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Chemometrics in biomonitoring: Distribution and correlation of trace elements in tree leaves

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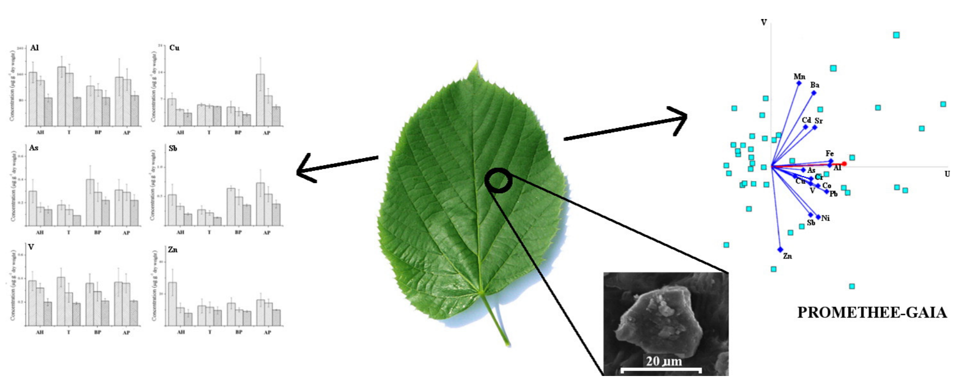
HIGHLIGHTS

- Surface and in-wax fractions showed different trace element distributions.
- The fractions removed by washing represent air derived deposition.
- Al, V, Cr, Cu, Zn, As, Cd and Sb were easily removed from the leaf surface by washing.
- Additional information on classified/ranked samples was provided.
- For the assessment of correlations among variables, clr transformation was needed.

GRAPHICAL ABSTRACT



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ABSTRACT

The concentrations of 15 elements were measured in the leaf samples of *Aesculus hippocastanum*, *Tilia* spp., *Betula pendula* and *Acer platanoides* collected in May and September of 2014 from four different locations in Belgrade, Serbia. The objective was to assess the chemical characterization of leaf surface and in-wax fractions, as well as the leaf tissue element content, by analyzing untreated, washed with water and washed with chloroform leaf samples, respectively. The combined approach of self-organizing networks (SON) and Preference Ranking Organization Method for Enrichment Evaluation (PROMETHEE) aided by Geometrical Analysis for Interactive Aid (GAIA) was used in the interpretation of multiple element loads on/in the tree leaves. The morphological characteristics of the leaf surfaces and the elemental composition of particulate matter (PM) deposited on tree leaves were studied by using scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) detector. The results showed that the amounts of retained and accumulated element concentrations depend on several parameters, such as chemical properties of the element and morphological properties of the leaves. Among the studied species, *Tilia* spp. was found to be the most effective in the accumulation of elements in leaf tissue (70% of the total element concentration), while *A. hippocastanum* had the lowest accumulation (54%). After water and chloroform washing, the highest percentages of removal were observed for Al, V, Cr, Cu, Zn, As, Cd and Sb (>40%). The PROMETHEE/SON ranking/classifying results were in accordance with the results obtained from the GAIA clustering techniques. The combination of the techniques enabled extraction of additional information from datasets. Therefore, the use of both the ranking and clustering methods could be a useful tool to be applied in biomonitoring studies of trace elements.

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1. Introduction

Airborne particulate matter (PM) pollution is recognized as a serious problem in urban environments, since it can cause respiratory problems and decrease life expectancy (WHO, 2005). Deciduous trees in urban areas capture PM on their leaf surfaces and act as sinks for PM (McDonald et al., 2007). Thus, trees have an important role in removing of PM and associated trace elements from the urban air (Nowak et al., 2006; Sæbø et al., 2012). Depending on their chemical properties, particulates enriched with the trace elements can be deposited on the leaves, either on the leaf surface or in the epicuticular wax, or accumulated in the leaf tissue (Dzierżanowski et al., 2011; Sæbø et al., 2012). Anatomical and morphological features, as trichomes and epicuticular wax, may increase the retention of PM and trace elements. Assessment of deposition and vegetation uptake of airborne trace elements can be a complex task, and may involve several parameters, i.e., a choice of the tree species and morphological traits of the leaves, properties of trace elements, etc.

Preference Ranking Organization Method for Enrichment Evaluation (PROMETHEE), often aided by Geometrical Analysis for Interactive Aid (GAIA), is an outranking method for a finite set of alternative actions to be ranked and selected among criteria, which are often conflicting (Behzadian et al., 2010). As a multicriteria decision making method (MCDM), the PROMETHEE was used to rank sites based on the level of the air pollution (Nikolić et al., 2010) and for the concentration analysis of heavy metals in road-side sediments (Herngren et al., 2006). However, according to available literature, the PROMETHEE-GAIA has not been applied in biomonitoring of trace elements using tree leaves. The Self-Organizing Network (SON) (Kohonen, 1982a, 1982b) is a type of artificial neural networks (ANNs) with unsupervised learning for multi-dimensional data reduction and display (Kohonen, 2001). A recent study recommended the SON as a complementary tool for the Self-Organizing Maps (SOM) analysis applied for seasonal and temporal trace element accumulation (Deljanin et al., 2015).

Recently, several studies on the PM fractions deposited on the leaves and differences between species in their accumulation capacity have been carried out (Dzierżanowski et al., 2011; Popek et al., 2013; Sæbø et al., 2012; Song et al., 2015). However, little is known on the relation between chemical composition of PM deposited on the leaf surfaces and in the epicuticular wax. Thus, one of the objectives was to carry out a chemical characterization of the leaf chemical content in different fractions: on the leaf surface, in the epicuticular wax and in the leaf tissue, in order to assess the species-specific leaf ability for the PM, i.e. trace element entrapment. Another aim of this study was to evaluate whether a combined approach of SON and PROMETHEE-GAIA, by providing an integrated interpretation of multiple measured variables, can be useful in assessment of trace element loads on tree leaves.

2. Materials and methods

2.1. Study area

The study was carried out in Belgrade, Serbia, at four urban parks located in the heavy traffic areas, viz. botanic garden (B), Karađorđev Park (K), Studentski Park (S), situated in the center of Belgrade, and Zemunski Park (Z) located in Zemun, cca. 6 km from the city center (Fig. 1). At botanic garden, samples were collected from the traffic-exposed streets bordering it.

2.2. Sampling and chemical analysis

Leaves from four deciduous trees common in this area: *Aesculus hippocastanum* L. (horse chestnut) (AH), *Tilia* spp. (T), *Betula pendula* Roth (European white birch) (BP) and *Acer platanoides* L. (Norway maple) (AP) were sampled in May and September 2014. Leaves were cut off with stainless steel scissors, at about 2 m height above the ground and collected wearing polyethylene gloves. Subsamples of 10–30 fully developed leaves were taken from five different trees of approximately the same age per species and per site. Leaves were collected randomly from all sides of the trees. The subsamples were packed in polyethylene bags and transported to laboratory. *B. pendula* was not sampled at Studentski park, since this species was absent at this site.

In the laboratory, half of the leaves were rinsed twice with deionized water (18.2 MΩ cm^{-1}), while the other half was left unwashed. The leaf samples collected at the botanic garden in September 2014 were divided into three groups. One group was left untreated, the second group was shortly rinsed (two times, 3–5 s each) with deionized water and the third one was firstly rinsed with deionized water as described above, and then washed with 250 mL of chloroform (Sigma-Aldrich, Chromasolv, ≥99.8%, GC) for 40 s. Afterwards, the samples were dried in the oven at 60 °C for 24 h, ground in the agate mortar, packed in polyethylene bags and kept in stable laboratory conditions until chemical analysis. Approximately 0.2 g of the dry leaf sample was digested for 1 h in a microwave oven (Speedwave™ MWS-3^{+}, Berghof) with 3 mL

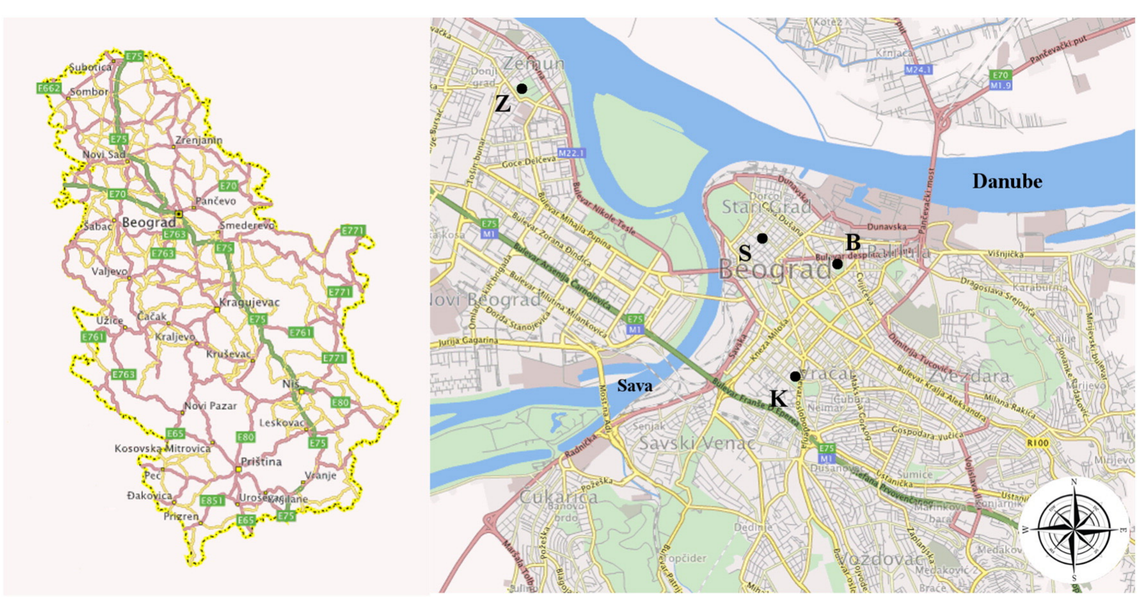

Fig. 1. Map of the study area: B — botanic garden, K — Karađorđev Park, S — Studentski Park, Z — Zemunski Park.