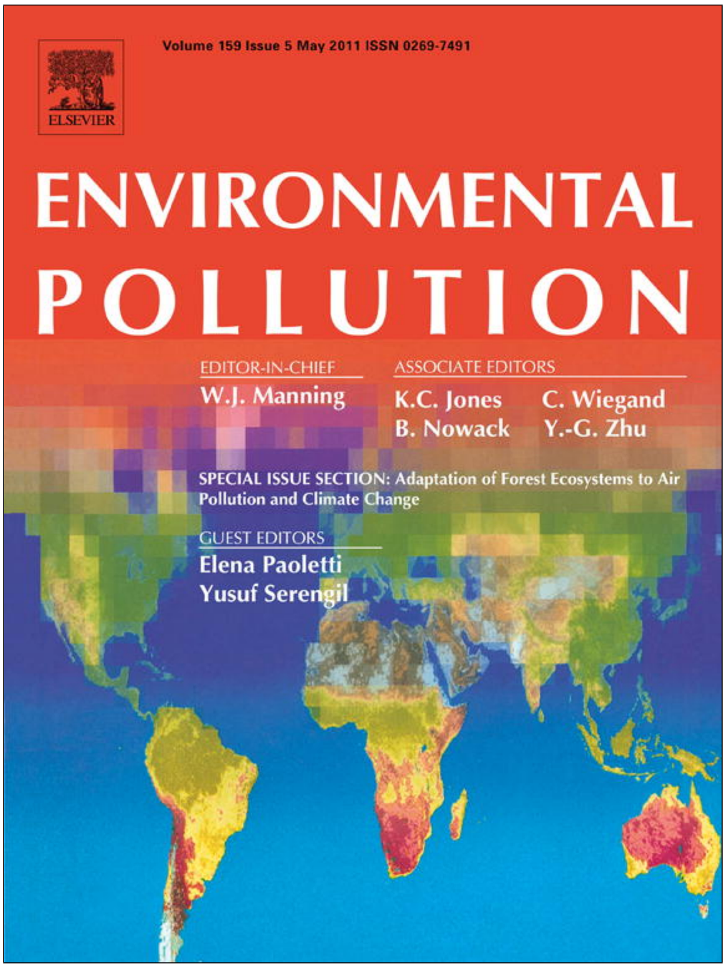
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Air pollution assessment based on elemental concentration of leaves tissue and foliage dust along an urbanization gradient in Vienna

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Studying the elements (Al, Ba, Ca, Cu, Fe, K, Mg, Na, P, S, Sr, Zn) in dust and leaves along an urbanization gradient in Wien, Austria we found that the elemental concentrations of foliage dust were significantly higher in the urban area than in the rural area for Al, Ba, Fe, Pb, P and Se, and concentrations of leaves were significantly higher in urban than in rural area for Mn and Sr.

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A B S T R A C T

Foliage dust contains heavy metal that may have harmful effects on human health. The elemental contents of tree leaves and foliage dust are especially useful to assess air environmental pollution. We studied the elemental concentrations in foliage dust and leaves of *Acer pseudoplatanus* along an urbanization gradient in Vienna, Austria. Samples were collected from urban, suburban and rural areas. We analysed 19 elements in both kind of samples: aluminium, barium, calcium, copper, iron, potassium, magnesium, sodium, phosphor, sulphur, strontium and zinc. We found that the elemental concentrations of foliage dust were significantly higher in the urban area than in the rural area for aluminium, barium, iron, lead, phosphor and selenium. Elemental concentrations of leaves were significantly higher in urban than in rural area for manganese and strontium. Urbanization changed significantly the elemental concentrations of foliage dust and leaves and the applied method can be useful for monitoring the environmental load.

1. Introduction

Plants are especially useful as biological indicators to assess air pollution because of their wide distribution (Kardel et al., 2010). Several plant species have already been applied as bioindicator (Aksoy et al., 2000; Celik et al., 2005; Baycu et al., 2006; Mingorance and Oliva, 2006). Heavy metals and inorganic contaminants can be emitted into the environment by transportation, industry, fossil fuels (Celik et al., 2005). The settling contaminants can deposit on the surface of leaves from air (Salma et al., 2001), and increase their harmful effects on human health (Temesi et al., 2003).

Some studies reported that *Acer pseudoplatanus* is used as bioindicator in air contamination of risk assessment (André et al., 2006; Watmough and Dickonson, 1996). This is a pioneer species, which is often found in contaminated and urban ecosystem in Europe (André et al., 2006). Another species, *Populus alba* grows on river banks in South and Central Europe and it is also used as ornamental urban tree (Madejón et al., 2004). This species was also applied as bioindicator in some studies (Balestrazzi et al., 2009; Chehregani and Malayeri, 2007). Both of these species can be applied as bioindicators in environmental studies because their leaves capture the dust. The leaf surface, the size of stomata and stomatal density are the most important factors controlling the amount of captured dust and heavy metal (Abbruzzese et al., 2009).

Vienna is a most populated city in Central Europe. It is characterized by vehicular traffic and industrial activity, which causes a high pollution pressure on the biota (Krommer et al., 2007). The increase of sulphur dioxide (SO_2), nitrogen oxides (NO_x), ozone (O_3) and trace elements were reported in this region (Smidt and Englisch, 1998; Zechmeister and Riss, 2009; Zechmeister et al., 2009). The aim of our study was to assess the level of environmental pollution in urban, suburban and rural areas among a gradient of urbanization in Vienna, Austria. The foliar dust may be also helpful to detect toxic elements in the air (Alfani et al., 2000); thus, we determined the elemental concentration of foliage dust samples. The elemental analysis of leaf tissues also provides information about the elemental concentration in the environment (Alfani et al., 2000). Therefore, in our study we also analysed the elemental concentration of leaf tissues to assess the anthropogenic impact along the urbanization gradient.

Our hypothesis was that the concentration of heavy metals in foliage dust and leaves tissue is lower in the rural area than urban area because of the higher level of traffic and industrial activity in the latter.

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2. Materials and methods

2.1. Study area

Sampling sites were located in and around the city of Vienna (North Eastern Austria). With around 2 million inhabitants, the capital of Austria represents one of the largest cities by population in the European Union. The city has a long historical background, with cultural and political importance, resulting in high population density and a dense urban and infrastructural network. It features lots of historical forested park facilities and adjacent national parks, but also well established traffic networks.

To assess the potential effects of air pollution caused by human impact, three sampling areas (urban, suburban and rural) were chosen along a gradient representing different levels of urbanization. The gradient extended over a distance of approximately 10 km within the boundaries of the city, and in the surrounding national park. Distance among the studied areas was at least 1 km. All sampling areas were along the Danube River in alluvial forests with typical tree species like *Acer pseudoplatanus* or *Populus alba*. Four sites, at least 50 m from each other were selected within each sampling area (urban, suburban and rural).

The urban sampling site was in the *Prater* (DU 48°12′ N 16°24′ E). This is an over 200 year old park, and a world-famous touristic attraction in Vienna. It is also a summer amusement park, the city's favourite recreation area since the 18th century (Porter and Prince, 2009). The suburban area (DS 48°11′ N 16°26′ E) was selected within the largest park facility of Vienna which covers around 600 ha and contains large remnant alluvial forests. The urban part of the park has a higher ratio of surrounding built-up area, higher pedestrian frequencies and more managed character like the suburban part.

The rural area (DR 48°10′ N 16°31′ E) was selected within the national park *Donauauen*. With 9300 ha, the national park represents one of the largest intact alluvial forests. It is protected by IUCN (International Union for Conservation of Nature) category II. Forest management was strongly reduced, traffic and visitors pressure was also decreased which resulted in a more natural and undisturbed character of this area. Human impact was only represented by an oil refinery at the border of the national park.

2.2. Leaves and foliage dust collection and preparation

Acer pseudoplatanus occurred in the three investigated areas while *Populus alba* occurred only in the rural area. Sampling was made during August 2009. Four sampling sites were selected in each of the areas and five trees were chosen randomly. After collection the leaf samples were pooled according to sampling sites within the investigated areas. Samples were collected in plastic bags and stored at +4 °C in the dark before preparation for analysis (Margitai and Braun, 2005).

The foliar dust was washed down from leaves by deionised water. The leaves were put into a 500 ml plastic box and 250 ml of deionised water was added. The samples were shaken for 10 min. The dust containing suspension was filtered through a 150 μm sieve. The leaves were washed with 50 ml deionised water again and this was filtered and added to the samples. This 300 ml of dust containing suspension was transferred into a microwave oven where the volume of water was reduced to 20–30 ml. Then the suspension was transferred into 50 ml glass beakers and the rest of water was evaporated at 105 °C. The beakers were reweighted to determine the dry weight of dust. Samples were prepared for analysis in the same vessels. They were digested using 5 ml 65% (m/m) nitric acid and 2 ml 30% (m/m) hydrogen-peroxide at 80 °C for 4 h. Digested samples were diluted to 10 ml using 1% (m/m) nitric acid.

Wet weights of leaves were determined, then the leaf samples were dried for 24 h at 105 °C and their dry mass was weighted for measuring their water content. Then, the samples were homogenised with electric mixer and stored in plastic tubes until pretreatment. For elemental analysis 0.2 g of plant tissue was 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 in 300 W and subsequently 5 min in 600 W. Digested samples were diluted to 25 ml with deionised water.

The elemental analysis was performed by inductively coupled plasma optical emission spectrometry (ICP-OES) using IRIS Intrepid II XSP instrument. We used six-point calibration procedure with multi-element calibration solution (Merck ICP multi-element standard solution IV).

2.3. Statistical analysis

Calculation was made by the SPSS/PC+ statistical software package. Concentration of data was log $(x + 1)$ transformed for the elemental concentrations of foliage dust and leaves. Homogeneity of variances was tested by Levene test. The elemental concentrations of dust and leaves in the studied areas (urban, suburban and rural) were compared with ANOVA. In case of significant differences, Tukey's Multiple Comparison test was used. Canonical discriminant Analysis (CDA) was also used for evaluating the elemental concentration of foliage dust and leaves (Zar, 1996).

3. Results

3.1. Discriminant analysis

Based on the concentrations of the measured elements of foliage dust and leaves two canonical discriminant functions were used in each cases. In the case of foliage dust, the canonical discriminant functions were marginally significant ($P = 0.06$). The first discriminant function showed a significant negative correlation with phosphorus and sulphur, but positively correlated with sodium, barium and strontium (Table 1). The concentrations of phosphorus and sulphur decreased in the urban area, while the concentrations of sodium, barium and strontium increased (Fig. 1). Significant negative correlation was found between the second discriminant function and the concentration of lead, iron, selenium, aluminium, copper, cobalt, magnesium, arsenic and calcium (Table 1). This means that the concentrations of these elements increased in the urban area.

In the case of element concentrations in leaf tissues the first discriminant function was significant ($P < 0.01$). Significant positive correlation was found between the first function and the concentration of phosphorus, potassium, cadmium, barium and lithium which indicated the increase of these elements in the urban area (Fig. 1). The concentrations of zinc, manganese, magnesium, copper and calcium positively correlated with the second discriminant function. While other elements like sodium, sulphur, iron, strontium and aluminium showed negative correlation with it. The effect of the second discriminant function was not significant; therefore, elements correlated significantly with it can be less discriminative in the comparison of different sampling sites.

Table 1
Canonical discriminant analysis of elemental concentration in dust and leaves of *A. pseudoplatanus* from urban, suburban and rural areas. Significantly correlated results are in bold face.

	Dust samples			Leaves samples	
	Discriminant function			Discriminant function	
	I	II		I	II
Eigenvalue	24.36	9.50	Eigenvalue	85.14	18.91
Percentage of variance	71.95	28.05	Percentage of variance	81.82	18.18
Cumulative percentage	71.95	100.00	Cumulative percentage	81.82	100.00
Canonical correlation	0.98	0.95	Canonical correlation	0.99	0.97
Wilks' lambda	0.00	0.10	Wilks' lambda	0.00	0.05
Chi-square	27.92	11.76	Chi-square	37.24	14.96
df	18	8	df	18	8
Significance	0.063	0.162	Significance	0.005	0.060
Structure matrix			Structure matrix		
Na	**0.663**	0.404	P	**0.412**	0.404
P	**−0.649**	−0.114	K	**0.144**	−0.016
Ba	**0.213**	−0.055	Cd	**0.141**	−0.065
Sr	**0.199**	0.172	Ba	**0.097**	0.063
S	**−0.142**	−0.009	Li	**0.049**	0.022
Pb	0.142	**−0.584**	Na	−0.295	**−0.657**
Fe	0.099	**−0.400**	S	−0.294	**−0.598**
Se	−0.299	**−0.385**	Zn	0.283	**0.453**
K	−0.142	**0.310**	Fe	0.094	**−0.396**
Zn	−0.031	**0.281**	Mn	0.031	**0.270**
Al	0.090	**−0.270**	Sr	−0.120	**−0.151**
Cu	0.038	**−0.235**	Al	−0.007	**−0.129**
Co	0.064	**−0.150**	Mg	0.031	**0.108**
Mg	0.043	**−0.120**	Cu	0.001	**0.100**
As	0.048	**−0.082**	Ca	0.040	**0.082**
Ca	−0.019	**−0.082**			

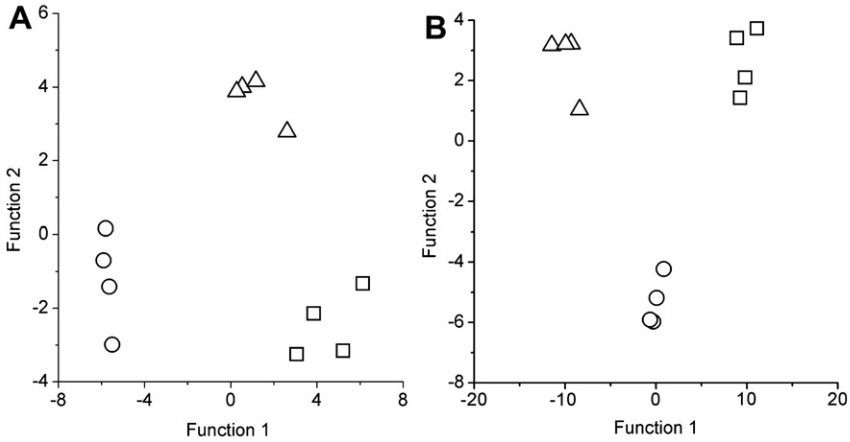

Fig. 1. Canonical discriminant analysis of elemental concentrations (mg kg^{-1}) of foliage dust (A) and leaves (B) of *A. pseudoplatanus*. Notations: open square = urban area, open circle = suburban area, open triangle = rural area.

3.2. Elemental concentrations in foliage dust and leaves of *A. pseudoplatanus*

In the case of foliage dust no significant differences were found in the concentrations of aluminium, arsenic, calcium, cobalt, copper, magnesium, sodium, sulphur, strontium and zinc along the urbanization gradient ($P > 0.05$) (Table 1, Supplementary data). The concentrations of aluminium, iron, lead, phosphorus and selenium was significantly higher in the urban areas than the in rural areas ($P < 0.05$) (Table 2). Significant differences were not found in the concentrations of these elements when the urban and suburban areas were compared ($P > 0.05$) (Table 2). In the case of potassium, we found significantly higher concentration in the rural area than in the urban area ($P < 0.05$). The concentrations of cadmium (<0.4 mg kg^{-1}), lithium (<0.6 mg kg^{-1}) and manganese (<0.9 mg kg^{-1}) were below detection limits in foliage dust.

We found significant differences in the case of cadmium, iron, potassium, manganese and strontium concentration in leaves of *A. pseudoplatanus* in the studied areas ($P < 0.05$) (Table 2, Supplementary data). Significantly higher cadmium, potassium, manganese and strontium concentrations were found in the urban area than in the rural area ($P < 0.05$) (Table 2). The iron concentration was significantly higher in the suburban area than in the urban and rural area ($P < 0.05$). The iron concentration in the leaves did not differ significantly between the urban and rural area ($P > 0.05$). In contrast to the elemental concentrations of foliage dust the arsenic (<0.8 mg kg^{-1}), cobalt (<0.5 mg kg^{-1}) and lead (<0.3 mg kg^{-1}) concentrations were below detection limits in the leaves of *A. pseudoplatanus*.

3.3. Elemental concentration of *Acer pseudoplatanus* and *Populus alba*

The measured elemental concentrations of leaves and foliage dust of *A. pseudoplatanus* and *P. alba* from rural area are shown in Table 3. *P. alba* was found only in rural area therefore, this comparison was based on the data of the rural area. Significant differences were not found between the foliage dust concentrations of *A. pseudoplatanus* and *P. alba* in the cases of all elements ($P > 0.05$). The concentration of cadmium, copper, potassium, magnesium, strontium and zinc was significantly higher in the leaves of *A. pseudoplatanus* than the leaves of *P. alba* ($P < 0.05$).

4. Discussion

We found that the elemental concentration of foliage dust and leaves of *A. pseudoplatanus* were significantly different in the urban area compared to the rural area. Wei and Yang (2010) reported that the concentration of lead was wide-spread in urban road dust and our results corroborate that report. Although, we found lower lead

Table 2
Summary statistics of elemental concentrations (mg kg^{-1} dry weight) in dust and leaves of *A. pseudoplatanus*. Different letters indicate significant differences ($P < 0.05$).

	Dust samples (mean ± SE)				Leaves samples (mean ± SE)		
	Urban	Suburban	Rural		Urban	Suburban	Rural
Al	828 ± 175^{a}	478 ± 85^{ab}	360 ± 77^{b}	Al	134 ± 18	168 ± 14	156 ± 18
As	1.6 ± 0.3	1.3 ± 0.3	1.2 ± 0.2	Ba	15.7 ± 1.2	11.2 ± 1.7	10.4 ± 1.0
Ba	37.3 ± 3.7^{a}	25.0 ± 1.5^{b}	31.1 ± 3.1^{ab}	Ca	31,786 ± 3497	23,628 ± 4841	29,640 ± 4445
Ca	29,427 ± 4258	31,518 ± 7307	25,480 ± 3973	Cd	0.12 ± 0.02^{a}	0.09 ± 0.02^{ab}	0.4 ± 0.2^{b}
Co	1.6 ± 0.5	1.0 ± 0.4	0.7 ± 0.2	Cu	5.1 ± 0.7	3.8 ± 0.9	9.5 + 2.6
Cu	30.0 ± 5.0	24.7 ± 1.6	20.1 ± 2.3	Fe	165 ± 11^{a}	219 ± 14^{b}	156 ± 19^{a}
Fe	2136 ± 414^{a}	1164 ± 226^{ab}	705 ± 156^{b}	K	9745 ± 1095^{a}	7095 ± 1224^{ab}	5897 ± 887^{b}
K	107,337 ± 8995^{a}	148,734 ± 14,818^{ab}	162,430 ± 11,309^{b}	Li	1.4 ± 0.4	0.9 ± 0.4	1.0 ± 0.3
Mg	15,574 ± 4731	11,103 ± 2745	8476 ± 1235	Mg	4683 ± 430	3744 ± 496	4832 ± 451
Na	10,124 ± 9351	1465 ± 194	5019 ± 363	Mn	211 ± 34^{a}	107 ± 14^{ab}	66 ± 10^{b}
Pb	18.0 ± 2.2^{a}	13.6 ± 0.7^{a}	5.8 ± 0.7^{b}	Na	829 ± 571	497 ± 73	439 ± 59
P	11,972 ± 2890^{a}	9075 ± 1754^{ab}	4459 ± 237^{b}	P	4306 ± 1183	2864 ± 219	4146 ± 581
Se	2.4 ± 0.2^{a}	2.0 ± 0.2^{ab}	1.4 ± 0.2^{b}	S	2182 ± 82	2099 ± 146	2515 ± 203
S	5489 ± 655	4962 ± 666	10,028 ± 2521	Sr	106 ± 19^{a}	54 ± 10^{ab}	68 ± 11^{b}
Sr	108 ± 25	97 ± 15	166 ± 20	Zn	65 ± 12	44 ± 3	182 ± 71
Zn	311 ± 53	285 ± 43	203 ± 20				

Table 3
Elemental concentrations (mg kg^{-1} dry weight) in leaves of *P. alba* and *A. pseudoplatanus* from rural area. Notices: n. d. = not detected, a = significant differences ($P < 0.05$).

Elements	Dust		Leaves	
	Populus	*Acer*	*Populus*	*Acer*
Al	341 ± 71	360 ± 77	135 ± 11	177 ± 34
As	1.4 ± 0.3	1.2 ± 0.2	n.d.	n.d.
Ba	54.1 ± 24.8	31.1 ± 3.1	9.8 ± 1.1	11.0 ± 1.9
Ca	26,806 ± 1250	25,480 ± 3973	23,842 ± 1568	35,437 ± 8205
Cd	n. d.	n. d.	0.02 ± 0.01	0.7 ± 0.3[a]
Co	1.6 ± 0.3	0.7 ± 0.2	n. d.	n. d.
Cu	21 ± 5.4	20.1 ± 2.3	5.1 ± 1.0	13.8 ± 4.2[a]
Fe	645 ± 152	705 ± 156	130 ± 8	182 ± 33
K	157,321 ± 23,198	162,430 ± 11,309	4475 ± 241	7319 ± 1504[a]
Li	n. d.	n. d.	0.7 ± 0.1	1.4 ± 0.5
Mg	12,414 ± 3996	8476 ± 1235	4079 ± 142	5584 ± 743[a]
Mn	n. d.	n. d.	76 + 16	55 + 11
Na	5078 ± 870	5019 ± 363	414 ± 67	465 ± 107
Pb	4.5 ± 1.1	5.8 ± 0.7	n. d.	n. d.
P	5990 ± 778	4459 ± 237	3548 ± 155	4744 ± 1145
Se	1.3 ± 0.1	1.4 ± 0.2	n. d.	n. d.
S	8833 ± 1490	10,028 ± 2521	2249 ± 35	2781 ± 379
Sr	202 ± 23	166 ± 20	46 ± 5	90 ± 17[a]
Zn	321 ± 107	203 ± 20	55 ± 7	309 ± 111[a]

concentration in foliage dust in the urban area compared to other studies (Christoforidis and Stamatis, 2009; Faiz et al., 2009). In contrast with earlier studies (Aksoy and Sahin, 1999; Baycu et al., 2006; Qiu et al., 2009), significantly higher cadmium concentration was found in the rural area than in the urban area. Margitai and Braun (2005) studied heavy metal concentration of foliage dust in different European cities. According to our present results the zinc concentration in foliage dust is higher in the urban area of Vienna, than in Brussels, Munich, Debrecen and Oradea (Margitai and Braun, 2005). In contrast to the results in other cities, the cadmium concentration of foliage dust was below detection limit (0.4 mg kg^{-1}) in Vienna. As Margitai and Braun (2005), we also studied the elemental concentration of sulphur which also indicates the level of air pollution. Remarkably higher sulphur concentration was found in foliage dust in Vienna than in Munich, Debrecen, Oradea and Cluj-Napoca (Margitai and Braun, 2005). In the case of iron, arsenic, copper and zinc also higher concentrations were found in foliage dust in Oradea and Cluj-Napoca than in Vienna (Braun et al., 2007). In an earlier study, Zechmeister and Riss (2009) used moss species to assess the air pollution in Austria and they reported less cadmium (0.4 μg/g), copper (5.9 μg/g), sulphur (1263 μg/g) and zinc (32.7 μg/g) concentrations compared to our results.

We also studied whether the elemental concentrations may differ between species. We compared the elemental concentrations of foliage dust and leaves of *Populus alba* and *Acer pseudoplatanus*. Our results showed that there were no remarkable differences in elemental concentrations of foliage dust between *P. alba* and *A. pseudoplatanus*. In contrast, the concentrations of cadmium, copper, potassium, magnesium, strontium and zinc were significantly higher in leaf tissues of *A. pseudoplatanus* than in *P. alba*. Madejón et al. (2004) analysed *P. alba* leaves from non-affected area, and the copper and manganese concentrations were similar to our results in leaves. The cadmium, iron and zinc concentrations were higher in their study (Madejón et al., 2004). In an earlier study, Baycu et al. (2006) reported higher zinc and cadmium concentrations in *Populus* leaves than in *Acer*. In contrast with their results, we found higher zinc and cadmium concentrations in *Acer* species than in *Populus*. The comparison of species demonstrates the effects of urbanization on elemental concentrations in leaves but the results may also depend on the morphological and anatomical parameters of leaves (Kardel et al., 2010). *Populus* leaves had small surface, small stomata and high stomatal density (Abbruzzese et al., 2009). In an earlier study, the highest stomatal density was found in *Acer* species compared to other species (Woodward and Bazzaz, 1988). Royer (2001) reported that stomatal index may be suitable to assess the paleoatmospheric CO_2 concentration. In this study *Acer* species had higher stomatal index than *Populus* species (Woodward and Bazzaz, 1988; Ceulemans et al., 1995). The higher stomatal density in *A. pseudoplatanus* leaves may be the reason why the elemental concentration of *P. alba* leaves is lower.

The high aluminium, barium, iron and lead concentrations in foliage dust and the high manganese concentration of leaf tissues characterise the air quality in the urban areas. Although there is an oil refinery company in the vicinity of Vienna, an earlier study (Zechmeister and Riss, 2009) and our study also demonstrated that the high levels of heavy metals were not caused by this activity. Therefore, the results demonstrated that the accumulation of trace elements and heavy metals depend on the traffic and urbanization levels (Mingorance and Oliva, 2006). Our results show that the effects of urbanization on elemental concentrations in foliage dust and leaves tissue are remarkable and based on elemental concentrations of these samples the effects of air pollution in urban, suburban and rural areas can be assessed.

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Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.envpol.2011.01.034.

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