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Trace element concentrations in soils along urbanization gradients in the city of Wien, Austria

Edina Simon · Andreas Vidic · Mihály Braun · István Fábrián · Béla Tóthmérész

Received: 29 February 2012 / Accepted: 11 July 2012 / Published online: 29 July 2012
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Abstract Urban soil is an important component of urban ecosystems. This study focuses on heavy metal contamination in soils of Wien (Austria) and results are compared to those for a few large European cities. We analysed the elemental contents of 96 samples of topsoil from urban, suburban and rural areas in Wien along a dynamic (floodplain forest) and a stable (oak–hornbeam forest) urbanization gradient. The following elements were quantified using ICP-OES technique: Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Pb, P, S and Zn. For heavy metals PI (pollution index) values were used to assess the level of pollution. The PI values indicated high level of pollution by Pb in the suburban and rural area of stable gradient and in the urban area of dynamic gradient; moderate level of pollution was indicated for Cd in the urban area of stable gradient. The level of pollution was moderate for Co in the suburban and rural area of the stable gradient, and for Cu in suburban area of stable gradient, and urban area of dynamic gradient. The pollution level of Zn was moderate in all areas. Urban soils,

especially in urban parks and green areas may have a direct influence on human health. Thus, the elemental analysis of soil samples is one of the best ways to study the effects of urbanization. Our results indicated that the heavy metal contamination was higher in Wien than in a few large European cities.

Keywords Pollution index · Heavy metals · ICP-OES · Urbanization

Introduction

The urban environment is an increasingly important ecosystem because the majority of the human population spends their lifetime there (De Miguel et al. 1998) and soils are directly linked with humans in urban environment (Poggio et al. 2008). The urban soil is a vital component of the urban ecosystems (Lu et al. 2007). Heavy metals in urban soils may be harmful for human health because these metals can enter the human body via food chains or inhalation of dust (Lu et al. 2007). Thus, the study of urban environment is also important from the aspect of human health risk assessment. In the last few years, many studies focused on investigation of urban soils (Lee et al. 2006; Zhang 2006).

The concentration of heavy metals in urban soil can be increased by human activities such as traffic emission (Hafen and Brinkman 1996), industrial emission (Li et al. 2008) and atmospheric deposition (Han et al. 2006). Therefore, the urbanization and industrial growth rate causes the increase of air and soil pollution level (Golia et al. 2008). Heavy metals may be sent into the air with these human activities and the metals are deposited into urban soil (Chen et al. 2005).

Wien is one of the cultural centres in Europe and the most populated city among Austrian provinces, so studying the

Responsible editor: Zhihong Xu

Electronic supplementary material The online version of this article (doi:10.1007/s11356-012-1091-x) contains supplementary material, which is available to authorized users.

E. Simon (✉) · B. Tóthmérész
Department of Ecology, University of Debrecen,
Debrecen, PO Box 71, 4010, Hungary
e-mail: edina.simon@gmail.com

A. Vidic
Department of Conservation Biology, Vegetation Ecology
and Landscape Ecology, University of Vienna,
Althanstrasse 14,
1090 Vienna, Austria

M. Braun · I. Fábrián
Department of Inorganic and Analytical Chemistry,
University of Debrecen,
Debrecen, PO Box 21, 4010, Hungary

heavy metal pollution in this area has great environmental relevance. In this study, we focus on the element concentrations in the soils of different areas along two urbanization gradients, representing urban, suburban and rural stages of urbanization. One gradient (so-called dynamic gradient) run along the Danube River and represents high habitat dynamics with regular flooding in the past and/or recent years. The other gradient was at a higher elevation, covered by forests; therefore, this is a more stable gradient compared to the flood-disturbed area.

Using the PI (pollution index), we assessed the pollution levels of Wien based on soil samples. Our hypothesis was that the element concentrations, especially heavy metal concentrations were higher in urban than suburban and rural areas. In accordance, we assumed that the level of pollution changed significantly along and the urbanization gradients. Thus, this index may be useful to assess the level of pollution. It is also expected that different altitudes and vegetations of the dynamic and stable gradients cause differences in the levels of pollution.

Materials and methods

Study area

Sampling sites were located in and around the city of Wien (Austria). Geographic coordinates of the locations of research sites are provided as advised by Shapiro and Báldi (2012). Wien is an important administrative and cultural centre of Austria. About two million people are living in this region and the population density is about 4,000 inhabitants/km². Climatically, Wien is located in a transitional zone with an average annual temperature of 10–20 °C and rainfall of 1,000–2,000 mm. The traffic emission is the most important pollution source caused by numerous roads and motorways with heavy traffic.

Two urbanization gradients were chosen to study the effects of urbanization on element concentrations in various habitats and soil types. Each gradient extended over a distance of approximately 10 km. The dynamic gradient was along the Danube River in remnant floodplain forests. All sampling areas along this gradient were characterised by their formerly high habitat dynamics and therefore display specific soil parameters and vegetation types. High soil water content (>25 %), alkaline pH value (~8) and remaining of sandy sediments or rubble are typical characteristics of alluvial forest soil (Ellenberg and Leuschner 2010). Typical tree species of floodplain forests like *Fraxinus excelsior* or *Populus alba* were present in these sampling areas. Along the gradient, three areas were selected: urban, suburban and rural area. The urban area was in the *Wiener Prater* (48°12'N, 16°24'E), near to the city centre. The suburban area was in the district of *Leopoldstadt*

(48°11'N, 16°26'E), further away from the *Wiener Prater*. The rural area (48°10'N, 16°31'E) was along the *Donau–Oder Kanal* within the national park *Donauauen*. Habitat characteristics of the three areas are shown in Fig. 1. The stable urbanization gradient started from the urban area of *Schönbrunn* (48°10'N, 16°18'E), over the suburban area (48°14'N, 16°17'E) of the *Pötzleinsdorfer Schlosspark* to the rural area (48°14'N, 16°16'E) of *Michaelerwald* within the Biosphere Reserve *Wienerwald*. This is a forested area; typical vegetation type is oakhornbeam forest. The soil is a brown forest soil. Soil water content is less than 18 %, pH values become more acid toward the rural stable gradient area (~6.4) (Fig. 1).

Soil sampling, chemical and statistical analyses

Soil samples ($N=96$) were collected along the two gradients representing urban, suburban and rural areas. At each sampling site, four repeated bulk samples were collected. All samples were taken at a depth 0–20 cm. From all samples, 50–100 g soil was dried at room temperature. After drying, stones, plant roots and residues were removed with plastic tweezers. Samples were sieved in 2-mm plastic sieve. Then the samples were homogenised with agate mortar and stored in plastic tubes until pre-treatment. For elemental analysis 0.2 g of soil samples were digested using 4.5 ml 65 % (m/m) nitric acid and 0.5 ml 30 % (m/m) hydrogen-peroxide in a microwave digestion unit (Milestone 1200 Mega) for 5 min at 300 W and for 5 min at 600 W. Digested samples were diluted to 25 ml with deionised water. Elements were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES).

PCA biplot was used to display the physicochemical parameters and major elemental concentrations of the soil of dynamic and stable gradients. In the case of PI, canonical discriminant analysis was used to assess the pollution levels in all investigated sampling areas along the dynamic and stable gradient. Homogeneity of variance was examined by Levene's test. General linear model (GLM) was applied to test the significant differences in the elemental concentrations of the studied areas. We used t test to compare the differences in the elemental concentrations between the same stages of the two gradients.

Assessment of the level of pollution

The PI is used to further assess the pollution levels of urban soils (Wei and Yang 2010). It is defined as a ratio of heavy metal concentration and the background concentration of elements (Chen et al. 2005; Faiz et al. 2009):

$$PI = c_n/B_n,$$

where c_n is the measured concentration and B_n is the background concentration. The following pollution categories

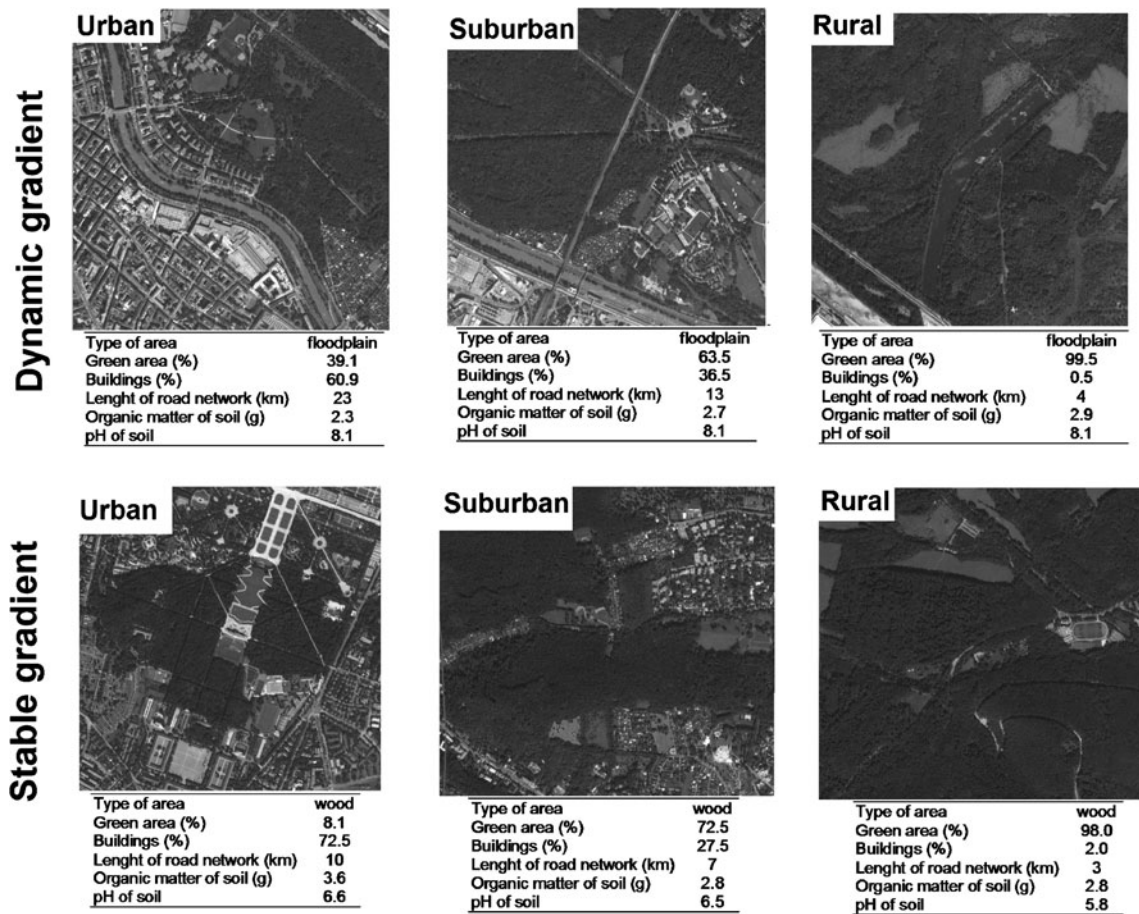


Fig. 1 Characterization of areas of dynamic and stable gradients in a plot of 1.5 by 1.5 km

are used (Lu et al. 2007): $PI \leq 1$ low level of pollution, $1 < PI \leq 2$ moderate level of contamination, $2 < PI \leq 5$ high level of pollution, $PI > 5$ extremely high level of pollution. The background concentrations of the elements were used from the Geochemical Atlas of Europe Part 1 (Salminen et al. 2006).

Results

Characterization of soil

The first principal components explained 85.3 % of the total variances; the first component (PC1) contributed 50.7 % of total variance and the second one (PC2) contributed 21.4 %. The results show the total separation of dynamic and stable gradients from each other based on soil main elemental concentration and physicochemical parameters (Fig. 2). We found that pH, P, S, Ca and Mg correlated with the PC1. This correlation indicates that the value of pH (Fig. 1) and the concentration of these elements were significantly higher in the soil of dynamic gradient which was alkaline. There were negative correlations between the Mn, Al, Fe and K concentrations and the PC1; thus, the concentrations of these elements

were significantly higher in the soil of stable gradient indicating its non-alkaline soil type. The organic matter and water content were significantly higher in the urban area of stable

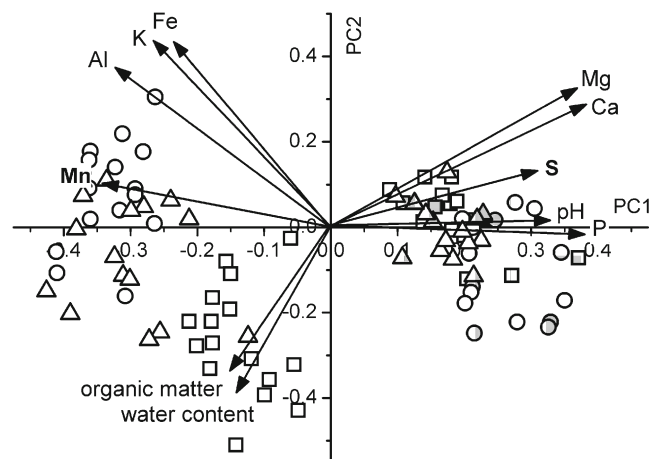


Fig. 2 Principal component biplot of the soil samples and the physicochemical parameters and main elemental concentrations of soil. Notations: open square—urban area of stable gradient, open circle—suburban area of stable gradient, triangle—rural area of stable gradient, grey square—urban area of dynamic gradient, grey circle—suburban area of dynamic gradient, grey triangle—rural area of dynamic gradient

gradient (Fig. 1) which was indicated by the negative correlation of PC2. The following elemental concentrations were obtained along the urbanization gradients. In the case of Al (urban, 7.8 g kg⁻¹; suburban, 7.9 g kg⁻¹; rural, 6.3 g kg⁻¹), Fe (urban, 13 g kg⁻¹; suburban, 14 g kg⁻¹; rural, 11 g kg⁻¹), Mg (urban, 18 g kg⁻¹; suburban, 20 g kg⁻¹; rural, 16 g kg⁻¹), Mn (urban, 346 mg kg⁻¹; suburban, 327 mg kg⁻¹; rural, 244 mg kg⁻¹) and P (urban, 618 mg kg⁻¹; suburban, 581 mg kg⁻¹; rural, 688 mg kg⁻¹) significantly higher concentration was found in the urban and suburban area of dynamic gradient than in the rural area ($P<0.05$). In the case of Ca, significant differences were found from urban to rural areas (urban, 52 g kg⁻¹; suburban, 57 g kg⁻¹; rural, 47 g kg⁻¹). Within the stable gradient, the Al (urban, 8.5 g kg⁻¹; suburban, 16 g kg⁻¹; rural, 13 g kg⁻¹), K (urban, 2.5 g kg⁻¹; suburban, 4.6 g kg⁻¹; rural, 2.8 g kg⁻¹) and Mn (urban, 501 mg kg⁻¹; suburban, 734 mg kg⁻¹; rural, 818 mg kg⁻¹) concentrations were significantly lower in the urban area than in the suburban and rural area ($P<0.05$). In the case of Fe (urban, 12 g kg⁻¹; suburban, 20 g kg⁻¹; rural, 17 g kg⁻¹), Mg (urban, 1.9 g kg⁻¹; suburban, 3.3 g kg⁻¹; rural, 2.6 g kg⁻¹) and P (urban, 422 mg kg⁻¹; suburban, 176 mg kg⁻¹; rural, 223 mg kg⁻¹) the elemental concentrations differ significantly among the different type of areas. These results indicate anomalies which may be caused by anthropogenic influences.

Pollution index

Using canonical discriminant analysis the dynamic and stable gradients were separated from each other based on PI values (Fig. 3). The following metals reached PI values

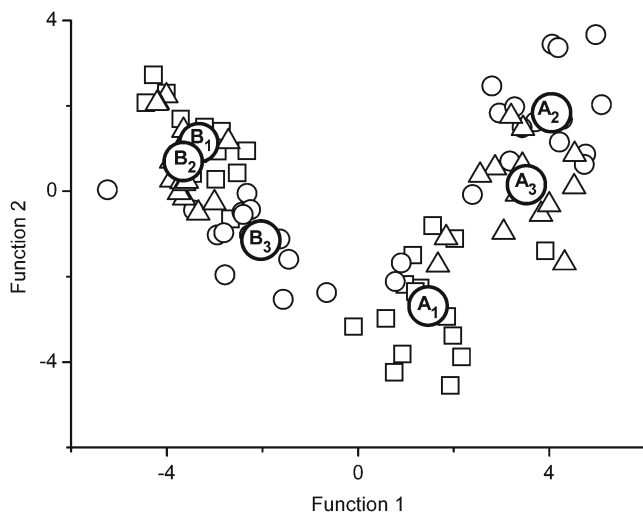


Fig. 3 Canonical discriminant analysis based on PI values. Notations: open square—urban, open circle—suburban, triangle—rural, A1—discriminant centroid of urban area of stable gradient, A2—discriminant centroid of suburban area of stable gradient, A3—discriminant centroid of rural area of Stable gradient, B1—discriminant centroid of urban area of dynamic gradient, B2—discriminant centroid of suburban area of dynamic gradient, B3—discriminant centroid of rural area of dynamic gradient

corresponding to a low level of pollution (0–1): as, Ba and Cr. The highest PI values were found for Pb in the urban area of dynamic gradient (2.0) and in the suburban area (2.15) and rural area (2.09) of stable gradient (Table 1). In the other areas, the PI values showed moderate level of pollution. PI values indicating a moderate contamination level (1–2) were detected for Cd in the urban area of stable gradient, for Co in the suburban and rural area of stable gradient and for Cu in the urban area of dynamic gradient and in the suburban area of stable gradient. In the case of Zn, the PI values indicated moderate level of pollution in all areas along both gradients. The high PI values (>1) indicated a pollution level mainly caused by anthropogenic activities.

Metal concentrations

Along the dynamic gradient, all metals differ significantly among the urban, suburban and rural areas, except for Cu (Electronic supplementary material (ESM) Table 1). We compared the metal concentrations referring to the different areas. In the case of Ba, Pb and Zn, significantly higher concentration was found in the urban areas than in the suburban and rural area (Table 2). Using the Tukey multiple comparison test, the differences were not significant between suburban and rural areas. In the case of As, Co and Cr, the metal concentration was higher in the urban and suburban area than in the rural area ($P\leq 0.05$). Difference was found in the case of Cd between suburban and rural areas. Significant differences between metal concentrations were also found along the stable gradient, except in the case of As and Cd (ESM Table 2). We found that the Cu and Zn concentrations were significantly higher in the suburban than in the urban area (Table 2). The concentrations of Ba, Co, Cr and Pb decreased in the urban area compared to the rural and suburban areas.

Differences between sampling areas among urbanization gradient

We also compared sampling areas of the same urbanization stages of the dynamic and stable gradients. In this comparison, the average metal concentration of the site ($df=3$) was analysed for all metals. We found significantly higher concentration for As, Cr, Cu, Pb and Zn in the dynamic urban area than in the stable urban area (As, $P=0.003$; Cr, $P=0.001$; Cu, $P=0.019$; Pb, $P=0.020$; and Zn, $P=0.019$). The concentrations of Ba, Co, Cu and Zn differed significantly between the dynamic and stable suburban areas (Ba, $P=0.016$; Cd, $P=0.002$; Co, $P=0.001$; Cu, $P=0.022$ and Zn, $P=0.006$). Similar results were found in the cases of rural areas, where the concentrations of As ($P=0.021$) and Cr ($P=0.001$) were higher in the rural area of the dynamic

Table 1 Pollution Index (PI) values of heavy metals in soil samples of dynamic and stable gradient

Elements	Dynamic gradient			Stable gradient		
	Urban	Suburban	Rural	Urban	Suburban	Rural
As	0.69	0.42	0.59	0.41	0.44	0.40
Ba	0.17	0.13	0.13	0.19	0.31	0.24
Cd	4.86	3.80	4.53	4.49	6.41	5.35
Co	0.84	0.67	0.88	0.63	1.41	1.22
Cr	0.84	0.70	0.91	0.33	0.55	0.48
Cu	1.05	0.87	0.94	0.62	1.23	0.92
Pb	2.00	1.68	1.40	1.66	2.15	2.09
S	0.97	1.10	0.95	0.75	0.65	0.57
Sr	0.63	0.55	0.63	0.10	0.17	0.16
Zn	1.43	1.17	1.07	1.11	1.54	1.28

gradient than that of the stable gradient. While in the case of Ba ($P=0.009$), Cd ($P=0.012$), Co ($P=0.009$) and Pb ($P=0.002$), higher concentration was found in the rural area of stable gradient than in the rural area of dynamic.

Discussion

The main elemental concentration and the physicochemical parameters of soil indicated different soil types between dynamic and stable gradients. Physical and chemical

Table 2 Concentrations of heavy metals (mean \pm SD, milligrams per kilogram) in the soil samples of dynamic and stable gradient

Elements	Urban	Suburban	Rural
Dynamic gradient			
As	8.0 \pm 0.4a	6.9 \pm 0.6a	4.9 \pm 1.4b
Ba	69 \pm 6a	52 \pm 6b	51 \pm 3b
Cd	0.2 \pm 0.1ab	0.2 \pm 0.03a	0.1 \pm 0.01b
Co	8.8 \pm 0.2a	9.2 \pm 0.8a	7.0 \pm 0.3b
Cr	80 \pm 3a	86 \pm 3a	66 \pm 7b
Cu	18 \pm 2a	16 \pm 2a	15 \pm 3a
Pb	65 \pm 10a	46 \pm 3b	55 \pm 17b
Zn	97 \pm 7a	73 \pm 4b	80 \pm 4b
Stable gradient			
As	4.8 \pm 0.1a	5.2 \pm 0.2a	4.6 \pm 0.7a
Ba	75 \pm 12a	122 \pm 14b	95 \pm 6b
Cd	0.3 \pm 0.1a	0.3 \pm 0.1a	0.3 \pm 0.1a
Co	6.5 \pm 0.5a	15 \pm 1b	13 \pm 2b
Cr	31 \pm 5a	52 \pm 2b	45 \pm 2b
Cu	11 \pm 1a	21 \pm 2b	16 \pm 3ab
Pb	54 \pm 2a	70 \pm 3b	68 \pm 3b
Zn	75 \pm 5a	105 \pm 5b	87 \pm 5ab

Different letters indicate significant differences in the ANOVA by Tukey test ($P<0.05$)

parameters of soil (pH and organic matter) affect the bio-availability of elements and heavy metals (Imperato et al. 2004). Soil pH, one of the most important factors among physicochemical parameters, is an indication of the acidity or alkalinity of soil (Gupta et al. 2008). The higher P, S, Ca and Mg concentration and the value of pH indicated floodplain soil type with rich calcium carbonate content in the dynamic gradient which is typical soil type in the area of dynamic gradient (www.eusoils.jrc.ec.europa.eu). At the same time, our results show higher Mn, Al, Fe and K concentration in the soil of stable gradient, which demonstrates the brown forest soil type in the area of stable gradient (www.eusoils.jrc.ec.europa.eu). So, these results indicated anomalies in soils among Austrian provinces. The relationship between physicochemical parameters and main elemental concentration of soil indicated that in the area of dynamic gradient, the higher pH values resulted in higher Ca and Mg concentrations in floodplain soil (Ogbodo 2011). In the case of P in this area, the effect of higher pH value was similar to that, because organic P may become soluble (Ogbodo 2011). In the case of stable gradient, lower pH value resulted in higher concentration of H⁺ ion which increases the solubility of Al, Mn and Fe concentrations (Whelan and Alexander 1986). So, in the stable gradient, the concentrations of these elements are higher than in the dynamic gradient. Acid soil results in high concentration of soluble Al, Fe and Mn. When the soil pH is lower than 6.0, the availability of the P, K Ca Na and Mg is decreased (Vangronsveld et al. 1996). Similar to an earlier study, our results indicated that most elements were more soluble or available in acid soil than in natural or slightly alkaline soils (Vangronsveld et al. 1996). Organic matter also plays important role in aggregate stability, and it influences to soil porosity. Complex porosity may results the metal exhibition with more mechanistic and diffusion through media. Soil porosity and pore size distribution are important factors to control the water and solute flow and the retention of the

chemical in soils (Ersahin et al. 2008). The pore size of alkaline soil is higher (>4 mm diameter) than in the case of non-alkaline soil (2 mm diameter) (Barral et al. 1998; van der Wal et al. 2007). The pore size of soil matrix may increase the effect of filtration which result the main elemental concentration between alkaline and non-alkaline soil (Darlington et al. 2009).

We used PI to assess the pollution level of soils in Wien. Some earlier studies reported the contents of heavy metals in European urban, suburban and rural soils. Using results of different studies, we assessed the pollution level of several European cities and compared them to our findings. In the case of Cu, higher PI values were found in the suburban area of stable gradient than in Kayseri (Aksoy and Sahin 1999) and Denizli (Celik et al. 2005). In the rural area, we found higher PI values for Cu than in Kayseri (Aksoy and Sahin 1999) and Denizli (Celik et al. 2005). In the urban areas, the PI values for Pb were lower than in other cities, expect for Warsaw (Czamowska 1980) and the rural area of Kayseri (Aksoy and Sahin 1999) and Denizli (Celik et al. 2005). The PI values of Zn were higher than in our study, expect for Denizli where the rural areas showed lower PI values than in Wien (Celik et al. 2005) (Table 3). We found lower PIs of metals in our study in Wien, especially in the urban area, compared to the other studied cities, where higher anthropogenic activities, such as mining and smelting were in and/or nearby the studied city (Aksoy and Sahin 1999; Celik et al. 2005; Douay et al. 2008). In the dynamic gradient, higher PIs of metals were found than reported in other papers; in

this area, the floodplain soil type was dominant which may be contaminated by surface and groundwater during flooding events (Bleeker and van Gestel 2007). The sediment-bound metals may be deposited in floodplain soil (Hudson-Edwards et al. 2001). This may cause higher PIs in the studied sites than in earlier studies. Our results indicated that there are clear differences in PIs among the European cities. The life quality is healthier in Wien than in many other cities because of the lack of smelting and mining activities.

Our results indicate that the pollution level differs between the investigated gradients. In the urban area of dynamic urbanization gradient, some heavy metals (Co, Cu, Pb and Zn) were found in higher concentrations than in urban area of stable gradient. A closer distance to the city centre and vicinity to Austria's most frequented highway may cause these higher concentrations at the sampling areas of dynamic gradient. On the other hand, the suburban and rural areas of the stable gradient showed higher soil contamination levels than areas of the dynamic gradient. This difference may be caused by the soil type and the anomalies in soil which is caused by anthropogenic activities. Similar to our study, Hanesch and Scholger (2002) also reported anomalies when Austrian provinces were studied, which may be related to the wind deposition of heavy industry complexes in the Czech Republic and Germany. The Wienerwald is like a strainer in west–east direction. Stohl and Kromp-Kolb (1994) reported that winds are from north-west or from southeast in Wien. The prevailing wind

Table 3 Pollution index (PI) values in European cities based on earlier studies

City	Type of area	Studied elements							Reference
		As	Cd	Co	Cr	Cu	Pb	Zn	
Kayseri	Urban		6.7			1.7	3.7	2.0	Aksoy and Sahin (1999)
	Suburban		4.4			<i>0.9</i>	2.2	1.6	
	Rural		2.4			<i>0.6</i>	<i>1.2</i>	<i>1.0</i>	
Denizli	Urban		15.1			4.0	10.3	7.4	Celik et al. (2005)
	Suburban		4.8			<i>1.0</i>	2.3	1.2	
	Rural		1.7			<i>0.5</i>	<i>1.1</i>	<i>0.2</i>	
Metaleurop	Urban	1.6	66.2	1.6	5.6	6.5	31.4	71.0	Douay et al. (2008)
Umicore	Urban	2.2	54.2	1.2	5.8	4.1	34.3	19.7	Douay et al. (2008)
Walverhampton	Urban		3.2			16.1	7.1	10.3	Fountain and Hopkin (2004)
Belgrade	Urban		31.3	2.5	6.8	7.1	10.7	3.9	
Madrid	Urban			0.6	7.2	4.1	4.9	3.1	De Miguel et al. (1998)
London	Urban		3.5			4.2	9.0	2.7	Thornton (1991)
Rome	Urban		1.1				10.1		Angelone et al. (1995)
Warsaw	Urban		2.6	0.5	3.1	1.8	<i>1.7</i>	2.4	Czamowska (1980)
Glasgow	Urban		1.9			5.6	6.6	3.0	Gibson and Farmer (1986)
Krakow	Suburban		17.9			0.4	7.4	7.7	Purchart et al. (2010)

Values indicated in italics are smaller than the PI values reported in this paper

direction is southwest in the west of Wien. The hilly terrains of Wienerwald cause this southwest wind direction. The stable gradient is situated in the west of Wien; the southwest wind direction transport metals with deposition from urban to suburban and rural areas. This may be the reason causing higher Cu, Cr, Co, Ba, Pb and Zn concentration.

Differences of heavy metal concentrations and PIs between dynamic and stable gradient reflects soil type, anthropogenic activities and different wind direction along the two gradients. In the dynamic gradient, the prevailing wind direction is northwest and southwest (Stohl and Krom-Kolb 1994). By contrasting this, the prevailing wind direction is southwest in the area of stable gradient (Stohl and Krom-Kolb 1994). The difference in soil type also cause differences in heavy metal concentration between dynamic and stable gradient. In the floodplain soil of dynamic gradient, the sediment-bound metals are deposited in the soil, which is a sink for heavy metal deposition (Hudson-Edwards et al. 2001). The deposition lasts for years or centuries, so the floodplain soil can indicate long-term contamination (Hudson-Edwards et al. 2001). In the case of brown forest soil of stable gradient, metals can accumulate in soil only from atmospheric deposition. In the case of stable gradient, industrial activities are lower than in the dynamic gradients. This also may cause differences in heavy metals and IPs between dynamic and stable gradient. Our results show that the values of PI are adequate indicators to assess the level of pollution based on soil sample analysis in urban ecosystems.

Conclusions

In this study, the element concentrations of soils were used to explore the effects of urbanization on the urban ecosystem in Wien. Using the PI, we found moderate level of contamination for Cu, Pb and Zn. Our results indicate that the traffic emission may be the major source of these metals in Wien, because of the concentration of these metals are higher than their background concentration. Our results also show that the elemental analysis of soil samples is useful to study the effects of urbanization.

Acknowledgment The research was partially supported by the TÉT Research Fund (AT-20/2008) and the OeAD (HU 17/2009). The work is supported by the TÁMOP 4.2.1./B-09/1/KONV-2010-0007 project. The project is implemented through the New Hungary Development Plan, co-financed by the European Social Fund and the European Regional Development Fund.

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