Cd, Pb, Zn and Ni Contents of Urban Soils in Istanbul

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Abstract

In this study, 104 soil samples at depths ranging from 0-5 cm and 20-25 cm were taken from 9 sampling sites within the urban parts of Istanbul city and 1 site (control) outside of urban part between May and September 1999. Cd, Pb, Zn, Ni contents and some soil properties of these samples were determined. According to soil characteristics and heavy metal contents we can conclude that the urban soils of some part of Istanbul have started to become polluted with Pb and Zn. Analysis of soil samples showed the presence of Pb in all of the soil samples at varying concentrations ranging from 24.87-445.6 mg kg^{-1} in spring 23.23-1121.20 mg kg^{-1} in autumn. In spring, the Zn and Ni contents in the examined soils were found between 30.27-310.0 mg kg^{-1} and 12.27-36.20 mg kg^{-1}, respectively and it ranged between 57.36-528.11 mg kg^{-1} and 15.43-45.05 mg kg^{-1}, respectively in autumn.

Keywords: Heavy metals, Istanbul, lead, soil pollution, urban soils

1. Introduction

Soil heavy metal contamination is a great concern worldwide. Even though geochemical processes poses certain level of these contaminant, the main source of pollution is originating from human activities such as mining, metal smelting and surfacing industry, traffic and combustion of fossil fuels, agricultural use of pesticides, wood protection chemicals, fertilizers and sewage sludges (Alloway, 1999; Lu et al., 2007). Heavy metals tend to spread through air and water from these anthropogenic pollution sources. Especially traffic activities generate heavy metals, particulate matter and aerosols in the urban roadway environment. Lagerwerff and Specht (1970) reported that Cd, Ni, Pb and Zn in roadside soil contamination was related to the composition of gasoline, motor oil and automobile tires and to roadside deposition of residues of these

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materials. Unlike the organic pollutants, metals do not biodegrade and are generally not mobile, therefore their residence time in the soil is thousands of years (Adriano, 2001; Vassilev et al., 2004). Urban soils are the recipients of large amounts of heavy metals from a variety of sources (Manta et al., 2002) and thus, heavy metals in urban soils have been shown to be very useful indicators of environmental pollution (Kelly et al., 1996). In areas where public gardens and parks are exposed to significant pollution levels of heavy metals may have toxic effects on plants, animals and human beings (Sánchez-Camazano et al., 1994). Pruvot et al. (2006) found a broad range of metal concentration from the upper horizons of the urban soils close to the former Pb smelter in Northern France. Pb concentrations which present in crops and vegetables were also found high due to the atmospheric emissions and deposition of the contaminated dust. It is usually known that these particles are key routes of exposure to Pb for younger children, in particular via hand-to-mouth transfer. Heavy metal accumulation in soil and in plants may also cause toxicity and affect metabolic processes of plants (Kabata-Pendias and Pendias, 1992; Bayçu et al., 2006). Providing information about heavy metal deposition in urban soils resulting from road traffic received special attention in scientific research for many years (Olivares, 2003). Urban soils are becoming more polluted with heavy metals compare to forest and agricultural soils. Topsoils from green areas in the cities show higher heavy metal concentrations than the natural ones. Distribution patterns of the pollutant metals were suggested that vehicle traffic represents the most important pollutant source for the studied environment in Palermo (Manta et al., 2002). García-Miragaya et al. (1981) reported strong Pb pollution in roadside soils at Caracas, Venezuela, due to heavy traffic of motor vehicles and utilization of leaded gasoline. Pb added to fuel as tetra ethyl and it is discharged into the environment as small inorganic Pb particles (Mengel and Kirkby, 2001). According to the same authors, only motor vehicles bought after the year 2000 use unleaded gasoline in Venezuela and consequently the same or higher levels of Pb contamination prevail. The degree of anthropogenic influence on the heavy metal distribution in soils was studied in the metropolitan area of Mexico City and nearby forested areas. Urban samples exposed to different traffic conditions were taken from a metropolitan zone with almost no industrial influence and were analyzed for Cd, Cu, Pb and Zn. The Pb levels were related to the traffic conditions and soils exposed to heavy traffic conditions had the highest Pb concentrations (Morton-Bermea et al., 2002). Pb had the highest enrichment factor in forest soils and Cu, Cd and Zn, with lower enrichment factor than Pb in polluted urban areas of Mexico City (Morton-Bermea et al., 2002). Turkey is a developing country with large majority of population inhabiting cities. Heating is mostly achieved through fossil fuel burning during the winter months and caused intensive air pollution together with industry and traffic emissions of leaded gasoline. Especially Pb is being released into the environment because of industrial uses and from the combustion of fossil fuels. The high heavy metal content in roadsides and urban soils is mostly due to the density of the traffic, which is considered one of the major sources of heavy metal contamination in Turkey, because unleaded gasoline was expensive and drivers mostly preferred leaded gasoline for many years (Aksoy et al., 2000). Istanbul is the biggest and mostly populated city of Turkey including highways with dense automobile traffic and industrial enterprises located around the city.

We aimed to determine total concentrations of Cd, Pb, Zn and Ni in the urban soils from different locations of Istanbul and to investigate the relationships with certain physicochemical properties of soils and seasonal variations. The work is intended to be a base for future investigations of exhaust emissions leading to seasonal changes in concentrations of Cd, Pb, Zn and Ni. While the production and usage of premium gasoline started to decrease, the production and usage of unleaded premium gasoline has started to increase especially in the year of 2000. According to Yener (2007), heavy metal concentrations in the soils of Istanbul are decreasing, presumably because of the initiation of unleaded gasoline in 2000 and the transfer of industrial establishments outside the city. For this reason, our investigation will bring an idea about the last basic data of urban soil pollution before the unleaded gasoline usage in Istanbul, Turkey.

2. Materials and Methods

2.1. Sampling locations

Istanbul lies both on the Asian and European continents (28° 08'-29° 55' east longitudes and 41° 33'-40° 48' north latitudes) and with the Bosphorus in between it is the most populated city of Turkey. Soil samples were taken in May and September in 1999 from nine locations including urban parks and roadsides of Istanbul under the influence of varying traffic densities and from one control site (S1) at Istanbul University Research Forest (Figure 1 and Table 1).

2.2. Sampling methods

In May and at the end of September 1999, tree soil samples were taken from different points at depth levels of 0-5 cm and 20-25 cm from 8 of the 10 sample sites. Soil samples were taken only from 2 points at site S8 and 1 point from site S9. And due to the soil being too rocky at the depth of 20-25 cm, only 2 points at site S2 and S3 were taken. In this way, a total of 104 (52 in May and 52 in September) soil samples were collected for analysis. Totally 104 core soil samples (100 cm^3) which were taken from topsoils at 20-25 cm depths they were air-dried in a room temperature.

2.3. Soil analysis

Air dried soil samples which were passed through a 2- mm sieve, were dried at 105 °C for 14-15 hours. The following physical and chemical properties were determined according to the procedures referred by Gülçur (1974): texture (particle diameter) by the Bouyoucous hydrometer method, pH in a soil–water ratio of 1:2.5 by Hanna Microprocessor pH Meter, organic carbon content by the Walkley–Black wet oxidation procedure, total nitrogen by Kjeldahl method, electrical conductivity of soil-water exracts at 1:5 ratio by InoLab Cond Level 1 brand equipment, $CaCO_3$ by Scheibler calcimeter. Cadmium (Cd), lead (Pb), zinc (Zn), nickel (Ni) and potassium (K) concentrations of the sieved (0.25-mm mesh), oven dried (105 °C, 3 days) and wet-digested (100 mg dw/5 ml 65 % HNO_3, 300 °C, 4 days) soil samples were determined by atomic absorption spectrophotometry (Shimadzu AA-680) (modified Sastre et al., 2002).

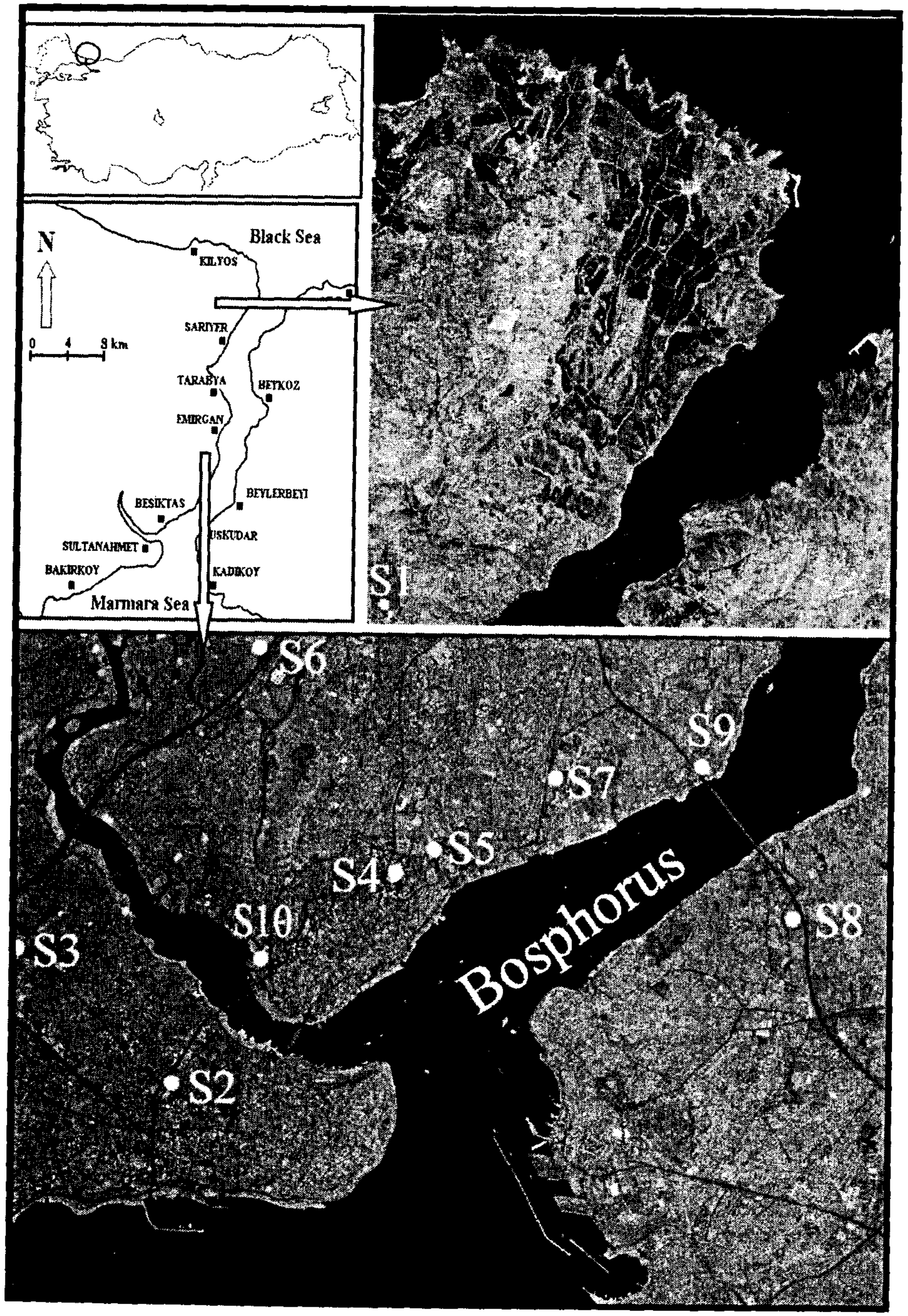

Figure 1. Location of the sampling sites.
Şekil 1. Örnek alanların yerleri.

Table 1. Distribution of sampling sites.
Tablo 1. Örnek alanların dağılımı.

No.	Location
S1	Istanbul University-Faculty of Forestry/Education and Research Forest-Bahçeköy (Control)
S2	Saraçhane Urban Park-Saraçhane
S3	Old City Walls Vicinity-Edirnekapı
S4	Taksim Urban Park-Taksim
S5	Democracy Urban Park-Maçka
S6	Çağlayan Urban Park-Çağlayan
S7	Yahya Kemal Urban Park / Barbaros Boulevard-Beşiktaş
S8	Bosphorus Bridge / Asian Side Exit (E-5 Highway)-Beylerbeyi Intersection
S9	Bosphorus Bridge / European Side Exit (E-5 Highway) vicinity
S10	Cezayirli Hasan Paşa Urban Park-Kasımpaşa

2.4. Statistical analysis

The SPSS 10.0 for Windows program was used for all statistical analyses (SPSS, Chicago, IL, USA). Correlations among different analyzed parameters were tested using Pearson's correlation coefficient. Results were considered significant at $P < 0.05$.

3. Results

In this study the soil samples taken from the control site (S1) at the Research Forest are considered to be natural. On the other hand, those taken from the urban parks and roadsides of the city are generally made up of soils and other materials brought in from elsewhere.

The soil on the sampling sites ranged from loamy clay and sandy-loamy clay. soil pH displayed a significant increase in fall comparing to season. Electrical conductivity was measured below 500 μS cm^{-1}. There was no lime in the S1 site; the highest level of lime was found at S2 (top soil) and at S3 (subsoil) (Table 2).

The organic carbon content in the soils obtained from the city and also from the control site displayed a higher level in the topsoil as compared to the subsoils in both spring and autumn. Generally, total nitrogen content of the topsoil samples taken in both seasons is higher in comparison to the subsoils. Nitrogen and potassium values for the subsoil vary between 0.05-0.2 % and 0.2-0.7 %, respectively (Table 2).

Cd concentrations were generally higher at the S2, S9 and S10 sample sites. Generally, cadmium tends to accumulate more in topsoils, however, in this study Cd accumulation at the top soils tends to remain at lower concentrations (Table 3).

Table 2. Some physical and chemical properties of the soil samples.
Tablo 2. Toprak örneklerinin bazı fiziksel ve kimyasal özellikleri.

Sampling No.	Depths	Sand (%)	Silt (%)	Clay (%)	pH (1:2.5 H_2O)		EC (1:5 H_2O $\mu S\ cm^{-1}$)		$CaCO_3$ (%)	
					Spring	Autumn	Spring	Autumn	Spring	Autumn
S1	0-5	65.0 ± 7.0	16.7 ± 5.8	18.3 ± 1.5	6.29 ± 0.68	6.68 ± 0.45	321 ± 113	428 ± 202	0.0	0.0
	20-25	49.7 ± 8.7	20.3 ± 3.2	30.0 ± 6.6	6.32 ± 0.79	6.67 ± 0.50	82 ± 31	91 ± 50	0.0	0.0
S2	0-5	72.0 ± 4.4	13.0 ± 4.4	15.0 ± 0.0	7.38 ± 0.21	8.29 ± 0.34	528 ± 150	767 ± 56	21.45 ± 5.29	22.57 ± 2.92
	20-25	74.5 ± 13.4	13.0 ± 8.5	12.5 ± 4.9	7.91 ± 0.00	8.37 ± 0.06	300 ± 19	299 ± 36	22.34 ± 3.77	27.67 ± 0.87
S3	0-5	60.3 ± 8.4	16.0 ± 3.5	23.7 ± 4.9	7.62 ± 0.24	8.23 ± 0.09	389 ± 26	734 ± 377	4.03 ± 1.20	6.49 ± 6.00
	20-25	59.5 ± 9.2	16.0 ± 1.4	24.0 ± 7.1	8.17 ± 0.25	8.16 ± 0.30	302 ± 29	376 ± 88	32.58 ± 0.87	34.22 ± 2.61
S4	0-5	58.3 ± 11.0	17.7 ± 3.5	24.7 ± 7.2	7.56 ± 0.19	7.81 ± 0.06	335 ± 18	406 ± 109	10.31 ± 6.93	10.31 ± 7.96
	20-25	57.0 ± 12.5	15.3 ± 4.0	27.7 ± 11.0	7.78 ± 0.06	8.12 ± 0.28	199 ± 32	262 ± 55	14.34 ±11.28	16.60 ± 12.75
S5	0-5	81.3 ± 5.1	10.0 ± 3.0	8.7 ± 2.3	7.13 ± 0.33	7.73 ± 0.13	396 ± 86	409 ± 47	2.18 ± 1.86	2.53 ± 0.43
	20-25	74.7 ± 1.2	11.3 ± 1.2	14.0 ± 0.0	7.91 ± 0.24	8.14 ± 0.20	196 ± 23	262 ± 59	8.74 ± 0.32	6.76 ± 2.17
S6	0-5	70.7 ± 9.1	16.0 ± 4.0	14.0 ± 5.3	7.41 ± 0.08	7.83 ± 0.09	395 ± 98	554 ± 99	8.16 ± 1.43	5.53 ± 2.14
	20-25	67.0 ± 7.5	15.7 ± 1.5	17.7 ± 6.0	7.84 ± 0.03	8.26 ± 0.11	189 ± 20	243 ± 23	9.49 ± 5.41	8.32 ± 3.05
S7	0-5	47.3 ± 8.1	20.0 ± 4.6	32.3 ± 5.1	7.26 ± 0.34	7.70 ± 0.52	389 ± 92	568 ± 468	1.98 ± 1.51	2.14 ± 1.20
	20-25	49.7 ± 19.4	20.3 ± 6.4	29.7 ± 12.9	7.21 ± 1.31	7.55 ± 1.36	134 ± 48	181 ± 86	2.80 ± 3.24	4.85 ± 4.26
S8	0-5	49.5 ± 0.7	22.0 ± 0.0	28.5 ± 0.7	7.42 ± 0.23	7.92 ± 0.09	361 ± 30	479 ± 8	8.50 ± 8.26	7.28 ± 6.81
	20-25	50.5 ± 3.5	18.5 ± 2.1	30.5 ± 0.7	7.66 ± 0.22	7.97 ± 0.20	192 ± 3	228 ± 33	9.32 ± 9.42	6.36 ± 5.51
S9	0-5	60.0	18.0	22.0	7.39	7.83	403	317	8.40	14.75
	20-25	43	25	32	7.68	8.11	209	282	2.87	13.52
S10	0-5	68.0 ± 4.6	16.3 ± 3.8	15.7 ± 1.2	7.39 ± 0.47	8.16 ± 0.27	469 ± 118	533 ± 23	7.58 ± 3.84	7.44 ± 4.63
	20-25	53.3 ± 15.0	21.0 ± 4.0	26.0 ± 13.2	7.77 ± 0.16	8.23 ± 0.11	334 ± 266	266 ± 69	6.63 ± 5.41	5.88 ± 5.69

Table 2. continued.
Tablo 2'nin devamı.

Sampling No.	Depths	Corg (%)		N (%)		K (%)	
		Spring	Autumn	Spring	Autumn	Spring	Autumn
S1	0-5	6.55 ± 1.46	6.01 ± 1.41	0.447 ± 0.109	0.473 ± 0.105	0.523 ± 0.191	0.568 ± 0.308
	20-25	1.75 ± 0.12	0.98 ± 0.42	0.142 ± 0.036	0.117 ± 0.017	0.385 ± 0.045	0.827 ± 0.289
S2	0-5	4.30 ± 0.94	4.89 ± 0.19	0.426 ± 0.080	0.480 ± 0.037	0.272 ± 0.060	0.452 ± 0.075
	20-25	1.34 ± 0.17	1.66 ± 0.17	0.108 ± 0.047	0.108 ± 0.002	0.253 ± 0.033	0.256 ± 0.110
S3	0-5	0.87 ± 0.24	0.79 ± 0.32	0.088 ± 0.007	0.100 ± 0.010	0.351 ± 0.072	0.310 ± 0.065
	20-25	0.86 ± 0.06	0.90 ± 0.11	0.077 ± 0.004	0.059 ± 0.019	0.392 ± 0.057	0.396 ± 0.179
S4	0-5	2.56 ± 0.68	3.18 ± 0.40	0.238 ± 0.033	0.288 ± 0.017	0.456 ± 0.071	0.425 ± 0.067
	20-25	0.82 ± 0.08	0.95 ± 0.23	0.109 ± 0.010	0.114 ± 0.009	0.495 ± 0.064	0.461 ± 0.086
S5	0-5	2.96 ± 1.37	3.34 ± 0.47	0.284 ± 0.108	0.320 ± 0.106	0.318 ± 0.025	0.244 ± 0.041
	20-25	0.63 ± 0.47	0.85 ± 0.54	0.069 ± 0.010	0.135 ± 0.086	0.424 ± 0.212	0.452 ± 0.131
S6	0-5	4.61 ± 2.21	6.06 ± 1.30	0.355 ± 0.198	0.477 ± 0.130	0.357 ± 0.096	0.267 ± 0.068
	20-25	0.90 ± 0.20	0.39 ± 0.09	0.099 ± 0.020	0.070 ± 0.011	0.435 ± 0.208	0.397 ± 0.228
S7	0-5	2.96 ± 0.41	4.46 ± 1.25	0.318 ± 0.080	0.419 ± 0.128	0.504 ± 0.242	0.409 ± 0.126
	20-25	0.79 ± 0.12	0.69 ± 0.17	0.080 ± 0.020	0.104 ± 0.020	0.509 ± 0.217	0.280 ± 0.048
S8	0-5	5.96 ± 0.45	5.64 ± 1.14	0.447 ± 0.028	0.470 ± 0.018	0.665 ± 0.158	0.421 ± 0.015
	20-25	1.46 ± 0.23	1.38 ± 1.02	0.151 ± 0.055	0.173 ± 0.071	0.639 ± 0.285	0.644 ± 0.211
S9	0-5	3.95	4.19	0.261	0.261	0.653	0.204
	20-25	1.14	1.14	0.109	0.112	0.667	0.325
S10	0-5	4.86 ± 1.14	5.75 ± 1.76	0.391 ± 0.067	0.531 ± 0.123	0.332 ± 0.098	0.448 ± 0.157
	20-25	1.67 ± 1.20	1.42 ± 1.38	0.139 ± 0.076	0.149 ± 0.086	0.364 ± 0.052	0.314 ± 0.033

Table 3. Total heavy metal concentrations in soil samples (mg kg^{-1}).
Tablo 3. Toprak örneklerinin toplam ağır metal konsantrasyonları (mg kg^{-1}).

Sampling No.	Depths	Cd Spring	Cd Autumn	Pb Spring	Pb Autumn	Zn Spring	Zn Autumn	Ni Spring	Ni Autumn
S1	0-5	0.49±0.25	0.04±0.07	24.87±4.20	38.53±12.72	58.02±18.05	125.39±11.69	15.40±3.40	36.07±14.01
	20-25	0.34±0.23	0.07±0.12	26.03±4.15	40.27±21.99	43.30±17.10	115.70±29.92	18.57±9.39	38.19±18.60
S2	0-5	0.28±0.13	0.72±0.22	247.23±118.43	746.49±72.56	155.48±46.23	529.11±78.82	22.90±2.74	45.05±3.16
	20-25	0.18±0.25	0.08±0.11	290.45±37.55	464.85±176.56	72.73±24.50	138.76±61.32	20.95±7.71	15.43±1.65
S3	0-5	0.16±0.10	0.12±0.15	26.63±5.93	32.87±17.17	30.27±3.11	57.36±13.35	19.57±6.60	29.04±4.60
	20-25	0.10±0.13	0.14±0.19	73.85±17.8	82.75±6.86	53.25±5.09	64.73±31.41	27.00±5.94	27.31±8.47
S4	0-5	0.06±0.06	0.26±0.28	79.80±28.54	91.80±46.82	72.00±19.71	126.78±35.60	20.53±6.33	33.51±3.59
	20-25	0.18±0.29	0.05±0.09	88.93±33.25	129.68±121.76	63.45±11.64	111.57±43.07	30.88±3.08	25.46±1.32
S5	0-5	0.15±0.23	0.08±0.06	29.53±6.36	23.23±2.74	40.38±5.49	63.71±3.56	12.27±3.91	17.55±5.22
	20-25	0.10±0.10	0.02±0.03	53.97±28.12	86.69±27.63	70.33±13.01	156.19±29.08	16.03±4.20	33.71±6.73
S6	0-5	0.18±0.09	0.33±0.12	114.63±12.00	102.37±28.30	163.75±42.77	269.46±145.60	16.72±3.91	25.51±6.76
	20-25	0.05±0.07	0.24±0.16	62.70±14.90	62.32±57.45	87.77±24.19	131.36±66.62	24.00±7.88	24.76±16.32
S7	0-5	0.15±0.03	0.23±0.06	44.13±20.44	108.39±99.69	80.48±17.59	92.76±24.64	17.80±3.56	34.28±14.60
	20-25	0.28±0.08	0.23±0.11	52.67±33.75	110.23±103.50	65.08±23.38	64.79±12.45	21.10±1.93	21.92±2.58
S8	0-5	0.23±0.32	0.31±0.23	112.40±16.83	86.50±9.76	149.90±61.94	139.46±62.37	29.90±4.45	34.47±2.90
	20-25	0.26±0.02	0.31±0.02	35.00±18.24	27.00±12.02	68.95±10.54	104.61±2.40	35.25±3.18	34.25±1.62
S9	0-5	0.33	0.12	437.90	1121.20	310.00	380.20	24.55	19.02
	20-25	0.49	0.13	445.60	126.65	113.20	321.73	36.20	20.27
S10	0-5	0.44±0.03	0.24±0.12	99.80±62.79	77.31±63.92	161.45±28.53	225.79±51.65	24.33±9.69	32.31±7.33
	20-25	0.26±0.24	0.23±0.10	123.40±134.04	63.70±49.71	125.33±83.16	135.64±73.32	27.23±1.27	31.87±1.00

Pb concentrations in the soils obtained from within the city were generally higher in comparison to the control site, except Pb concentration of S5 at 0-5 cm depth in autum. The highest concentrations of Pb for both seasons were found at sample site S9 followed by sample site S2 at 20-25 cm depth in autumn. Pb content at S9 and S2 can be categorized as "very polluted" (Table 3).

Zn concentrations in the topsoils -with the exception of a few sites- were generally higher in comparison to the subsoils and increased during autumn. The topsoil Zn values were generally 'high' at S2, S6, S8 and S10 but "very high" at S9 in spring (Table 3).

Ni content of the soils -both in spring and autumn- generally remained below the limit value, but we have also found higher concentrations in some of the samples (Table 3).

It is observed that there are seasonal variations in Cd, Pb, Zn and Ni when examined in relationship to soil characteristics and with one another (Table 4).

4. Discussion

Large amounts of heavy metals from a variety of pollutant sources –vehicle emissions, industrial wastes etc.- accumulate on the topsoil and vegetation (dry deposition) and then reach to the subsoil through rainfall (wet deposition) and leak (Sánchez-Camazano et al., 1994).

In this study, Cd accumulation in the topsoils tends to remain at lower concentrations. According to Alloway (1999), Cd content in soil mostly stays between 0.01-1 mg kg^{-1}. When evaluating the Cd content, in all the sample sites it was observed that no value exceeded 1 mg kg^{-1}. In Austria, soils having a Cd level of between 1.01-3.0 mg kg^{-1} are accepted as being "polluted" (Smidt, 2000). So, according to this data, Istanbul soils have not yet started to become polluted by Cd.

Soils having a Pb content of above 100 mg kg^{-1} are accepted as being 'polluted', while 200 mg kg^{-1} and higher is considered as "very polluted" (Smidt, 2000). During spring, the Pb concentrations in the soils of various regions of Istanbul varied between 24.87 - 445.6 mg kg^{-1}. On the other hand, in a significant number of the sites there was an increase in Pb quantity in autumn which was found to range between 23.23-1121.20 mg kg^{-1} (Table 3). The Pb contents at S9 and S2 were generally 5-6 times higher than the threshold values and can be categorized as generally "very polluted". Our results may be owing to the intensive traffic and Pb content of the exhaust gases. According to an investigation (Ona et al., 2006) carried out in the central parts of Philippines, the average soil Pb concentrations in San Fernando, Olongapo, Malolos, Balanga and Cabanatuan cities exceeded maximum value of Pb concentration (25 mg kg^{-1}) which was measured in natural soil . Only San Juan in Site 4 had a Pb concentration of > 250 mg kg^{-1}. Data gathered from the study areas showed that elevated levels of Pb in soil were due primarily to vehicular emissions and partly to igneous activity. When making a comparison with certain other cities, in autumn the average Pb concentrations in the soil of 0-5 cm depth in Istanbul which are quite higher than many other cities (e.g. Madrid, Seville, Bangkok, Hong Kong, Stockholm, Antalya) indicate that the major source of Pb contamination in urban soils is vehicular emission (Table 5).

Table 4. The relationships between the Cd, Pb, Zn, Ni concentrations and some properties of the soil samples taken from the urban sites in spring and autumn seasons (n = 52) (* Significant at $P \leq 0.05$, ** Significant at $P \leq 0.01$, *** Significant at $P \leq 0.001$).
Tablo 4. Cd, Pb, Zn, Ni konsantrasyonları ile ilkbahar ve sonbahar mevsimlerinde kentsel alandan alınan toprak örneklerinin bazı özellikleri arasındaki ilişkiler (n = 52) (* önem düzeyi $P \leq 0.05$, ** önem düzeyi $P \leq 0.01$, *** önem düzeyi $P \leq 0.001$).

	Spring											
	Sand	Silt	Clay	pH_{H2O}	EC	$CaCO_3$	N	C_{org}	K	Cd	Pb	Zn
Cd	- 0.035	0.200	- 0.067	- 0.292*	0.146	- 0.102	0.247	0.316*	0.029	1		
Pb	0.109	0.043	- 0.173	0.244	0.156	0.352**	0.074	0.082	-0.002	0.180	1	
Zn	0.093	0.166	- 0.210	0.098	0.457***	0.168	0.462***	0.494***	0.121	0.288*	0.614***	1
Ni	- 0.391**	0.398**	0.354**	0.354	- 0.125	0.271	- 0.107	- 0.117	0.345*	0.120	0.327*	0.274*
	Autumn											
	Sand	Silt	Clay	pH_{H2O}	EC	$CaCO_3$	N	C_{org}	K	Cd	Pb	Zn
Cd	- 0.008	0.071	- 0.046	0.185	0.306*	0.191	0.318*	0.269	- 0.167	1		
Pb	0.228	- 0.191	- 0.227	0.254	0.253	0.483***	0.186	0.211	- 0.108	0.379**	1	
Zn	0.272	- 0.153	- 0.299*	0.195	0.348*	0.286*	0.473***	0.451***	0.046	0.540***	0.718***	1
Ni	- 0.203	0.216	0.181	- 0.171	0.277**	- 0.109	0.347*	0.248	0.631***	0.190	0.089	0.327*

Table 5. Comparison of average heavy metal concentrations in the urban soils ($mg\ kg^{-1}$).
Tablo 5. Kent topraklarındaki ortalama ağır metal konsantrasyonlarının karşılaştırılması ($mg\ kg^{-1}$).

City		Depth (cm)	n	Cd	Pb	Zn	Ni	References
Coruna		0-5	15	0.3	309	206	28	Cal-Prieto et al. (2001)
Madrid		0-20	55		161	210	14.1	De Miguel et al. (1998)
Seville		0-10	31		137	145	21.9	Madrid et al. (2002)
		10-20	31		163	131	23.2	
Naples		0-2	173		262	251		Imperato et al. (2003)
Palermo*		0-10	70	0.68	202	138	17.8	Manta et al. (2002)
Stockholm		0-5	42	0.40	101	171	12.8	Linde et al. (2001)
Bangkok		0-5	30	0.29	47.8	118	24.8	Wilcke at al. (1998)
Hong Kong		0-10	594	2.18	93.4	168		Li et al. (2001)
Hong Kong		0-15	152	0.62	94.6	125	12.4	Li et al. (2004)
Antalya		0-5	73	1.33	36.5	189	81.5	Güvenç et al. (2003)
Istanbul	Spring	0-5	27	0.24	98.61	107.23	19.74	In this study
		20-25	25	0.21	98.69	74.75	24.64	
	Autumn	0-5	27	0.25	183.60	190.01	31.41	
		20-25	25	0.15	110.18	123.35	28.08	
Soil range				0.01-2.0	2-300	1-900	2-750	Alloway (1999)
Critical values				3-8	100-400	70-400	100	Alloway (1999)

* Median

In a classification done for Austrian soils, Zn concentrations between 21-50 mg kg^{-1} are designated as being "normal"; between 51-150 mg kg^{-1} are "above normal"; between 151-300 mg kg^{-1} are 'high'; and above 300 mg kg^{-1} are 'very high' (Smidt, 2000). When evaluating Zn content in soils in the light of this information, very few sample sites lie within the "normal" category (21-50 mg kg^{-1}). It is seen that the major portion of the soils lie within the "above normal" category ranging between 51-150 mg kg^{-1}. In comparison to other cities, the average Zn content in Istanbul soils of 0-5 cm depth are lower in spring but higher all other cities in autumn with the exception of Madrid, Coruna and Naples (Table 5). The Zn content in soil is dependent on the parent material mineralogy and its content tends to change as a result of human activity. The accumulation of Zn is mostly caused by anthropogenic sources, atmospheric deposition, mixing of sludge wastes in soils, fertilization with organic or synthetic fertilizers, liming and usage of pesticides in agriculture (Kiekens, 1999). The high amounts of Zn in the soils of Istanbul may be due to various sources of emission. As mentioned earlier the traffic at sites S2 and S9 is particularly dense. Thus, the high Zn concentrations at these two sites may be attributed to the exhaust gases. Zn may have also accumulated in soil (S10) during the production or maintenance of ships in the Golden Horn shipyard.

Ni values in soils vary between 2-750 mg kg^{-1}, with the highest value accepted as being 50 mg kg^{-1} (McGrath, 1999). Ni content in the sample soils both in spring and autumn generally remained below the 50 mg kg^{-1} limit value. However, average Ni concentrations of soil in autumn were higher in comparison with other cities except Antalya (Table 5). McGrath (1999) states that in sandy soils Ni amounts decrease, whereas in clay soils it shows an increase (Table 4).

When we evaluate the sample sites with one another it can be seen that the quantities of almost all four elements at the Saraçhane (S2), European side exit of the Bosphorus Bridge (S9) and Kasımpaşa (S10) are higher in comparison to the remaining sample sites.

Furthermore, there is also a variation in the concentrations of heavy metals in the soils in terms of season. Even if not in all the soils, a majority displayed an increase especially in Pb, Zn and Ni quantities during autumn.

From the results of analysis and comparisons among topsoil samples collected from rural, urban and mostly industrial sites in the vicinity of the Gulf of Izmit, Turkey, it was clearly shown that urban and industrial soils were contaminated more than rural soils (Yılmaz et al., 2003). According to the same authors, Cd was not detected in any of the soil samples but Pb enrichment in urban and industrial soils was thought as a result of gasoline combustion. Comparison of obtained average metal concentration levels with the world average ones indicated elevated values for Pb and Zn (37 and 72 mg kg^{-1}, respectively). Our Cd concentrations were also low but Pb and Zn levels were observed quite high compare to this investigation.

As the effects of air pollution were being examined, heavy metal contents in soils were mostly concentrated upon. However, certain physical and chemical characteristics of the soils were also evaluated. In particular, alkaline pH reactions, clay, organic matter and lime contents affect soil's cation exchange capacity and cause buffered heavy metal quantities to increase. In both spring and autumn, Zn showed positive correlations with Cd, Pb and Ni. In spring there was a positive correlation between Pb and Ni. Another positive relationship was determined between Pb and Cd in autumn. Also in spring, when other soil characteristics (sand-silt-clay proportions, EC, C_{org}, N and K) were examined with Cd and Pb concentrations, no positive or negative relationships were determined. Except that, a negative correlation between pH and Cd and a positive correlation between $CaCO_3$ and Pb were found. Again in spring, there is seen to be a positive relationship between Zn and EC, N, C_{org} content. In this season, Ni concentrations showed a negative correlation with sand and a positive correlation with silt and clay proportions (Table 4). McGrath (1999) stated decreases of Ni concentrations in sandy soils, and some increases in clay soils. We have also determined a positive correlation of Ni with K. In autumn there was a negative correlation only between clay proportions and Zn concentrations. In this season, EC and N values showed significant positive correlations with Ni, Zn and Cd. There was a positive relationship between Pb and Zn with $CaCO_3$. According to the results of the statistical analysis, there was also a positive correlation between C_{org} and Zn. In this study, neither spring nor autumn results showed a relationship between soil pH levels and heavy metal contents (except Cd in spring) (Table 4). Buffering and adsorption of the heavy metals in soil also increased with the increase of pH levels. The obtained result appears to be contrary to this general information. It must be due to the pH values of the urban soils over a narrow range (from 6.29 to 8.29). Manta et al. (2002) has also detected similar results. Heavy metal concentrations in autumn were higher then those of spring. Annual distribution of the rainfall may also affect the rise in heavy metal concentrations. According to the weather conditions, autumn and spring seasons are usually rainy in Istanbul but a dry period also exists in summer. For these reasons, heavy metals can easily leach downwards from the topsoil in wet seasons and they can be accumulated on topsoil by dry depositions in summer.

When comparing heavy metal content in the soils with either the control site or with that of other cities it can be understood that the values for Istanbul are high. Attention should especially be paid as to the rather high quantities of Pb and Zn in the some sampling sites. When considering that the number of vehicles in Istanbul is exceeding 1 million and a significant amount of leaded gasoline is consumed still, it is quite understandable why these results were obtained in such high amounts in the sampling time.

In the future studies, seasonal changes of heavy metal contents should be observed including monthly variations throughout the year. It will be appropriate to analyses yearly approximate fuel consumptions in Istanbul as these significantly affect heavy metal concentrations in soils. Comparison with data from other investigations regarding air pollution with the long-range transport of metals from other parts of the city should be under consideration (Steinnes et al., 1997). Results of urban soil research should be transferred to urban planning and development. Prognosis and simulation of changing soil properties related to urban development; atmospheric deposition; evaluation of soils in the context of urban planning and land use requirements should be also under consideration (Norra and Stüben, 2003). Various precautions may be taken in order to prevent the soils in Istanbul becoming polluted by the heavy metals. Firstly, emissions should be reduced, more restrictions should be placed on the usage of leaded gasoline. Tolerant and accumulator tree and shrub species should be used in parks and gardens within the city to withstand heavy metal contamination. Such vegetation which can absorb heavy metals from the soil and accumulate them in plant parts should be given preference -e.g. *Ailanthus, Populus, Robinia* (Bayçu et al., 2006). In such a way which is also known as phytoremediation, heavy metal contents in soil can be reduced.

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İstanbul'da Kent Topraklarının Cd, Pb, Zn ve Ni İçerikleri

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Kısa Özet

Çalışmada İstanbul'un kentsel alanından 9 ve kent dışından 1 örnekleme noktasından (kontrol) Mayıs ve Eylül 1999 tarihlerinde 0-5 cm ve 20-25 cm derinlikten toplam 104 toprak örneği alınmıştır. Bu örneklerde Cd, Pb, Zn, Ni içerikleri ile bazı toprak özellikleri incelenmiştir. Toprak özellikleri ve ağır metal içerikleri değerlendirildiğinde İstanbul kent topraklarının bir kısmının Pb ve Zn ile kirlenmeye başladığı belirlenmiştir. Pb değerlerinin ilkbaharda 24,87-445,60 mg kg^{-1}, sonbaharda 23,23-1121,20 mg kg^{-1} arasında değiştiği bulunmuştur. Ayrıca toprakların Zn ve Ni içeriklerinin ilkbaharda 30,27-310,00 mg kg^{-1} ve 12,27-36,20 mg kg^{-1}, sonbaharda ise 57,36-528,11 mg kg^{-1} ve 15,43-45,05 mg kg^{-1} arasında değiştiği belirlenmiştir.

Anahtar Kelimeler: Ağır metaller, İstanbul, kurşun, toprak kirliliği, kent toprakları

1. Giriş

Toprakların ağır metal içerikleri çevre kirliliğinin ulaştığı boyutların anlaşılmasında en önemli göstergelerdendir. Çünkü toprak en zor ve en son kirlenen yaşama ortamıdır. Ağır metallerin doğadaki konsantrasyonlarının artmasına neden olan en önemli kaynaklar fosil yakıtlar ve trafik, madencilik, tarım ve ormancılıkta kullanılan gübreler, pestisitler, odun koruma ilaçları vb, arıtma çamurları, evsel ve sanayi kaynaklı atıklar, metal işleyen endüstriler, şeklinde sıralanabilir.

Bu çalışmada öncelikle İstanbul'un çeşitli bölgelerindeki parklar ile yol kenarlarındaki toprakların toplam Cd, Pb, Zn ve Ni içeriklerinin araştırılması hedeflenmiştir. Araştırmada ayrıca toprakların bazı fiziksel ve kimyasal özellikleri ile

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yukarıda belirtilen ağır metallerin içerikleri arasındaki ilişkiler irdelenmiş ve ağır metal içeriklerinin mevsime bağlı olarak değişip değişmediği de incelenmiştir. Araştırma kurşunlu yakıt kullanımının yasaklandığı 2000 yılından önce yapılmış olup, araştırma sonuçlarının kurşun içeren yakıtların kullanımdan sonraki durumu inceleyen çalışmalara temel oluşturacaktır.

2. Materyal ve Metod

İstanbul'da Mayıs ve Eylül 1999 sonunda 1'i kontrol 10 örnek alandan, 0-5 cm ve 20-25 cm derinlik kademelerinden 104 (52 adedi Mayıs 1999, 52 adedi Eylül 1999 tarihinde) toprak örneği alınmıştır (Şekil 1 ve Tablo 1). 10 örnek alanın 8 tanesinden 3 farklı noktadan 0-5 cm ve 20-25 cm derinlik kademelerinden toprak örneği alınmıştır. S8 numaralı alanda 2, S9 numaralı alanda 1 noktadan örnek alınmıştır. S2 ve S3 numaralı örnek alanlardan 20-25 cm derinlik kademesinden çok taşlı olması sebebiyle ancak 2 noktadan örnek alınabilmiştir.

Hava kurusu halindeki toprak örnekleri öğütülüp, 2 mm lik elekten geçirilmiştir. Toprak örneklerinde tekstür (Bouyoucous hidrometre metodu ile) pH değerleri (toprak-su oranı 1:2,5 olan çözeltide), elektriksel iletkenlik (EC) (toprak-su oranı 1:5 olan çözeltide), $CaCO_3$ (Scheibler kalsimetresi ile) organik karbon miktarı (Corg) (Walkley-Black ıslak yakma yöntemi ile) toplam azot (semi-mikro Kjeldahl metodu ile) belirlenmiştir. Toprakların Cd, Pb, Zn, Ni ve K içeriklerinin belirlenebilmesi için, topraklar fırın kurusu halde %65'lik HNO_3 ile özel tüplerde berrak çözeltiler elde edilinceye kadar yakılmıştır. Cd, Pb, Zn, Ni ve K ölçümleri Atomik Absorpsiyon Spektrofotometresinde (Shimadzu AA-680) yapılmıştır.

3. Sonuçlar ve Tartışma

Örnek alanlardaki toprakların ortalama Cd içerikleri 0,02-0,72 mg kg^{-1} arasında değişmektedir (Tablo 3). Kirlenmemiş toprakların kadmiyum içerikleri çoğunlukla 0,01-1 mg kg^{-1} arasında kalmaktadır. Tüm örnek alanlarda bu değerin aşılmadığı görülmektedir.

İstanbul'un değişik bölgelerinde toprakta ortalama Pb konsantrasyonları ilkbaharda 24,87-445,60 mg kg^{-1} arasında değişmektedir. Sonbaharda ise örnek alanların önemli bir bölümünde topraktaki kurşun miktarı artmış olup, ortalama 23,23-1121,20 mg kg^{-1} arasında bulunmuştur (Tablo 3). 100 mg kg^{-1} değerinin üzerinde Pb içeren topraklar "kirlenmiş", 200 mg kg^{-1} üzerinde ise "çok kirlenmiş" olarak kabul edilmektedir (Smidt, 2000). Bu bilgilere göre trafiğin oldukça yoğun olduğu Boğaziçi Köprüsü Avrupa Yakası Çıkışında (S9) kurşun içerikleri, "çok kirlenmiş" sınıfına girmektedir. Aynı şekilde Saraçhane Parkından (S2) alınan topraklardaki Pb içeriği de oldukça yüksektir.

İncelenen toprakların ortalama Zn konsantrasyonlarının ilkbaharda 30,27-310,00 mg kg^{-1}, sonbaharda 57,36-528,11 mg kg^{-1} arasında kaldığı belirlenmiştir (Tablo 3). İncelenen toprakların önemli bir kısmı "normalden yukarı" olarak tanımlanan 51-150 mg kg^{-1} arasında çinko içermektedir. İlkbahar mevsiminde sadece Boğaziçi Köprüsü

Avrupa Yakası Çıkışında (S9) üst topraktaki çinko miktarı çok yüksekken (300 mg kg^{-1} ın üzerinde), sonbaharda bu alanın yanında S2 numaralı alanda da üst toprakta Zn konsantrasyonları çok yüksektir. Hem Pb, hem de Zn değerlerinin yüksek olduğu S2 ve S9 numaralı alanlar trafiğin yoğun olduğu bölgelerdir.

Toprakların ortalama nikel konsantrasyonları ilkbaharda 12,27-36,20 mg kg^{-1}, sonbaharda 15,43-45,05 mg kg^{-1} arasında değişmektedir (Tablo 3). Topraklardaki Ni değerleri kabul edilebilir sınır değer olan 50 mg kg^{-1}'in altındadır.

İlkbaharda ve sonbaharda Zn ile Cd, Pb ve Ni arasında pozitif bir ilişki bulunmuştur. Ek olarak sonbaharda Pb ve Cd miktarları arasında da pozitif bir ilişki mevcuttur. İlkbaharda Zn içerikleri ile toprak özelliklerinden EC, N ve Corg içerikleri arasında pozitif ilişkiler mevcuttur. Bu mevsimde Ni konsantrasyonları ise kum oranları ile negatif, toz ve kil oranları ile pozitif bir korelasyon göstermektedir. Ayrıca çalışmamızda nikel ve potasyum değerleri arasında da pozitif ilişki olduğu belirlenmiştir. Sonbaharda kil oranları ile sadece Zn konsantrasyonları arasında negatif bir korelasyon bulunmaktadır. Bu mevsimde EC ve N değerleri ile Pb haricinde incelenen diğer üç element arasında pozitif yönde anlamlı ilişkiler bulunmaktadır. Pb ve Zn ile $CaCO_3$ arasında anlamlı pozitif bir ilişki vardır. İstatistik analiz sonuçlarına göre sonbaharda Corg ile sadece Zn arasında pozitif ilişki mevcuttur (Tablo 4).

İstanbul'un bazı noktalarındaki 0-5 cm derinlikteki toprakların özellikle sonbahardaki Pb içeriklerinin diğer bazı kentlerden (Madrid, Seville, Bangkok, Hong Kong, Stockholm, Antalya)* yüksek olduğu belirlenmiştir. Yine sonbaharda 0-5 cm derinlikteki toprakların ortalama Zn içerikleri Madrid, Coruna ve Naples haricindeki kentlerden, Ni içerikleri ise Antalya haricindeki kentlerden daha yüksektir (Tablo 5).

Çalışma sonuçlarına göre incelenen noktalardan bazılarında topraklar Pb ve Zn ile kirlenmeye başlamıştır. Bu nedenle kent içindeki ve yollara yakın park ve bahçelerde ağır metal kirliliğine dayanıklı ağaç ve çalı türleri kullanılmalıdır. Topraktan yoğun şekilde ağır metal alıp biriktiren bitki türleri tercih edilmelidir. Böylece topraktan daha fazla ağır metal alınarak bu bitkilerde biriktirilebilecek ve topraktaki ağır metal konsantrasyonları fitoremediation yoluyla azaltılabilecektir.

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