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Characterization of trace metal particles deposited on some deciduous tree leaves in an urban area

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Abstract

In 1996 and 1997 horse chestnut (*Aesculus hippocastanum* L.) and Turkish hazel (*Corulys colurna* L.) leaves were sampled at 2 m height in the Belgrade Botanic Garden, located in an urban area with heavy traffic. Using a scanning electron microscope with an energy dispersive X-ray spectroscopy (SEM-EDAX), the size, size distribution, morphology and chemical composition of individual particles were examined on the adaxial and abaxial surfaces of leaf discs of both species. The majority of particles observed on leaves belonged to a class of fine particles ($D < 2$ μm). Morphological and chemical composition indicated that the most abundant particles were soot and dust with minor constituents such as Pb, Zn, Ni, V, Cd, Ti, As and Cu. Using an electrochemical technique (DPASV), it was possible to measure trace metal concentrations (Pb, Cu, Zn) in a water-soluble fraction of deposits on each single leaf. Trace metal contents in the leaf deposits, increased during the vegetation period for both species and were considerably higher in *A. hippocastanum* due to different epidermal characteristics. The higher trace metal concentrations in deposits in 1997 reflected greater atmospheric pollution in the Belgrade urban area.

Keywords: Airborne particles; Trace metals; Tree leaves; Urban pollution; SEM-EDAX

1. Introduction

In industrial zones of the northern hemisphere, most trace metals in forest ecosystems originate from atmospheric wet and dry deposition. Dry deposition depends on the physical characteristics of the particles, such as size and shape, on meteorological conditions, such as wind speed and thermal stability, and also on the morphological characteristics of the biological surface (Seinfeld and Pandis, 1998; Harrison and Yin, 2000). Moreover, as an additional parameter, the characteristics of the plant species contribute to the degree of deposition. As trees are very efficient in trapping atmospheric particles, which is especially important for urban areas (Coe and Lindberg, 1987; Freer-Smith et al., 1997; Bargagli, 1998; WHO, 2000) plant leaves have been used as indicators and/or monitors of trace metal pollution (Nriagu, 1989). In general, higher plants generally are not as suitable biomonitors as lichens and mosses. However, in industrial and in urban areas, where those forms of vegetation are often missing, higher plants can act as

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biomonitors. Also, in some cases higher plants may give better quantifications for pollutant concentrations and atmospheric deposition than non-biological samples. Therefore, using plant leaves primarily as accumulative biomonitors of trace metal pollution has attained great ecological importance (Markert, 1993; Bargagli, 1998; WHO, 2000).

The aim of this work was to set up a reliable methodological approach in sampling and analytical procedures for investigation of the material deposited on tree leaves, i.e. to estimate the validity of the use of broad tree leaves of two species (*A. hippocastanum* and *C. colurna*) to monitor urban trace metal pollution. It was the first step towards later foliar analyses (trace metal contents in single leaves are to be presented in the following paper). Two sequential experimental years (1996 and 1997) with very different air quality conditions in an urban area of Belgrade were chosen. The morphological (shape, size, size distribution) and chemical characteristics of deposited individual particles were investigated using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDAX). The concentrations of trace metals (Pb, Cu, Zn, Cd), in the water-soluble fraction of deposits on single leaves were measured with differential pulse anodic stripping voltammetry (DPASV).

2. Experimental

2.1. Sampling

Leaves were sampled from two deciduous tree species: horse chestnut (*Aesculus hippocastanum* L.) and Turkish hazel (*Corulys colurna* L.) in the Botanic Garden, which is located in an urban area of Belgrade with heavy traffic. It is situated within a triangle of busy streets, a lower area of the city. There is a small foundry for arts and crafts about 300 m in the N–NE direction from the sampling site, as well as a thermal plant about 1500 m in the N–NW direction. Samples for DPASV analyses were taken, in a dry period, at the beginning (May and June) and end (September) of the seasonal vegetation cycles in 1996 and 1997 and at the end of September in 1997 for SEM-EDAX. Wearing polyethylene gloves, leaves growing at 2 m height were cut off with clean scissors. Each leaf was placed horizontally in a polycarbonate Petri dish and transferred to a Class 100 clean room, with the specific conditions required for analyses of low concentrations of trace metals (Vukmirović et al., 1996), where the samples were prepared for trace metal analyses and electron microscopy.

2.2. Sample preparation and SEM-EDAX analyses

Six leaves from each tree species were picked up from the 2 m height for SEM-EDAX analysis. Samples were prepared for both adaxial and abaxial leaf surfaces of both tree species. Discs of 10 mm diameter were cut from unwashed leaves with a sharp device, wearing polyethylene gloves. Each leaf disc was mounted on an aluminum stub, over double-sided stick tape. The stubs were placed on a perforated round Teflon plate, cut to fit in a polycarbonate Petri dish. Leaf samples were dried in air in the clean room. To minimize charge build-up on the samples from exposure to the SEM electron beam the samples were coated with 100–150 Å layer of high purity carbon using vacuum evaporator (Balzers/Union FL-9496) prior to analyses.

An SEM Philips XL30 apparatus equipped with a thin-window EDAX DX4 system for energy dispersive X-ray microanalysis was used to analyze the particles deposited on the leaf samples. The SEM observations were carried out at magnifications up to 2000× while the electron beam energy was fixed at 20 keV, and the working distance in most cases was about 10 mm and probe current was 100 pA. Particles were observed by backscattered electron images.

Three different leaf discs of the adaxial and abaxial surfaces for both tree species were examined in the same way. Ten photomicrographs were randomly taken of each 0.03 mm^2 area at 624× magnification and about 1800 particles per species were assessed to their morphology and about 900 for X-ray spectra analysis. For each tree species about 0.025% of the original leaf surface was examined.

An energy dispersive X-ray spectrum (EDS) was collected from the selected particles in the range between 0 and 15 keV for a preset time (live time) of 10–20 s. The total X-ray count rate was between 1000 and 2000 counts s^{-1}. The elements observed were: Al, Si, C, S, N, Cl, P, K, Ca, Na, Mg, Cr, Fe, Cu, Zn, Ni, Cd, As, Ti and V with detection limit >1 wt.%. The relative elemental composition of the particles, were computed directly with EDAX software, using the "ZAF" (atomic number, absorption, fluorescence) correction. As the particles deposited on leaves have complex shapes, quite different from an ideal flat sample, there may be over- or underestimation of the actual atomic concentration, but this does not prevent identification of the most important particle types. Periodical checks of the X-ray peak identification, were conducted. EDX spectrometer gain calibration was accomplished by using a gold/copper standard since X-ray lines from these two elements span almost the entire spectral range of the detector.

2.3. Determination of trace metal concentration in the water soluble fraction of leaf deposits

Six single leaves of each species were analyzed for particular sampling episode. Each leaf was washed in bidistilled, deionized water, using an ultrasonic bath.