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Full Length Research Paper

Heavy metals in surface soils of groves: A study from Istanbul, Turkey

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Green urban spaces and groves provide important entertainment and recreation opportunities for city residents. Many such places include historical structures, and so are also open to tourism activities. The present study determined the heavy metal contents in surface soils of some groves in Istanbul and investigated the interaction between some heavy metals (CU, Ni, Zn and Pb). In addition, the extent of the pollution was examined by calculating enrichment factors (EF) for these heavy metals. The maximum EF values for Cu and Pb were determined for soil samples from Gulhane Park (30.125 for Cu, 125.77 for Pb). The highest EF values for Zn and Ni were observed in soil samples from Fethipasha Grove (39.61 for Zn, 69.78 for Pb). In conclusion, different levels of heavy metal pollution were detected in the topsoils of the investigated groves.

Key words: Enrichment factor, grove, heavy metals, Istanbul, soil pollution.

INTRODUCTION

Soil is a complex and heterogeneous mixture of organic and inorganic matter, as well as different components that determine the physical, chemical and biological properties of the soil. There are at least 68 trace elements in soil, representing only about 0.6% of their total composition, while 12 minor and major elements —Si, Al, O, Ca, Fe, K, Ti, Mg, Mn, Na, Cr, Ni— account for the rest. However, significant local or regional imbalances (relative to gross pedological averages) may occur in the soil composition (Galinha et al., 2010). In contrast to soils in agricultural areas, soils in urban environments, particularly in parks and gardens, have a direct influence on public health that is unrelated to production of food because they easily come into contact with humans and are transferred to them, either as suspended dust or by direct contact (Mielke et al., 1999; Madrid et al., 2002).

Furthermore, even though urban soils are rarely used for food production, they receive higher than normal loads of contaminants from traffic and industrial activities in heavily industrialized cities (Madrid et al., 2002; Manta et al., 2002; Imperato et al., 2003; Chen et al., 2005). Heavy metals in soils can also generate airborne particles and dusts, which may affect the environmental air quality (Bandhu et al., 2000; Cyrys et al., 2003; Gray et al., 2003, Chen et al., 2005). Humans are exposed to dusts through three main routes: 1) ingestion, 2) inhalation, and 3) dermal absorption. In dusty environments, adults may ingest up to 100 mg dust/day (Leung et al., 2008). Children are usually exposed to greater amounts of dust than adults due to play behaviors and instances of pica (Ren et al., 2006; Chiodo et al., 2007; Cao et al., 2011). Heavy metal enrichment factors have been proposed as indicators for diffuse soil contamination. Various analytical techniques are used to measure heavy metal concentration in soils using different geochemical mapping programs. The enrichment factor can be dependent on the analytical method applied (Tarvainen and Schmidt-Thomé, 2003).

The behavior of a given element in soil (that is, the determination of its accumulation or leaching) may be established by comparing concentrations of a trace element with a reference element (Kabata-Pendias and Pendias, 1985). The obtained result is described as an enrichment factor (EF), given by the following equation:

$$EF = (C_n/C_{ref}) / (B_n/B_{ref})$$

in which C_n is content of the examined element in the soil, C_{ref} is content of the examined element in the earth's crust, B_n is content of the reference element in the soil, and B_{ref} is content of the reference element in the earth's crust. A reference element is "conservative" (that is, one in which the content in samples originates almost exclusively from the earth's crust). The most common reference elements in the literature are aluminum (Al), zirconium (Zr), iron (Fe), scandium (Sc), and titanium (Ti), although there are also attempts to use other elements such as manganese (Mn), chromium (Cr) and lithium (Li) (Loska et al., 2005). Generally, the enrichment factor is used to assess soil contamination (enrichment), and its interpretation is as follows:

EF < 2—depletion to minimal enrichment;
EF 2–5—moderate enrichment;
EF 5–20—significant enrichment;
EF 20–40—very high enrichment;
EF > 40—extremely high enrichment (Sutherland, 2000).

EF can also be used to evaluate element depletion in soil (Blaser et al., 2000). All EF values less than 1 may indicate that leaching and consumption of an element take precedence over its accumulation in soil (Loska et al., 2005). Deely and Fergusson (1994) also used Fe as reference element for the normalization of elements, because Fe content is unrelated to that of other metals.

In the present study, urban groves were chosen for sampling because their soils have usually not been cultivated for a long time and thus, they could be expected to reflect the long-term accumulation of metals in the urban environment. In this study, a general characterization is given for topsoils in the city of Istanbul. Then, the concentration data for 5 heavy metals (Pb, Cu, Zn, Ni and Cd) are presented and discussed. In order to highlight the extent and severity of contamination, heavy metal contents were compared to the mean values of the earth's crust and enrichment factors were calculated.

MATERIALS AND METHODS

Study area and soil sampling

Istanbul is a very densely populated city, located near the sea (bordered Black Sea to the north, Marmara Sea to the South and the Bosporus Strait) and is one of the largest urbanized and most densely populated areas in the world. According to the Parks Department of Istanbul Metropolitan Municipality, there are 12 groves under the control of the department. The groves, accessible to the public with their conserved patterns, cover an area of approximately 380,000 ha and host all kinds of recreation, promenade, picnic and sport activities as well as festivals (www.ibb.gov.tr).

In the present study, topsoil samples (depth=0 to 10 cm) were collected from six of the groves in Istanbul (Fethipasha, Florya Ataturk, Emirgan, Mihrabad, Osmangazi, and Gulhane Parks). The locations of the six sampling sites are shown in Figure 1. Sampling sites were selected where the most recent human perturbations were at least 10 years ago and where chemicals (such as fertilizers, pesticides) and sewage sludges have not been used. Fethipasha Grove extends from the northern Uskudar district, on the Asian side of the city, to Kuzguncuk Hill. The grove is surrounded by walls and includes vehicular and pedestrian roads, running tracks, excursion spots, cafeterias, volleyball and basketball facilities. Fethipasha Grove was designated as a natural protected area by 3-numbered Cultural and Natural Heritage Conservation Council of Istanbul. Mihrabad Grove, on the Asian side of Istanbul, extends from 1.5 km north of Kanlica to the neighborhood of Cubuklu ferry port. Surrounded by residential areas on four sides, Osmangazi Grove is located between Umraniye and Dudullu districts.

The present area was established in 1970 through an afforestation program by the Ministry of Forestry. It provides promenade, entertainment and recreation opportunities to local people. Emirgan Grove, one of the most famous groves in Istanbul, is located on the European side, between Baltalimani and Istinye districts.

Florya Ataturk Grove was established in 1937 to protect the region against strong winds and storms and to meet the health-aesthetic and entertainment-recreation needs of local people. Gulhane Park, situated to the west of Topkapi Palace, was established as an outer yard of Topkapi Palace and transformed into a Park in 1920. It has an area of approximately 100,000 m^2 (www.ibb.gov.tr). At each sampling point, three sub-samples, with a 20x20 cm surface area, were taken and then mixed to obtain a bulk sample. All the samples were collected with a stainless steel spatula and kept in PVC packages at room temperature. Stones and foreign objects were removed by hand.

Analysis

Soil samples were air dried, sieved to pass a 2 mm mesh and stored in polypropylene bottles. The pH values of the soil samples were determined following standard procedures (Page et al., 1982), using a pH in water (1:2.5 soil: water ratio) extract. pH values were read using a pH meter (Jenway 3040 Ion Analyzer). The percentages (%) of C, H, N and S in the soil samples were determined in the detailed analysis laboratory of Istanbul University. Before being sent for elemental analysis, samples were dried at 50°C for 24 h and ground to a fine powder in a quartz mortar. Subsequently, the soil samples were analyzed using Thermo Finnigan 1112 Series Flash Elemental Analyzer for determining the percentages (%) of C, H, N and S of the samples. To determine the types of heavy metal in the soil samples, samples were analyzed using an XRD (X-Ray Powder Diffraction) spectrometer in the detailed analysis laboratory of Istanbul University.

Prior to analysis, samples were dried at 50°C for 24 h and then ground to a fine powder in a quartz mortar. The "Microwave Solubilization Method for Soil" was used to determine the metal concentrations of soil samples (EPA Method 3051A, 2007). For this purpose, 0.5 g homogenous dry soil was put in teflon containers. Ultra pure 9 ml HNO_3, 3 ml HCl, and 2 ml HF were added, and the teflon containers were then closed and placed in the microwave (Berghof MWS-2 microwave-system).

They were gradually heated up to 185°C in microwave and kept at this temperature for 10 min. The samples in teflon containers were filtered (MN 640 de, 125 mm Macherey-Nagel filter paper), taken into HDPE volumetric flasks and then filled with ultra pure water until 50 ml. The metal analysis of the prepared samples was utilized ICP optical emission spectrometer (Perkin Elmer Optima 7000 DV) combined with an autosampler (Perkin Elmer S10 Autosampler). Replicated measures of a reference material (NCS Certified Reference Material, NCS ZC73002 Soil), reagent blanks, and duplicated soil samples were used to assess contamination and precision. The analytical precision, measured as relative standard deviation, was routinely between 5 and 6%, and never higher than 10%.

Figure 1. Map of sampling groves.

Statistical analysis

Simple correlation analysis was used to examine the relationship between the analyzed metals and pH. To assess the soil environment quality, an enrichment factor (EF) of each metal was attributed to each park. The EF was defined as the ratio of the heavy metal concentration in the study to the geometric means of background concentration of the corresponding metal in the earth's crust (Taylor and McLennan, 1995).

RESULTS

In the present study, pH value was found to vary between 5.34 and 6.95 for all the collected soil

Table 1. Results of XRF analysis, elemental analysis and pH values.

Sample no.	Sampling location	Predominantly	In addition	In smaller quantities	C(%)	H (%)	N (%)	pH
1	Mihrabad Grove	SiO_2, Al_2O_3, Fe_2O_3	K_2O, MgO, CaO, TiO_2	CuO, Na_2O, SO_3, P_2O_5, MnO, Cr_2O_3, BaO, ZrO_2, NiO, SrO, ZnO, Rb_2O, Cl, PbO	2.85	1.21	0.21	6
2	Osmangazi Grove	SiO_2, Al_2O_3, Fe_2O_3	K_2O, TiO_2	MgO, CaO,SO_3, BaO, CuO, Na_2O, P_2O_5, MnO, Cr_2O_3, BaO, ZrO_2, SrO, ZnO, Rb_2O, Cl, PbO, Y_2O_3, Nb_2O_5, Ga_2O_3	1.22	0.80	0.16	5.34
3	Fethipasha Grove	SiO_2, Al_2O_3, Fe_2O_3	K_2O, MgO, CaO,	TiO_2, SO_3, BaO, CuO, Na_2O, P_2O_5, MnO, Cr_2O_3, BaO, ZrO_2, SrO, ZnO, Rb_2O, Cl, PbO, Y_2O_3, NiO	5.23	1.37	0.27	6.7
4	Emirgan Grove	SiO_2, Al_2O_3, Fe_2O_3	K_2O, MgO, CaO, TiO_2	SO_3, BaO, CuO, Na_2O, P_2O_5, MnO, Cr_2O_3, BaO, ZrO_2, SrO, ZnO, Rb_2O, Cl, PbO, Y_2O_3, NiO	4.11	1.07	0.20	5.4
5	Florya Ataturk Grove	SiO_2, Al_2O_3, Fe_2O_3, CaO	K_2O, MgO, TiO_2	SO_3, BaO, CuO, Na_2O, P_2O_5, MnO, Cr_2O_3, BaO, ZrO_2, SrO, ZnO, Rb_2O, Cl, PbO, Y_2O_3, NiO	2.37	0.79	0.14	6.9
6	Gulhane Park	SiO_2, Al_2O_3, Fe_2O_3, CaO	K_2O, TiO_2	MgO, CuO, Na_2O, SO_3, P_2O_5, MnO, Cr_2O_3, BaO, ZrO_2, NiO, SrO, ZnO, Rb_2O, Cl, PbO	3.89	1.21	0.25	6.95

samples (Table 1). Accordingly, soil samples had light acidic characteristics. As a result of XRF analysis performed for each soil sample, the soil major element composition was found to be SiO_2+Al_2O_3+Fe_2O_3. In addition, compounds of K_2O, MgO, CaO, and TiO_2 were detected in many soil samples. There were also low concentrations of MgO, CaO, SO_3, BaO, CuO, Na_2O, P_2O_5, MnO, Cr_2O_3, BaO, ZrO_2, SrO, ZnO, Rb_2O, Cl, PbO, Y_2O_3, Nb_2O_5, and Ga_2O_3 in soil samples (Table 1). In the elemental analysis of soil samples, the highest content of C (5.23%) was determined in the sample from Fethipasha Grove, while the lowest content was from Osmangazi Grove (1.22%). The H content of samples varied between 0.79 and 1.37 %, and N content between 0.16 and 0.27 (%). The lowest H and N contents were determined in the samples of Florya Ataturk Grove. Concentrations of Na, Mg, Ca, K, Al, Fe, Cu, Zn, Ni, Pb, and Cd in soils of Istanbul's Groves are listed in Table 2, together with median values, standard deviations and variability ranges.

For comparison purposes, concentrations of the same heavy metals both in soil samples and unpolluted soils (with the metal concentration in the earth's crust) (Taylor and McLennan, 1995) are reported in the same table. The highest Ni and Zn contents were determined in the soil sampled from Mihrabad Grove (Table 2). The highest Cu content was observed in the sample from Florya Ataturk Grove, and the highest Pb content was in the sample from Gulhane Park. Cd was not detected in any of the samples. In comparison with the mean metal contents in the earth's crust, Cu content exceeded the mean level only in the sample from Florya Ataturk Grove; in addition, Zn content of Mihrabad and Fethipasha Grove samples, Ni content of all samples except Osmangazi Grove, and Pb content of Fethipasha and Emirgan Grove samples were higher than the mean values of the earth's crust (Table 2).

Inter-element relationships provide interesting information on heavy metal sources and pathways. Cu was only weakly correlated with Zn (r^2=0.13), Ni demonstrates good correlation with Zn (r^2=0.78), but there is no good correlation between Cu and Pb. For the correlation of Ni with Cu and Pb, r^2 values were 0.018 and 0.25, respectively. There was a weak correlation between Zn

Table 2. Concentrations (mg/kg) of elements in topsoils from the groves of Istanbul listed together with minimum, maximum and mean values, standard deviations, and the mean metal content of earth's crust (mg/kg).

Element	1	2	3	4	5	6	Min.	Max.	Mean	SD	The mean metal content of earth's crust (Taylor and McLennan, 1995)
Na	1874.4	1162.4	1585.6	1395.2	1559.76	21.92	21.92	1874.4	1266.55	653.26	
Mg	117.2	9.68	0.4	7.76	69.12	37.12	0.4	117.2	40.21	45.48	
Ca	2148	342	601.6	469.2	2620.8	15.36	15.36	2620.8	1032.83	1075.30	
K	5784	8424	7538.4	9328	9468	10.72	10.72	9468	6758.85	3572.34	
Al	2920.8	4051.2	2115.2	4249.6	994.56	12.88	12.88	4249.6	2390.71	1683.62	80400
Cu	8.56	7.36	13.52	7.12	53.76	26.8	7.12	53.76	19.52	18.347	25
Fe	3041.6	2702.4	913.6	2601.6	5409.6	1240	913.6	5409.6	2651.47	1598.56	35000
Zn	98.16	37.176	73.42	58.46	47.2	40.93	37.18	98.16	59.24	23.16	71
Ni	40.528	11.648	36.43	32.66	28.0	13.94	11.65	40.53	27.2	11.93	20
Pb	10.936	20.136	29.46	32.59	9.38	89.12	9.382	89.12	31.94	29.55	20
Cd	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.98

ND: Not Detected

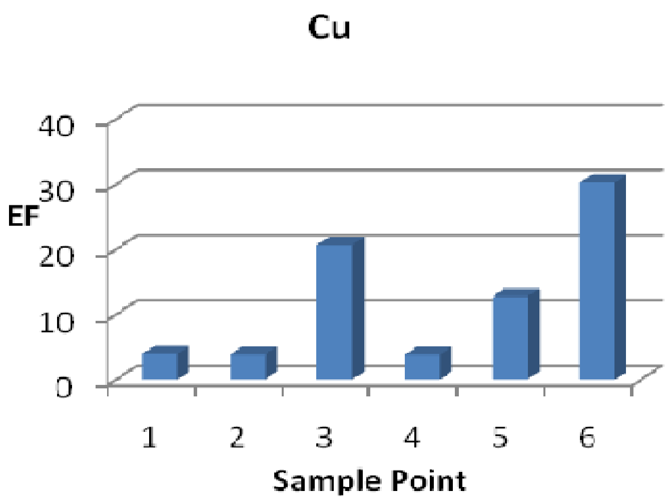

Figure 2. Enrichment factors for Cu in topsoil samples.

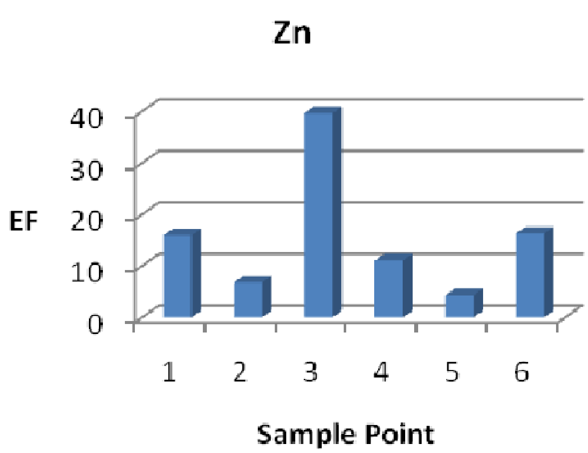

Figure 3. Enrichment factors for Zn in topsoil samples.

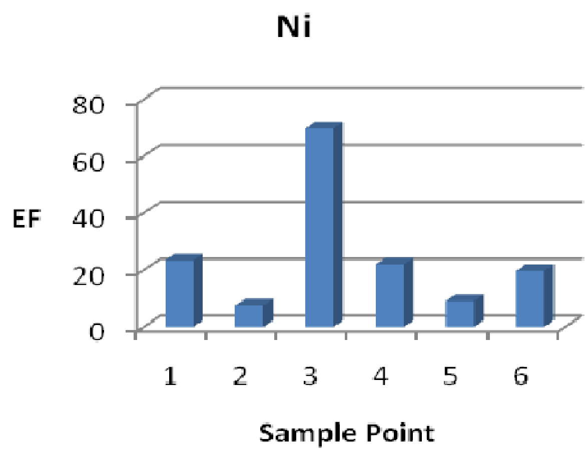

Figure 4. Enrichment factors for Ni in topsoil samples.

and Pb (r^2=0.16). Considering the correlation of four metals (Cu, Zn, Ni, Pb) with Al_2O_3 and Fe_2O_3: Cu and Pb were determined to have better correlation with these compounds (r^2=0.29 to 0.53) compared to Zn and Ni (r^2=0.009 to 0.04), which suggests Cu and Pb affinities for Al-oxides and Fe-oxides of the soils. In terms of the correlation with pH, all of the metals except Cu demonstrated rather weak correlations with pH(r^2=0.0013 to 0.13). However, there was a strong correlation between Cu and pH (r^2=0.52). Owing to the narrow pH range (5.34 to 6.95) measured in the samples, it has limited importance on the heavy metal distribution, substantially limiting their mobility because of the neutral-weakly acidic environment. Heavy metal enrichment factors (EFs) for the soil samples were calculated by assuming the mean metal concentrations in earth's crust shown in Table 2 (enrichment factors were calculated based on Fe). The results are represented in Figures 2, 3, 4 and 5.

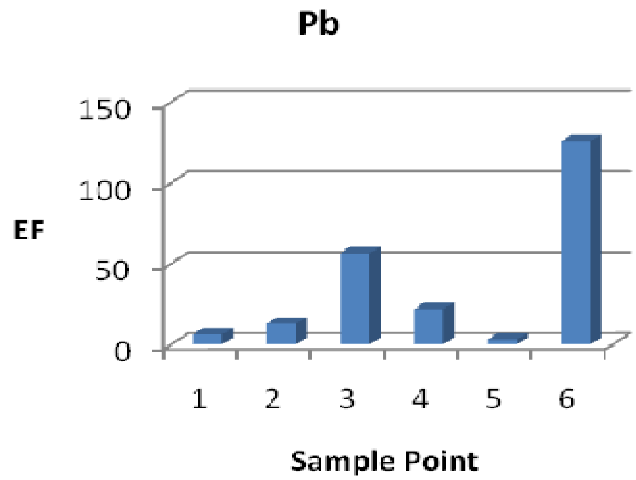

Figure 5. Enrichment factors for Pb in topsoil samples.

The highest EF values for Cu and Pb were determined in the soil samples of Gulhane Park (30.125 for Cu, 125.77 for Pb) (Figures 2 and 5). These EF values are indicative of high anthropogenic Cu pollution and extremely high anthropogenic Pb pollution. The highest EF values for Zn and Ni were determined in the soil samples of Fethipasha Grove (39.61 for Zn, 69.78 for Ni) (Figures 3 and 4). As can be concluded, there was very high anthropogenic Zn and Ni pollution in Fethipasha Grove. Considering the EF values for four heavy metals (Cu, Ni, Zn and Pb), both very high and extremely high anthropogenic pollution was detected in Fethipasha Grove (Figures 2, 3, 4 and 5). There was also very high and extremely high anthropogenic pollution in Gulhane Park. Levels of anthropogenic pollution were lower in Osmangazi and Florya Ataturk Groves compared to the other sampling locations (Figures 2, 3, 4 and 5).

DISCUSSION

The groves in Istanbul have been affected by human activities, leading to a high accumulation of heavy metals. The enrichment factor calculations indicated anthropogenic soil pollution in all of the groves. The levels of heavy metal pollution were elevated in Gulhane Park and Fethipasha Grove, which have been subjected to human activities for hundreds of years, compared to the more recently established public places (Florya Ataturk and Osmangazi Grove). In particular, with the exception of Florya Ataturk Grove, the high Pb content of the collected samples could be considered as an indicator of traffic-borne pollution.

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