ELEMENTAL CONCENTRATION IN DEPOSITED DUST ON URBAN TREE LEAVES DEPENDING ON APPLIED WASHING METHOD

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Abstract
In our study, the concentrations of elements were determined in leaves and deposited dust of *Quercus robur* and *Celtis occidentalis* which were washed with distilled water, rainwater and tap water. According to our results, each washing solutions had a significant effect on the elemental concentrations in the foliage dust. The highest concentrations of aluminum, chromium, copper, iron, manganese and zinc were detected in the foliage dust which was washed down with rainwater. The highest strontium and barium concentrations were found in the foliage dust which was washed down with tap water. We observed chromium and manganese accumulation in *Q. robur* leaves, while the concentrations of barium, copper and strontium were the highest in *C. occidentalis* leaves. Our results demonstrated the effect of rainwater on tree leaves which phenomenon occurs naturally. Rainwater may wash down the dry deposited foliage dust from the leaf surface, but it also delivers a certain concentration of elements through wet deposition.

Keywords: *Quercus robur, Celtis occidentalis*, MP-AES, tree leaves, dust

1. Introduction

Pollution of the urban areas by heavy metals is a growing problem. The sources of these contaminants are generally anthropogenic, and the main emission sources are industry, vehicular traffic and domestic heating (Simon et al., 2011; Alfani et al., 2000).

Biological indicators have been used to detect air pollutants and assess air quality in urban environment in the past few decades. The opportunity of long-term air pollution monitoring and inexpensive sampling is great advantage of these methods (Serbula et al., 2012). Elemental analysis of tree leaves and foliage dust have been proved useful to provide information about toxic elements in the air (Al-Khashman et al., 2011). Leaves are highly sensitive to air pollution, because they are directly exposed to air contaminants. Leaves can absorb gaseous pollutants via the stomata and they also passively collect dust via the trichomes on their surface. Based on this ability of the leaves, air pollution removal and air quality improvement by urban forests have been studied in various countries (Nowak et al., 2006; Escobedo – Nowak, 2009; Younis et al., 2013). The efficiency of pollutant accumulation and dust trap depends on morphological and anatomical parameters of leaves. On the other hand, leaf structure can be damaged by heavy loads of dust pollutants, which can cause stomatal clogging, leaf chlorosis and reduced photosynthetic activity (Younis et al., 2013).

Several studies have determined the levels of heavy metal contamination in washed and unwashed leaves from different species along urbanization gradients (Al-Khashman et al., 2011; Aksoy – Demirezen, 2006; Serbula et al., 2012). In these studies, leaves were divided into two subsamples. One subsample was washed with distilled water to remove atmospheric deposition, while the other subsample remained unwashed. Al-Khashman et al. (2011) determined the concentrations of iron, lead, zinc, copper, nickel and chromium in washed and unwashed leaves of *Phoenix dactylifera* L. collected from different sites with different degrees of metal contamination. Their study showed that removal of metals from the leaves was significant when comparing the amount of elements extracted from washed and unwashed leaves (Al-Khashman et al., 2011). Approximately 50% of the metals were removed by washing the leaves. The variance of elemental concentration according to the wind parameters, composition of dust and the values of pH was also reported (Al-Khashman et al., 2011). Similar observations were found by Aksoy – Demirezen (2005) when washed and unwashed leaves of *Fraxinus excelsior* L. were analysed from sites at different levels of urbanization. The amounts of metals removed by washing the leaves differed significantly among the study sites according to the varying atmospheric deposition (Aksoy – Demirezen, 2005). Generally, high levels of heavy metals were removed from leaves in the urban and roadside sites due to increased density of pollutants. Meanwhile, low levels of metals were removed by washing the leaves in the rural areas (Aksoy – Demirezen, 2006).

Simon et al. (2014) reported that *Celtis occidentalis* and *Quercus robur* are useful biological indicators for assessment of air pollution. Their study demonstrated that both of these species have large stomata size and high stomata density. The surface of *C. occidentalis* leaves is also covered by a large number of trichomes, so that this species is especially effective at decreasing the amount of dust from the air (Simon et al., 2014). The aim of the present study was to determine the elemental concentrations in leaves and deposited dust of *Q. robur* and *C. occidentalis* which were washed with distilled water, rainwater and tap water. The concentrations of aluminum, barium, chromium, copper, iron, manganese, lead, strontium and zinc were compared among different types of washing methods and between the two species.

2. Materials and methods

Study area and species

The sampling site was located in the city of Debrecen, in an urban area of the university campus with relatively light traffic around. Debrecen is the second largest city of Hungary and it lies on the flat terrain of the Great Hungarian Plain, at a height of 120 m above the sea level (Kircsi – Szegedi, 2003). Hungary itself works as a net sink for aerosols arriving from neighbor regions with the prevailing north-western wind, while the Mediterranean and Saharan aerosols can also influence air quality (Dobos et al., 2007). In urban areas, the accumulated pollution after a longer arid period can be washed out with a following intensive rainfall (Veres et al., 2013).

Leaves of *Q. robur* and *C. occidentalis* were used in this study. *Q. robur* is a large deciduous tree native to Europe and the dominant gymnosperm species in Hungary (Johnson, 2011). The surface of its leaves is smooth, as they lack trichomes. Relatively low stomata density and large stomata size was found in the leaves of *Q. robur* (Simon et al., 2014). *C. occidentalis* is a deciduous tree native to North America, but it is widely used in Hungary as street tree in cities and towns, because of its high tolerance for urban conditions (Johnson, 2011). *C. occidentalis* leaves have a high dust absorbing capability because of their high trichome density (Simon et al., 2014).

From the two species 150-150 leaves were collected on 1st September 2015.

After collection, leaves of both species were randomly divided into tree subsamples for the purpose of washing them with different types of washing solutions (distilled water, rainwater and tap water). The rainwater was collected in a plastic container from August to September 2015. Samples were stored in plastic bags at +4°C in the dark before preparation for analysis.

Sample preparation and elemental analysis

Foliage dust was washed down from leaves with distilled water, rainwater and tap water. Leaves were put into a 500 ml plastic box and 250 ml of the different type of washing solution (distilled water, rainwater and tap water) was added. Then the samples were shaken for 10 minutes. The dust containing suspension was filtered through a 150 µm sieve, and then the leaves were washed again with 50 ml of the same washing solution. This was also filtered and added to the samples. This 300 ml suspension was transferred into a microwave oven, where its volume was reduced to 20-30 ml. After the suspension was transferred into 50 ml glass breakers, the rest of the water was evaporated at 105 °C. The breakers were reweighted to determine the dry weight of foliage dust. Samples were prepared for analysis in the same vessels. They were digested using 4 ml 65% (m/m) nitric acid, 0.5 ml 30% hydrogen-peroxide and 2 ml of distilled water at 80 °C for 4 hours. Digested samples were diluted to 10 ml using 1% (m/m) nitric acid.

Leaf samples were dried at 60 °C and then they were homogenized with electric mixer. For elemental analysis 0.2 g of leaf tissue was digested using 4 ml 65% (m/m) nitric acid and 1 ml 30% hydrogen-peroxide in a microwave digestion unit. Digested samples were diluted to 25 ml with distilled water (Simon et al., 2011).

Microwave plasma-atom emission spectrometry (MP-AES, Agilent) was used during the elemental analysis. A six-point calibration procedure was used with multi-element calibration solution. The concentrations of aluminum, barium, chromium, copper, manganese, iron, lead, strontium and zinc were determined in the foliage dust and leaves tissue samples.

Statistical analysis

Calculations were performed by the SPSS/PC+ statistical software package. Data of elemental concentrations of foliage dust and leaves was log (x + 1) transformed for statistical analysis. For the comparison of elemental concentrations in cases of different washing solutions, ANOVA and Canonical Discriminant Analysis (CDA) were used. Homogeneity of variances was tested by Levene test. When distribution of variances was not homogeneous, Kruskal-Wallis test was applied. In case of significant differences, Tukey's Multiple Comparison test was used.

3. Results

Discriminant analysis

Based on the elemental concentrations in foliage dust and leaves, two canonical discriminant functions were used in both cases. In the case of foliage dust, CDA showed a total separation of the three washing method (Fig. 1a.). Both discriminant functions were significant ($P < 0.001$). The first function showed significant positive correlation with the concentration of chromium ($r = 0.320$), copper ($r = 0.285$), manganese ($r = 0.230$), iron ($r = 0.220$), aluminum ($r = 0.166$) and lead ($r = 0.121$). These correlations indicated that these elements were found in the lowest concentrations in the foliage dust which was washed down with tap water. The second discriminant function correlated positively with the concentrations of zinc ($r = 0.653$), strontium ($r = 0.397$) and barium ($r = 0.299$). The concentrations of these elements were the highest in foliage dust which was washed down with rainwater. Meanwhile, the concentrations of these elements were the lowest in the foliage dust which was washed down with distilled water.

In the case of elemental concentrations in leaf tissues, the first canonical discriminant function was significant (P = 0.001), which correlated negatively with the concentration of zinc (r = -0.506) and positively with strontium concentration (r = 0.015) (Fig. 1b.). This means that the concentration of zinc was the highest in the leaf tissue which was washed with tap water, while samples which were washed with distilled water had the highest concentration of strontium. Positive correlation was found between the second discriminant function and the concentrations of aluminum (r = 0.783), iron (r = 0.731), copper (r = 0.473), manganese (r = 0.422), barium (r = 0.413) and chromium (r = 0.340). This indicated that the applied washing methods had a slight effect on concentrations of these elements.

Variation of the elemental concentrations in foliage dust based on washing methods

In the case of foliage dust, significant differences were found in the concentrations of aluminum (P < 0.001), barium (P < 0.001), chromium (P < 0.001), copper (P < 0.001), iron (P < 0.001), manganese (P < 0.001), lead (P < 0.001), strontium (P < 0.001) and zinc (P < 0.001), when comparing washing methods. The concentrations of aluminum, chromium, copper, iron, manganese and zinc were significantly higher in the foliage dust which was washed down with rainwater. In the case of chromium, copper, iron and manganese, the concentrations of these elements were lower in samples which were washed with tap water than with distilled water. However, the aluminum and zinc concentrations did not differ significantly between these two washing methods. Significant differences were found in the concentrations of barium and strontium (P < 0.001) among all the studied washing solutions. The foliage dust washed down with tap water contained the highest concentrations of these elements; while the dust was washed down with distilled water contained the lowest. The lead concentration did not differ between the rainwater and distilled water methods, but it was below detection limits in samples treated with tap water (Table 1).

Significant difference was found between the foliage dust washed down from *Q. robur* and the *C. occidentalis* in the concentrations of barium (P<0.001) and strontium (P<0.05). The barium concentration was higher in the foliage dust from *Q. robur* than from *C. occidentalis* in the case of all washing methods. In the case of distilled water and rainwater, the dust from *Q. robur* leaves had significantly lower concentrations of strontium than the *C. occidentalis* leaves. Meanwhile, when tap water was used for

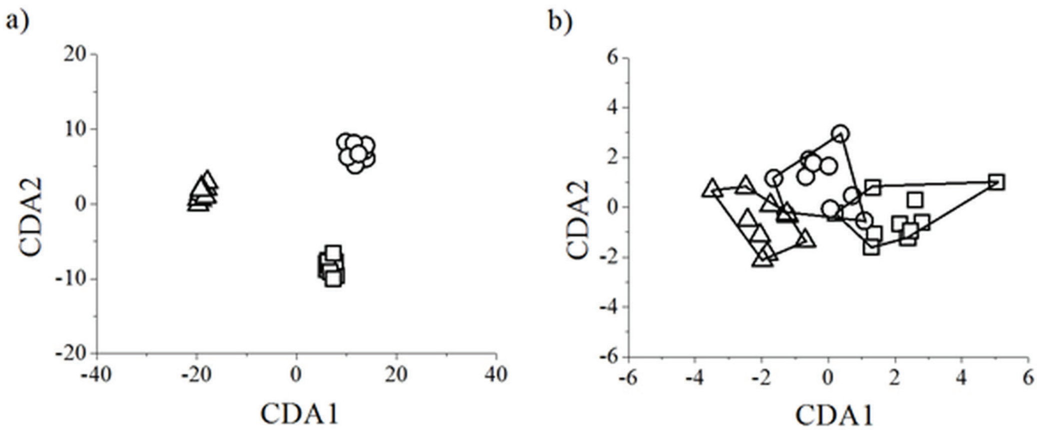

Fig. 1. Canonical discriminant analysis of elemental concentrations in foliage dust (a) and leaf tissue (b). Notations: open square = distilled water, open circle = rainwater, open triangle = tap water

washing, higher strontium concentration was found in the foliage dust on *C. occidentalis* leaves than on *Q. robur*.

Variation of the elemental concentrations in leaf tissue based on washing methods

Significant differences were found in aluminum ($P<0.05$), iron ($P<0.05$) and zinc ($P<0.001$) concentrations in leaf tissue, when comparing washing methods. The concentrations of aluminum and iron were the highest in the leaves which were washed with rainwater, while there was no significant difference between the distilled water and the tap water methods. In case of zinc, the concentration did not differ in the leaves when rainwater and tap water was used for washing, but the concentration of zinc was significantly higher than in the leaves washed with distilled water ($P<0.001$) (Table 2.).

In the case of leaf tissue, the concentration of most elements differed significantly by species. The concentrations of chromium ($P<0.001$) and manganese ($P<0.001$) were significantly higher in the leaves of *Q. robur* than *C. occidentalis*. Meanwhile, higher barium ($P<0.05$), copper ($P<0.001$) and strontium ($P<0.001$) concentrations were found in *C. occidentalis* leaves than *Q. robur*. In the case of zinc, the concentration was significantly higher in the leaves of *Q. robur* when distilled and tap water was used for washing. When rainwater was used for washing, the zinc concentration was higher in the leaves of *C. occidentalis* than *Q. robur*.

4. Discussion

In our study, the effects of different washing solutions were investigated on the elemental concentrations in foliage dust and leaf tissue. Distilled water, rainwater and tap water were used to wash down leaf samples as part of preparation for elemental analysis. Our results show that each washing method had a significant effect on the elemental concentrations of elements in the foliage dust. This can be explained with the composition of the samples eventually analyzed, which contained all the elements present in 300 ml of the washing solutions used at the sample preparation, along with the original amount of elements in the foliage dust. The highest concentrations of aluminum, chromium, copper, iron, manganese and zinc were detected in the foliage dust which was washed down with rainwater. This may be the consequence of the slightly acidic character of rainwater, which has a positive effect on the solubility and mobility of metals. Metals are emitted into the atmosphere through anthropogenic activities such as vehicular traffic in the means of brake and tire wear (Apeagyei et al., 2011). Iron, copper, chromium and zinc are typically vehicle-related metals which are present in the road dust and in the atmosphere, and they can be detected in the rainwater as well (Veres et al., 2013).

The highest strontium and barium concentrations were found in the foliage dust which was washed down with tap water. In a recent study, Simon et al. (2014) have measured the concentrations of air contaminants in foliage dust of *Q. robur* and *C. occidentalis* among other species. The concentrations of all elements in the foliage dust of *Q. robur* were similar to their findings. In comparison with their results, we have found slightly higher iron, lead and zinc concentrations in the case of *C. occidentalis* (Simon et al. 2014).

Significant differences were found between *Q. robur* and *C. occidentalis* only in the barium and strontium concentrations. According to our results, the washing solutions had a much greater effect on the elemental concentrations in foliage dust than the different species. Several studies have shown, that the amount of captured dust on leaves can be influenced by morphological and anatomical parameters (Serbula et al., 2012; Simon et al., 2014), but generally these conditions does not have a significant effect on the elemental composition of foliage dust.

Table 1. Elemental concentrations in foliage dust (mg kg^{-1}, mean ± SE)

Species	Washing solution	Al	Ba	Cr	Cu	Fe	Mn	Pb	Sr	Zn
Q. robur	distilled water	2605 ± 208	79.6 ± 2.3	10.1 ± 0.5	59.9 ± 1.5	4851 ± 484	460 ± 47	14.9 ± 1.5	36.1 ± 1.7	473 ± 27
	rainwater	5709 ± 501	134.1 ± 9.2	13.6 ± 1.1	123.3 ± 3.6	9832 ± 1113	1183 ± 34	23.3 ± 2.4	67.9 ± 8.9	6037 ± 261
	tap water	1460 ± 150	191.9 ± 6.3	2.8 ± 0.1	27.2 ± 1.8	1243 ± 109	140 ± 13	0.0 ± 0.0	611.8 ± 21.2	549 ± 66
C. occiden-talis	distilled water	2800 ± 625	62.3 ± 3.2	9.3 ± 0.7	41.8 ± 1.7	5320 ± 1258	387 ± 60	14.6 ± 1.0	52.7 ± 4.3	447 ± 36
	rainwater	5502 ± 312	104.3 ± 7.7	12.4 ± 0.8	114.9 ± 12.7	9570 ± 734	787 ± 44	21.9 ± 1.9	101.1 ± 9.5	6120 ± 798
	tap water	1057 ± 265	162.7 ± 5.8	2.4 ± 0.5	16.5 ± 0.4	1210 ± 428	66 ± 15	0.0 ± 0.0	529.8 ± 25.2	433 ± 16

Table 2. Elemental concentrations in leaf tissue (mg kg^{-1}, mean ± SE)

Species	Washing solution	Al	Ba	Cr	Cu	Fe	Mn	Sr	Zn
Q. robur	distilled water	168 ± 14	39.8 ± 4.3	0.7 ± 0.1	5.8 ± 0.2	208 ± 13	567 ± 58	24.3 ± 1.8	23.5 ± 2.8
	rainwater	243 ± 45	37.6 ± 4.3	1.0 ± 0.3	6.4 ± 0.2	257 ± 32	692 ± 43	25.0 ± 1.6	32.1 ± 2.0
	tap water	196 ± 14	35.7 ± 6.3	0.7 ± 0.0	6.8 ± 0.1	225 ± 12	620 ± 71	25.4 ± 2.6	51.0 ± 4.4
C. occidentalis	distilled water	218 ± 26	49.0 ± 7.5	0.3 ± 0.1	7.8 ± 0.4	242 ± 21	247 ± 71	154.4 ± 2.1	15.1 ± 3.2
	rainwater	399 ± 81	53.1 ± 5.8	0.4 ± 0.2	8.9 ± 0.3	369 ± 57	355 ± 55	145.7 ± 4.5	39.6 ± 4.7
	tap water	206 ± 55	33.6 ± 1.5	0.2 ± 0.1	6.9 ± 0.4	228 ± 43	132 ± 12	134.1 ± 6.8	25.9 ± 2.1

The washing methods influenced significantly the aluminum, iron and zinc concentrations in leaf tissues. Leaves which were washed with rainwater had significantly higher aluminum and iron concentrations compared to the distilled water and tap water. These are among the most common elements in the earth's crust and anthropogenic emissions. Thus, the rainwater contains many of these elements in dissolved forms or as solid particles, which are deposited on the leaf surface in the drying procedure after washing the leaves with rainwater.

When comparing the elemental concentrations of leaf tissues, we found that the different species had significant effects on most of the studied metals. We observed chromium and manganese accumulation in *Q. robur* leaves, while the concentrations of barium, copper and strontium were the highest in *C. occidentalis* leaves. Our findings are similar to the result of an earlier study of Baranyai (2012). They have also studied the elemental composition of *Q. robur* and *C. occidentalis* leaves in Debrecen. The concentrations of barium, copper, iron, manganese, strontium and zinc gained by their investigation are very similar to our results. They also recommended using these two species in biomonitoring researches, as they accumulated air pollution contaminants at a high ratio (Baranyai 2012).

5. Conclusions

The elemental concentration of both *Q. robur* and *C. occidentalis* leaf tissue did not differ significantly when washed with tap water and distilled water with the exception of zinc. This may indicate that tap water can be used instead of distilled water during sample preparation for the analysis of the other elements. However, the concentration of elements in the foliage dust varied significantly depending on the washing method, therefore in this case, the usage of rain or tap water is not recommended.

Our results also demonstrate the effect of rainwater on tree leaves which phenomenon occurs naturally. Rainwater may wash down the dry deposited foliage dust from the leaf surface, but it also delivers a certain concentration of elements through wet deposition.

6. References

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