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Heavy metal in leaves of twelve plant species from seven different areas in Shanghai, China

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Concentrations of heavy metals (Cu, Zn, Pb and Cd) were measured in leaves of twelve plant species from seven different locations in Shanghai, China. Unwashed and washed new and old leaves were considered, and the correlations among the heavy metal concentrations in soils and in plant leaves and deposited by the atmosphere were analyzed. In addition, scanning electron microscopy (SEM) was used to determine the stomatal density and structure of the leaves.

The background site (Chenshan Botanical Garden) had lower mean metal concentrations than the other sites. The highest Cu contents were found in *Nerium indicum* and *Platanus acerifolia*, the highest Zn content was found in *Pittosporum tobira*, and the highest Pb and Cd contents were found in *Cedrus deodara*. The lowest heavy metal contents were found in *Ginkgo biloba*, potentially because *Platanus acerifolia* and *Pittosporum tobira* leaves have higher densities of stomata than on *Ginkgo biloba* leaves (according to SEM results). However, *Magnolia grandiflora* had the highest metal accumulation index (MAI) (4.27), and *Cedrus deodara* had the lowest MAI (1.53). When comparing the heavy metal contents in the washed leaf samples with the unwashed leaf samples, *Nerium indicum* captured more rare-earth elements (determined using the capture rate (CR)), including Cu (92.7%) and Zn (36.9%). *Magnolia grandiflora* had higher CR values for Pb (63.4%) and Cd (49.1%), and *Cedrus deodara* had lower CR values for Cu (0), Zn (8.90%), Pb (5.93%) and Cd (2.97%). In addition, the Cu, Zn, Pb and Cd in plant needles potentially originate from the soil, and the Cu, Zn, Pb and Cd in the leaves of broad-leaved plants potentially originate from bulk atmospheric deposition. This hypothesis is supported by the relationship between the heavy metal concentrations in the soils and the washed new and old leaves. In addition, the concentration factor (CF) of heavy metals supported this model.

1. Introduction

With increasing urbanization and industrialization, the air quality in some urban areas has declined. In particular, heavy metal (Cu, Zn, Pb and Cd) pollution in urban air has become a serious problem during the last two decades because of transportation, industrial activity, and fossil fuel use (Celik et al., 2005; Wei and Yang, 2010). In addition, the health and quality of life of the urban population has been seriously threatened by continuous exposure to pollutants (Cocozza et al., 2016). Plants are essential components of ecosystems and may improve the quality of urban environments (Akbari, 2002; Brack, 2002). In addition, plants sequester CO_2, release O_2, moderate the air temperature and, more importantly, contribute to filtering ambient air by absorbing and accumulating significant quantities of potentially toxic substances (Piczak et al., 2003; McDonald et al., 2007; Dzierżanowski et al., 2011). Plants can take up and accumulate heavy metals through their root and leaf surfaces (Sawidis et al., 2001). Leaves are useful as biological indicators of pollutants when evaluating air pollution because they have a high distribution density (Moreno et al., 2003; Kardel et al., 2010). In addition, several plant species have already been used as bioindicators (Aksoy et al., 2000; Celik et al., 2005; Baycu et al., 2006; Mingorance and Oliva, 2006). For example, *Acer pseudoplatanus* L. has been used as a bioindicator for assessing air contamination (André et al., 2006) in urban ecosystems in Europe, and *Quercus ilex* L. has been used as a bioaccumulator for heavy metals in urban areas (Ugolini et al., 2013).

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However, most of the studies above only considered a single tree species (Aksoy et al., 2000; Mingorance and Oliva, 2006; Al-Alawi and Mandiwana, 2007), and few studies have investigated multiple plant species simultaneously (Piczak et al., 2003), especially evergreen species and deciduous species (Hu et al., 2014). The morphology and chemical properties of leaves have been reported to affect the accumulation of airborne particles and/or the retention of particles on leaf surfaces, thereby influencing the accumulation of heavy metals in the plants (Gratani et al., 2008). In addition, the efficiencies of heavy metal accumulation by different plant species are essential for developing planting designs that improve urban air quality (Dzierżanowski et al., 2011).

Therefore, the aims of this study were as follows: (1) to assess the differences between the heavy metal concentrations on the leaves of twelve plant species from seven different locations; (2) to evaluate why leaves contain different heavy metal concentrations by comparing unwashed and washed leaves and by determining the stomatal density and structure of plant leaves; (3) to identify the main source (from the soil or the air) of heavy metals in plant leaves based on the correlation analyses of the metal contents in the washed leaves, the soils and atmospheric deposition, the concentration factor (CF) of heavy metals, and the comparison of the heavy metal contents in new leaves and old leaves; and (4) to provide a scientific basis for selecting specific plant species for urban landscapes or green spaces.

2. Materials and methods

2.1. Study area

Shanghai (30°40′N–31°53′N, 120°51′E–122°12′E) is located on the east coast of China, and the Yangtze River flows along the northern region of Shanghai into the East China Sea. Shanghai covers an area of 6340.5 km^2, which is 0.06% of China, and has a subtropical monsoon climate with an annual average temperature of 17.2 °C and an annual average rainfall of 902.9 mm. The total population of Shanghai is 24.15 million, including both permanent and non-permanent residents (Shanghai Statistical Yearbook, China Statistics Press, Beijing, 2015). Currently, Shanghai is one of the regions in China with the most rapid economic development and the greatest amount of urban construction, and the large population and dense industrial activities in Shanghai have resulted in greater discharge of contaminants to the urban environment. To improve the quality of the urban environment, the total area of urban green spaces is being increased annually. At the end of 2014, green space coverage reached 38.43%, which was much higher than the green space coverage of 19.1% that was reported in 1998.

In this study, sampling was performed at seven sites at different locations in Shanghai along a transect from the suburbs to the city center. The six following sites were selected: People's Park (Site 1, built in 1952) and Fuxing Park (Site 2, built in 1946), which are located in the Huangpu District; Xujiahui Park (Site 3, built in 2000) and Shanghai Botanical Garden (Site 4, built in 1978), which are located in the Xuhui District; a public green space (Site 5, built in 1998) located near the Wujing industrial area of the Minhang District; and an area (Site 6) in the green belt of the outer traffic rings (built in 1993), which experience heavy vehicular traffic. In addition, a background site (BS) was established at Shanghai Chenshan Botanical Garden (newly constructed in 2007), which is located in the Songjiang District and is far from the city center. The Huangpu Districts are enclosed within the inner traffic ring, and the Xuhui District is located between the inner and middle traffic rings. Dense commercial and residential areas characterize these two districts. The Minhang District is located on the urban fringe between the middle and outer traffic rings and includes highly dense industrial and moderately dense residential areas. Songjiang District is located beyond the outer traffic rings and contains low-density residential areas. The sampling sites used in the present study are similar to those of Liang et al. (2016).

2.2. Plant materials and sampling

Twelve plant species (including seven trees and five shrubs; eight evergreen plant species and four deciduous plant species) that are extensively used in urban landscaping in Shanghai were selected in this study, and their characteristics are listed in Table S1. At each site, the tested species were randomized within test fields with relatively small areas (100 m^2), and the micro-scale differences in location were negligible within individual sites. The sampled plants were in good condition, with few diseases or pests. Leaves contaminated with pests or diseases were not sampled. For each species, leaves were sampled from four plants (replicates) on the 7th day after rain. In June and July 2015, which was during the vigorous growth period of each the plants, particularly for deciduous species, leaf samples were collected at 2–3 m above the ground from the outer areas (N, S, E, W) of the canopies using stainless steel pruning shears, taking care to minimize contact with the leaf surface.

To obtain a homogeneous sample, 40 one-year-old leaves (comparable in size and shape particularly, for the same species) were collected from each plant at each site and were mixed into a single sample before immediate transportation to the laboratory. Overall, 84 plant samples were acquired, with species sampled at each of seven sites. All samples were subsequently divided into two parts. One part of each plant leaf sample was cleaned using tap water and washed three times with deionized water in an ultrasonic cleaner (KQ-600B, Shanghai, China) for 10 min to remove dust from the leaf surface. The other part of the sample was not washed. Meanwhile, 40 fully expanded leaves (newer leaves) were also collected from *Magnolia grandiflora, Ligustrum lucidum, Pittosporum tobira* and *Prunus cerasifera* plants by using the same sampling method, and they were washed using the same washing method.

The fresh leaves were weighed and oven-dried at 75 °C until a constant weight was achieved. The water content was determined as the amount of weight lost by determining the dry weight of the fresh leaves. In addition, dried samples were mechanically ground using a stainless steel grinder and stored for heavy metal analyses. In this study, all of the results refer to the dry weight.

In addition, 7 soil samples were collected at each sampling site by using a random sampling method. Each sample was collected using a plastic scoop from below the corresponding sample tree and mixed to obtain one sample per sampling site. All homogenized samples were transported to the laboratory in airtight polythene bags and then air-dried, manually ground using a mortar and pestle and passed through a 100-mesh nylon sieve.

2.3. Heavy metal analyses

2.3.1. Analyses of heavy metal concentrations in the leaves

Approximately 0.25 g of each leaf sample was placed in a polytetrafluoroethylene (PTFE) vessel. Concentrated nitric acid (HNO_3), concentrated hydrochloric acid (HCl), and hydrogen peroxide (30%) were added, and the samples were then gently mixed and left to equilibrate overnight. The samples were digested in a microwave oven to determine the heavy metals concentrations (Cu, Zn, Pb and Cd) by using inductively coupled plasma-mass spectrometry (ICP-MS) (Perkin-Elmer Elan DRC-II). A plant standard (GSV-2), supplied by the Chinese National Research Center for Certified Reference Materials, was used for quality assurance and quality control (QA/QC). The recovery values for all elements were between 87% and 108%. Duplicate samples were analyzed to verify accuracy,