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Chemical composition of vegetation along urbanisation gradients in two European cities

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A B S T R A C T

Accumulation of particulate matter (PM) and metals on leaves of three deciduous woody species was studied along urbanisation gradients in Stavanger and Warsaw. Differences between rural and urban sites explained most of the observed variation in leaf chemistry, followed by differences between regions. Highest leaf accumulation of elements was found in Warsaw, but also composition of elements differed between the cities. Overall, species showed similar patterns of element accumulation, but differed in accumulation of specific elements. These differences could in part be explained by differences in epicuticular waxes and PM accumulation. Expected source of elements and their chemical characteristics did not explain the observed accumulation patterns. A better differentiation between elements taken up from soil and air would be required for his. Species specific accumulation of elements has to be taken into consideration using leaf samples for biomonitoring.

1. Introduction

Urban areas are often characterised by elevated levels of pollutants of anthropogenic origin, in most places from vehicular traffic. The pollution consists of gaseous pollutants and particulate matter (PM) with associated organic pollutants and metals. Trees are considered to be efficient in collecting particulate matter (McDonald et al., 2007) because of their size, large leaf area and crown structure, which creates turbulent air movements, leading to increased deposition on leaves (Fowler et al., 1989). Therefore, trees have been suggested for use in bioremediation of the air in urban areas (Nowak, 1994; Yang et al., 2005; Nowak et al., 2006). Nowak et al. (2006) reported relatively small effects from pollution deposition on urban vegetation on air quality, but Yin et al. (2011) recorded much higher values. The scale on which measurements and modelling are performed may be important, and the local effect may be most interesting (Sæbø et al., 2012). The difference between tree and shrub species in accumulation of PM has been well documented (Freer-Smith et al., 2005; Dzierżanowski et al., 2011; Sæbø et al., 2012; Popek et al., 2013). However, the subsequent fate of the pollutants after deposition can be affected by the weather conditions (Przybysz et al., 2014). Trees and shrubs may also be good bioindicators of pollution (Rai, 2013). However, different parts of the tree may yield different information, according to the total lifetime and exposure time of the tissue in question. Analysis of pollution on leaves may be obscured by elements transported from the soil, through root uptake and translocation, but not all pollutants are mobile in plant tissues. Wyttenbach et al. (1998) found that the distribution of elements in plants was not well correlated to that found in the soil. It is especially difficult to distinguish between low concentration of rare earth elements in plant tissues and that accumulated on plant surfaces. Elements such as lead (Pb), nickel (Ni), vanadium (V) and chromium (Cr) are good indicators of air pollution from traffic sources (Ny and Lee, 2011) since they are not easily taken up from the soil and transported to leaves. When such elements are found on leaves, air-pollution is the main source.

This study examined the following research questions: i) How does element composition of leaves differ along urbanisation gradients and cities? ii) How do differences in metal accumulation in

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leaves relate to PM accumulation and leaf properties?; and iii) Can patterns of metal accumulation be explained by chemical characteristics and origin (traffic, plant macro- and micronutrients, heavy metals *etc.*)? These issues are of interest in biomonitoring of pollutants and in use of plants to increase pollution deposition in order to amend air quality.

2. Materials and methods

PM and element accumulation on plant leaves was determined and the results analysed for a correlation between these two pollution fractions. Three woody species were established at one polluted and one clean site in or near each of two European cities, Stavanger, Norway, and Warsaw, Poland. Air quality data for the sites are shown in Table 1.

2.1. Plant material and field conditions

The plants used are commonly planted in urban areas, along roads, streets and highways in Europe. Two trees, *Tilia cordata* and *Acer platanoides* and the shrub *Sorbaria sorbifolia* were bought from a commercial nursery and planted in random order at each of the two sites near Stavanger. One of the sites was exposed to traffic pollution (near the city centre of Stavanger; 58°57′N 5°43′E), while the other was a clean rural site (Særheim; 58°45′N 5°39′E). Air quality was measured at two permanent stations in Stavanger, but not at the rural site of Særheim. However, the air quality at Særheim is usually high and, therefore, air quality data for the rural reference site of Birkenes (58°18′N 8°11′ E) were used instead (Table 1). In the test fields near Stavanger, the species were planted in 2009. At planting, the 3–4 years old trees were about 2 m tall and the shrubs were about 0.6 m tall. The ground under the woody species was covered with turf grass. For determination of accumulated PM and metal content, leaf samples were collected from these plants at the same day, when there was no precipitation, from about 50 cm (shrubs) to 170 cm (trees) above the ground from all sides of the plants in the field, with four replicates (plant individuals) per species at each harvest. A leaf area between 200 and 300 cm^2 was used per sample for analysis, collected just before natural leaf fall at the end of September in 2009 and 2010. Soil samples were collected for analysis only in the second year (2010).

At the polluted site in Warsaw city centre (52°14′N, 21°00′E), leaves were collected from the same species, but from already established vegetation. At the clean site (Pęhcin; 52°51′N, 20°34′E), the plants were bought from a commercial nursery and then established in 60-L containers filled with horticultural peat. The plants were of the same age and size as those in Stavanger, and the same methodology was used in the leaf harvesting process. Harvesting of leaves was done at the beginning of October in Warsaw, just before natural leaf fall. Leaf element concentrations were analysed for all species in two years (2009, 2010) and PM deposition was determined in one year (2009). The plants were in open areas in both sites and cities, but with a distinct urban setting, near trafficked roads in the two most urban sites.

The polluted and clean sites in Stavanger were quite near each other. Mean annual temperature in the region is around 7.5 °C and mean temperature for May, June, July, August and September (growing season) is 12.6 °C. Annual precipitation is 1250 mm and mean precipitation in the growing season is 517 mm. Mean annual temperature in Warsaw is about 7.8 °C and mean annual precipitation around 560 mm. Mean growing season temperature is 15.8 °C and precipitation for that period is 303 mm. Within each of the test fields, the conditions were homogeneous with respect to various growth factors. The plants analysed were in good condition, and any leaves with signs of contamination by pests or diseases were discarded.

Table 1
PM concentrations ($\mu g\ m^{-3}$; mean values for 2009 and 2010) at a downtown site in Stavanger, at Birkenes, a clean site in southern Norway, in Warsaw city centre ($PM_{2.5}$ in 2010 only) and at Pęchcin, a clean site in Poland (PM_{10} only).

Site:	Stavanger		Birkenes	Warsaw		Pęhcin
Month	PM_{10}	$PM_{2.5}$	PM_{10}	PM_{10}	$PM_{2.5}$	PM_{10}
Jan	41.4	18.2	5.7	65.1	39.4	81.2
Feb	30.0	14.2	3.2	66.1	45.2	56.5
March	35.6	10.5	3.9	60.4	40.3	38.0
Apr	34.0	10.3	5.2	61.5	35.4	39.8
May	22.6	8.6	4.1	46.0	24.8	22.3
June	21.5	8.7	4.3	41.4	24.0	17.8
July	20.9	9.2	4.8	42.1	21.8	15.2
Aug	17.5	8.4	3.0	35.8	24.8	19.5
Sept	19.1	8.7	3.6	44.8	25.7	19.8
Oct	20.4	9.2	6.4	49.6	35.4	37.9
Nov	32.4	12.9	2.2	48.2	22.4	33.4
Dec	32.6	18.7	2.5	55.6	39.3	52.3
Mean values	**29.3**	**11.5**	**4.1**	**51.4**	**31.5**	**36.1**

The bold values are the mean values for each of the columns.

2.2. Analysis of PM and wax

After collection of leaves, the samples were stored in paper bags at room temperature in a clean storage facility until analysis of PM on the leaf surfaces (water soluble) and in the waxes (soluble in chloroform), according to Dzierżanowski et al. (2011). After evaporation of the chloroform, wax amount was determined. Filters were weighed before and after filtration (XS105DU balance, Mettler-Toledo International Inc., Switzerland). When weighing, the filters were passed through a deioniser gate (HAUG, Switzerland), to avoid electrostatic charge on the filter surface. The water end chloroform was filtered through a 100 μm mesh before filtration. The filters used (Whatman, UK) were Type 91 (retention of 10 μm), Type 42 (retention of 2.5 μm) and PTFE membrane filters (retention of 0.2 μm). Thus, three fractions of particulate matter were collected on filters: (1) Large: 10–100 μm, (2) Coarse: 2.5–10 μm, and (3) Fine: 0.2–2.5 μm. PM was expressed as μg per cm^2 of one side leaf area of the washed leaves.

2.3. Analysis of metals

Leaves were collected and stored in paper bags before analysis. The plant material was milled with a silicon mill, in order to avoid metal contamination, in the preparation stages immediately before analysis. Soil samples were harvested from the two sites in Stavanger and pooled to three bulk samples (replicates) per site for analysis. Plant material samples were added 50% v/v HNO_3 and digested in Milestone UltraClave (UC), then diluted to 60 mL (61 ± 0.3 mL). Soil samples were mixed with 50% v/v HNO_3, digested in UC and then diluted to 109 mL (110.8 ± 0.5 mL). The samples were then analysed by high resolution ICP-MS, (Element 2 from Thermo Scientific).

2.4. Experimental design and statistical analysis

In Stavanger, the species were planted with a random distribution in the two test fields, with four individuals per species. In Warsaw, at the polluted site, established vegetation was used and leaves were harvested from these individuals, in four (PM analysis) or three (metal analysis) replicates. At the clean site (Pęhcin), the plants were positioned in random order. In both cases, four individual trees and shrubs were used.