense traffic(9). Airborne Pb settles out and accumulates on the ground. In this way, soil has become a major reservoir of Pb(10). Although, lead concentrations in soil and dust may range widely, lead occurs at an average concentration of 12 ppm in the earth's crust. In general the lead concentration of the surface is higher than the deeper layers(11). In Stockholm, lead concentrations on the soil surfaces were found to range between 30-300 μg Pb/g soil dry weight(12,13). In this study it is found that nonwashed surface samples had a mean of 46.69±14.70 ppm lead concentrations which was higher than that for the earth's crust as described by Philippe Grandjean(11) and the nonwashed deeper samples had 46.01±12.54 ppm with a significant difference ($p<0.05$).

The earth's crust contains an average cadmium concentration of 0.55 μg/g. Cadmium is a relatively mobile metal in soils(11). One of the main reasons of the high cadmium concentration of the soil is the combustion of petroleum, especially, of gasoline. The surface layers of the nonwashed soils had 3.24±0.37 ppm and deeper parts 3.03±0.41 ppm Cd concentrations. There was no significant difference between the surface and deeper layers ($p>0.05$). Harrison et al had found 0.96-4.91 μg/g Cd concentraitons in the roadside soil samples in Lancaster, England(3). Results of this study are higher than those found by Harrison et al.

While the average chromium concentration in the earth's crust is 300 μ/g(11), in this study it was found as 66.14 12.55 ppm for the nonwashed surface layers and 70.29 13.68 ppm for the nonwashed deeper layers and no significant difference was found between these layers ($p>0.05$).

The earth's crust has an average manganese content of 1000 μg/g(11). In this work, however, the mean Mn concentration of the surface soils was found as 364.27±45.03 ppm whereas the deeper layers had 354.83±44.54 ppm. Although our results are lower than the value given by Philippe Grandjean, there is a significant difference between the surface and the deeper layers ($p<0.05$). Morris et al have found 330 μg/g Mn concentration in the street sweepings from Newark, NJ, a heavy traffic city (2) which is similar with the results of this study.

Although the earth's crust contains an average nickel concentration of 80 μg/g(11), in this study the mean Ni concentration of the surface layers was found as 176.53±13.46 ppm while the deeper layers had 191.58±19.40 ppm, with a significant difference ($p<0.05$).

Zinc is a common and essential metal with a low toxic potential. Its concentration in the earth's crust is 40 mg/kg(11). In this study it is found that the surface layer of the nonwashed soil contained 62.13±24.25 ppm and the deeper parts had 61.57±25.74 ppm. There was no significant difference between the surface and deeper layers ($p>0.05$).

When the samples were washed, metal concentrations of the samples were found to decrease and there were significant differences between the washed and non-washed samples for all the surface samples ($p<0.05$ for all of the analyses).When deeper samples were examined, the same results were obtained. As for the controls, although we have found significant differences for the surface soils, the deeper layers showed no differences with respect to Pb, Cd and Cr (respectively $t=1.12$, $p<0.05$; $t= 0.99$, $p>0.05$; $t=1.81$, $p>0.05$).

Cr, Mn, Ni and Zn concentrations were found to increase in time and there were significant differences between the data corresponding to 31/3/1996, rainy days and 7/7/1996, dry season, for the subject soils for both nonwashed samples and washed samples and for both surface and deeper layers. For controls, however, there were significant differences regarding Cr, Mn, Ni and Zn with an acceptance of washed deep layers in terms of Cr ($t=0.8$, $p<0.05$). The Pb and Cd concentrations of the subject soils were decreasing with significant differences and a significant difference was found for Pb in the control specimens with an acceptance of washed surface soils for Cd.

Conclusion

A good correlation was found between the traffic intensity and Pb, Cd, Cr and Ni concentrations, while the correlation was not so good for Mn and Zn concentrations.

Traffic runoff was found to be the most significant source of metal contamination regarding Pb, Cd, Cr and Ni when compared to the control areas. These elements were also found to be sensitive to washing (also to rain) meaning that displacemont of the metal pollution is important for its impact on the environment.

References

1. Boon, Dy., Soltanpour, PN.: J. Environ Qual. 21, 82 (1992)
2. Bereket, G.,Yücel, E.: Doğa-Tr J Chemistry. 14, 266 (1990)
3. Harrison, R.M., Laxen, DP., Wilson. SJ.: Environmental Science&Technology 15, 1378 (1981)
4. Morris, MJ., Tobias, ED., Koehler, R., at all.: AJPH, 68(6), 557(1978)
5. Rondia, D.: Exposure and health effects In: Elvira, Di Ferrante. (Ed) Trace metals, pp. 117-134 Pergamon Press, Oxford, Newyork, Toronto, Sydney, Paris, Frankfurt 1978
6. Que Hee, SS., Boyle, JR.: Analyt. Chem. 60, 1033 (1988)
7. Vural, N.: Toksikoloji, pp. 315-324 A.Ü. Ecz. Fak. Yayın No:56: Ankara 1984
8. Vural, N., Gülvendik, G.: Biool. Trace. Elem. Res. 18, 85 (1988)
9. Patat, Ş., Kartal, Ş., Külcü, N.: IV. Kimya ve Kimya Mühendisliği sempozyumu Elazığ, özet kitabı pp. 542 (10-12 Haz 1987)
10. Mielke, HW., Water Air and Soil Pollution 57-58, 111 (1991)
11. Grandjean, P.: Health significance of metals. In: Maxy-Rosenau-Last (Ed.) Public Health and Preventive Medicine, pp:381-400 Prentice Hall International Inc., New Jersey 1990
12. Berglund, M., Lind, B., Lannero, E., at all: Arch. Environ. Contam. Toxicol. 27, 281 (1994)
13. Victorin, K., Dock, L., Vahter, M., at all.: IEM Report 4/90 (1990)

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