Particulate matter deposited on leaf of five evergreen species in Beijing, China: Source identification and size distribution

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HIGHLIGHTS
- By SEM and EDX, we found PM on leaf surface mainly come from natural source.
- The number density and mass quality of particles per leaf square centimeter were compared between species.
- On leaf scale, the Juniperus formosana accumulated most PM for its complex leaf structure.
- For one tree, Pinus bungeana, with the most leaf area, was most effective at mitigating airborne PM.

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GRAPHICAL ABSTRACT

ABSTRACT
Airborne particulate matter (PM) has become a serious problem, and urban plants can play important roles in reducing PM concentrations in the air. The morphology, size, and elemental composition of PM on tree leaves (five evergreen species) from Beijing, China, were obtained, together with number density of PM size fraction, by using scanning electron microscopy (SEM) and energy dispersive X-rays (EDX). The rinse and weigh method was used to characterize PM in three size categories (0.2–2.5 μm, 2.5–10 μm, and 10–100 μm). The results showed that PM up to 2 μm can get into the stomatal cavity, and the most furrowed areas of the leaf surfaces were sites of maximum PM deposition. The leaf-deposited PM mainly comprised C, O, Si, and Fe. The number of particles per leaf per cm² was 1.95 × 10⁷, and 96% of the particles were less than 2.5 μm. The mass concentration was 148.44 μg/cm², and PM₂.⁵ comprised only 2.09% by weight while PM larger than 10 μm comprised 79%. Juniperus formosana was most effective at mitigating airborne PM on the leaf scale. Pinus bungeana accumulated the most PM on the tree scale. The results showed that urban plants can play important roles in mitigating urban airborne PM.
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1. Introduction
Airborne particulate matter (PM) is a serious environmental problem in most cities around the world (Nowak et al., 2006; Shridhar et al., 2010), especially in developing countries (Jim
Fine PM (with a diameter less than 2.5 μm) poses a great threat to human health in urban areas (Sebe et al., 2012; Charron and Harrison, 2005; Putaud et al., 2010), which can reach the lungs and alveolar regions (Kampa and Castanas, 2008). Ultrafine PM (with a diameter less than 0.1 μm) can enter the bloodstream (Kaiser, 2005; Nemmar et al., 2002). Heavy PM pollution has reduced projected life expectancies by one year (WHO, 2003) to 5.5 years (Chen et al., 2013).

Airborne PM is recognized internationally as a key environmental and health issue, and the potential phytoremediation has received increased attention. Many studies have identified a beneficial impact on PM through increased urban greening (Nowak et al., 2006; Tiwary et al., 2009; Jim and Chen, 2008). Pugh et al. (2012) reported that green walls interacted with the increased residence time of PM in street canyons, producing a PM decrease of up to 60%. Tallis et al. (2011) used the Urban Forest Effects Model and estimated that the urban trees in London deposited 852 to 2121 tons of PM10 annually. However, there is controversy regarding urban vegetation increased particulate matter concentrations (Vos et al., 2013; Wania et al., 2012; Gromke and Ruck, 2012).

Based on experimental methods, urban plants appear to act as sinks for PM (McDonald et al., 2007) because plants capture PM on leaf surfaces (Yin et al., 2011) and absorb ultrafine PM (<0.1 μm) (Treshow, 2002) into leaf tissues through their stomata. At the leaf scale, PM deposition on leaf surfaces (accounting for most of the PM capture) occurs by four depositing processes: sedimentation caused by gravity; diffusion derived by Brownian motion; and impaction and interception resulting from turbulent flow (Freer-Smith et al., 2005; Sternberg et al., 2010). Sedimentation principally affects the deposition of large PM (Freer-Smith et al., 2005), impaction and interception affect fine and coarse particle deposition, and Brownian motion leads to the deposition of ultrafine particles. Blade roughness (Dzierzanowski et al., 2011), trichomes (leaf hairs) (Wang et al., 2006), and the thickness of the wax layer may affect the interception and adherence of PM. At the branches scale, plant characteristics determine the efficiency of deposition (Mitchell et al., 2010; Beckett et al., 2000a). Complex leaf structures on the crown of the tree are ideal for absorbing PM because they produce turbulent air movement (Popek et al., 2013; Beckett et al., 2000b; Fowler et al., 1989). At the individual tree scale, the leaf area index (Beckett et al., 2000c), commonly used in modeling studies of leaf PM capture (Vos et al., 2013), a higher leaf area means more PM deposition.

Although many researchers reported that vegetation plays an important role in the deposition of airborne PM, there were few studies on the source identification of PM on leaf surface. Much is known about the mass quality of PM accumulated on the leaf surface, but less is known about the number density of PM on the leaf surface. The number density is another important indicator used to express the volume of PM detention by plants, but was applied only a few times. In our study, we measured the number density and mass quality of PM in three size fractions, and compare the accumulation of PM deposited on the leaf surface of five typical evergreen species in Beijing.

2. Materials and methods

2.1. Sampling site

All of the test plants were grown on the campus of the research center for eco-environment sciences (RCEES), Chinese Academy of Sciences (40°0’ 28.40” N, 116°20’ 23.47” E) Beijing, China. The sampling sites were all located on the campus of the research center with distances less than 100 m, so the PM concentration, temperature, relative humidity, etc., of the different sites were nearly same. There were two motorways south and west of the RCEES (Fig. 1). There were no high polluting factories or power plants within 5 km, and the PM2.5 average in 2010 was 95.5 μg/m² (Wang et al., 2012). Plant leaves were collected from five typical evergreen species: Juniperus formosana, P. bungeana, Platycladus orientalis, Pinus tabulaeformis, and Euonymus japonicus. For each species, we had four individuals as replicates which had good growth conditions, an average size, and no deflections. The basic information of the trees used for testing is listed in Table 1. We sampled intact leaves, with no damage from insects and pests, from four directions of each tree at a height of 1.5 m. The samples were cut off with scissors, placed in paper bags, labeled, transported to the laboratory, and kept at an ambient temperature until analysis. We carefully conducted all of these processes and kept the PM deposited on the leaf from falling off. The date of the sampling and the dry periods before the sampling are listed in Table 2. There were at least 30 days with no precipitation before sampling. According to Liu et al. (2013), after 26 days of no rainfall, the plant leaves attained the maximum dust-retaining capabilities. We assumed the quality of PM on the leaf surface had approached the saturated value.

2.2. SEM and EDX analysis

For the needle leaves of P. bungeana and P. tabulaeformis, two 1 cm long needle sections were cut with scissors from the middle of whole needles. For J. formosana and P. orientalis, whole leaves were small enough to be mounted intact on the field emission scanning electron microscope stub. For E. japonicus, 1 cm² were cut from the center of the leaf. The prepared samples were attached to the stub with double-sided adhesive tape. The samples were gold-coated (with a thickness of less than 10 nm) to enhance electrical conductivity before analyzing them using a field emission scanning electron microscope (SEM, Hitachi S4800, Tokyo, Japan). Photographs were taken of randomly chosen spots at 1000× magnification, at 5 kV. Particle counting was performed using ImageJ software (for more information about this software please see http://rsbweb.nih.gov/ij), according to the method described by Ottelé et al. (2010). Only particles larger than 0.2 μm were counted, as we were limited by the image resolution. The PM composition was investigated by energy dispersive X-ray (EDX) analysis, with lower limits of 0.1 wt%.

2.3. The rinse and weigh method

The methods for rinse and weigh were those described by Dzierzanowski et al. (2011). The PM was rinsed off leaves with distilled water, resulting in the almost complete removal of the leaf-deposited PM (Fig. A.2). The rinse water was filtered using a sieve (bore diameter 100 μm) to remove PM larger than 100 μm. The water was then filtered sequentially, using 10 μm, 3 μm, and 0.2 μm filters (Millipore, USA), capturing large, coarse, and fine PM, respectively. Before and after their use, the filters were dried for 2 h at 60 °C, stabilized over 24 h (20–23 °C, and 30–40% relative humidity), and weighed using a BT25S balance (Sartorius Scientific Instruments Co. Ltd, Germany).
The PM in the wax was also measured by the rinse and weigh method. However, the distilled water was replaced by chloroform to dissolve the wax. We obtained the PM deposited in wax after the filtering process. The leaf area was measured using a scan root surface area analyzer (Zhejiang Advanced Instrument, GXY-A, China).

2.4. Estimation of PM deposited by the whole tree

We obtained the total leaf surface area of one tree using the LAI-2000 (Li-cor, USA) (Table 1). We hypothesized that the loading of PM on leaves from different parts of the tree were the same. We multiplied the masses of PM per specific area by the total leaf surface area of one tree to obtain the total amount of surface PM accumulated per tree of the five evergreen species in three size fractions.

3. Results and discussion

3.1. The specific location of PM on the leaf surface

The stomata (Fig. 2a), the furrowed areas (Fig. 2b), and leaf hairs (Fig. 2c) on the leaf surfaces were the optimum zones for particles to deposit because they were rough and adherent. That is why rough leaves captured PM more efficiently than smooth leaves. From the PM pictures, we found that PM up to 2 μm can get into the stomatal cavity and/or block the stomata (Fig. 2a). Many researchers (Burkhardt, 2010; Hwang et al., 2011) have reported that the rough leaf surface had more deposited PM, but these instances are rare. Our results directly demonstrated the specific location of PM deposition on leaf surfaces. Previous studies demonstrated that particles can be absorbed through stomata (Fowler, 2002; Ottélé et al., 2010) and indicated that a particle less than 0.1 μm can pass through the stomata. However, we found that fine PM can pass through the stomata, a conclusion similar to Lehndorff et al. (2006).

3.2. The morphological characteristics and elemental analysis of PM on leaf surface

Morphological analysis is one method used to identify PM sources. Particles with irregular shapes and angular edges came from natural sources, such as soil dust and/or from industrial or transport sources, resulting from particle abrasion (Fig. A.3 a–c). Spherical particles, which may come from coal firing (Shi et al., 2003) or biomass burning (Li et al., 2003), were easily identified by their smooth surfaces and regular shapes (Fig. A.3 d). Carbon particle aggregates larger than 10 μm, also called soot (Fig. A.3 e), were aggregates of fine or ultra fine particles that originated from vehicle exhaust and the burning of coal and biomass. Biological source particles included spores and pollens (Fig. A.3 f), which were also easily identified. Most bio-particles were large, with diameters ranging from 20 μm to 50 μm.

The EDX results indicated the main elemental composition of PM was O > C > Si > Fe > Ca > S > Mg > Pb > Al > Br > K > Na > Cl (Fig. 3). The particles mainly comprised C, O, Si, Ca, Na, and Mg may have come from natural sources, whereas particles containing Pb, Br, Fe, and Cl may have been the result of human activity (Ottélé et al., 2010; Yang et al., 2003). Dai et al. (2013) found that the main elements in PM on leaves of Sophora japonica in Beijing were C, O, Si, Ca, and Al, similar to our results. In our study, particles P1, P3, P5, and P8 (Fig. 4) had irregular shapes and have high concentrations of C, O, Si, and Al. These particles may have come from soil dust, as their diameters were less than 3 μm, but P8 was larger than 30 μm. P2, P7, and P9 (Fig. 4) had high concentrations of C, O, and Ca, with irregular shapes that indicated they may have come from building construction dust. Pb is a heavy metal known to be
harmful to human health and is mainly derived from anthropogenic sources, such as vehicle exhaust and coal. In our study, we found that particle P4 (Fig. 4) had high concentrations of Pb and Br. P4’s diameter was approximately 10 µm and it had a spherical shape, and its elemental composition, size and shape all indicated it came from vehicle exhaust. Fe can affect human body health. Maher et al. (2013) found high Fe content in the PM on leaves of roadside trees. We also found that particle P6 (Fig. 4), with a diameter of 3 µm, had 86% of Fe in weight. High concentrations of C, O, Si, Fe, and Ca meant the source of the PM was mainly from natural sources and partly from human activities. Wang et al. (2012) studied the airborne PM2.5 composition in RCEES, found that the mainly source of airborne PM2.5 were soil dust and construction dust. Similar source were for both airborne PM2.5 and particle deposited on leaves.

3.3. The number density of PM on leaf surface

The number density of particles, i.e., the number of particles on specific leaf areas, varied according to the size of the PM (Fig. 5). The number of particles had two peaks distributed from 0.2 to 0.8 µm and 2.5 to 5.0 µm. The number of particles with diameters larger than 5 µm was rare. J. formosana had a higher number density of PM in all of the size fractions when compared to the other species. The PM density was recalculated into three size categories: fine (0.2–2.5 µm), coarse (2.5–10 µm), and large (10–100 µm) (Table 3). The results showed that fine PM accounted for approximately 96% of the total PM number on leaf surfaces, while coarse PM accounted for 3.7%, and large PM comprised only 0.14%. J. formosana accumulated the most fine, coarse, and large PM, whereas E. japonicus accumulated the least amount of fine and coarse PM per unit area. P. bungeana accumulated the least amount of large PM per unit area.

3.4. The mass of PM on leaf surface

The results showed significant differences in the PM deposition between the different species (Fig. 6). The PM ranged from 72.31 µg/cm² (in P. tabulaeformis) to 231.84 µg/cm² (in J. formosana). The average deposition was 148.45 µg/cm². These results were comparable to a study by Sebø et al. (2012), which showed that Pinus sylvestris, a type of evergreen tree found in Norway, had 70 µg/cm² PM. The differences between these studies may be related to the PM concentration in the air, meteorological conditions, and/or differences in leaf architecture. E. japonicus, a type of

<table>
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<tr>
<th>Table 1</th>
<th>The basic characteristics of trees sampled (SE ± SD, n = 4).</th>
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<tr>
<td>Species</td>
<td>Height (m)</td>
</tr>
<tr>
<td>Pinus tabulaeformis</td>
<td>7.8 ± 2.5</td>
</tr>
<tr>
<td>Juniperus formosana</td>
<td>6.1 ± 1.2</td>
</tr>
<tr>
<td>Pinus bungeana</td>
<td>6.2 ± 2.1</td>
</tr>
<tr>
<td>Platycladus orientalis</td>
<td>4.1 ± 1.6</td>
</tr>
<tr>
<td>Euonymus japonicus</td>
<td>1.9 ± 0.7</td>
</tr>
</tbody>
</table>

* The foliage density of each tree was measured by LAI-2000 (Li-cor, USA).

<table>
<thead>
<tr>
<th>Table 2</th>
<th>The sampling date and dry periods before sampling.</th>
</tr>
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<tbody>
<tr>
<td>Sampling date</td>
<td>Dry period before sampling (days)</td>
</tr>
<tr>
<td>2013/5/26</td>
<td>50</td>
</tr>
<tr>
<td>2013/9/26</td>
<td>30</td>
</tr>
<tr>
<td>2013/11/25</td>
<td>35</td>
</tr>
<tr>
<td>2014/5/20</td>
<td>45</td>
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</tbody>
</table>

* Data come from Beijing urban ecosystem research station.

Fig. 2. Scanning electron micrographs of PM on leaf surfaces. (a) PM in and around stoma, (b) PM in the furrowed area, and (c) PM around leaf hairs.
shrub, was less efficient than *J. formosana* on the leaf scale.

The amount of surface PM deposited on foliage in different size fractions also differed significantly between the plants (Table 4). The fine PM (diameter 0.2–2.5 μm) accumulated on the leaves comprised 2.09% (by wt) of the total PM. Although a small percentage, this accumulation was significant because fine PM is the most harmful to human health. Although there were no significant differences between the species, *J. formosana* had most of the fine PM deposited on a specific area of the leaf surface.

Coarse PM (2.5–10 μm) comprised 18.88% (by wt) of the total PM deposited on leaf surfaces. The highest mass concentration of coarse PM was found on *J. formosana* leaves (49.14 μg/cm²), which was significantly higher when compared to the other species (Table 4) (*p* < 0.05). *P. tabulaeformis* accumulated the least amount of coarse PM (14.64 μg/cm²).

Large PM (10–100 μm) comprised 79% (by wt) of the total PM on
the foliage. Large PM accumulated on *J. formosana* leaves approximately three times more efficiently than on *P. tabulaeformis*. The percentage of the large PM fraction was lowest for *J. formosana*, which indicated that *J. formosana* leaves were more effective at accumulating small diameter (fine and coarse) PM. *E. japonicus* was more effective at accumulating large PM, but least effective in accumulating fine PM.

The large PM accounted for the majority of total PM (by wt), followed by coarse PM and fine PM. Dzierzanowski et al. (2011) reached similar conclusions. Popek et al. (2013) found the percentages of fine, coarse, and large PM were 14%, 21%, and 65%, respectively. The differences may be accounted for by the concentrations of each fraction in the air and by the leaf and structural characteristics of the studied plant species.

### 3.5. The PM deposited in wax

In terms of size fraction, *J. formosana* deposited the most fine and coarse PM in wax, 2.32 µg/cm² and 25.60 µg/cm², respectively. *P. bungeana* accumulated the most large PM in wax (34.86 µg/cm²). The highest mass of PM in wax was found on *J. formosana* leaves (54.70 µg/cm²), which was significantly higher than the other species (Fig. 7). *P. tabulaeformis* accumulated the least PM (42.91 µg/cm²). The particles fixed in wax were approximately 23% of the total PM on the leaf (PM on surface and PM in wax). Once PM is buried in the wax, it can be fixed on the leaf permanently and cannot return to the air again until the leaf falls off the tree.

### 3.6. The mass of PM deposited by the whole tree

*J. formosana* accumulated most PM per specific leaf area on the leaf scale. *P. bungeana* accumulated the most PM in all fractions on the tree scale: 7.83 g, 64.91 g, and 337.06 g for fine, coarse, and large PM, respectively (Table 5). While *Platycladus orientalis* deposited the least amounts of PM: 0.72 g, 6.16 g, and 19.85 g for fine, coarse, and large PM, respectively. The pine trees (*P. bungeana*, *P. tabulaeformis*) deposited more PM than the cypress trees (*J. formosana*, *Platycladus orientalis*). In terms of leaf area density, the closely
Species marked with different letters are significantly different as determined with one-way analysis of variance (ANOVA) (p < 0.05).

### Table 4
Total amount of surface PM accumulated on foliage of 5 evergreen species with respect to three size fractions. Data are mean ± SD, n = 16 (4 months with 4 replicates in each). Species marked with different letters are significantly different as determined with one-way analysis of variance (ANOVA) (p < 0.05).

<table>
<thead>
<tr>
<th>Species</th>
<th>The quality of PM on leaf (µg/cm²)</th>
<th>The percentage of different fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fine (0.2–2.5 µm)</td>
<td>Coarse (2.5–10 µm)</td>
</tr>
<tr>
<td>Juniperus formosana</td>
<td>4.19 ± 2.45 a</td>
<td>49.14 ± 23.02 a</td>
</tr>
<tr>
<td>Euonymus japonicus</td>
<td>3.10 ± 0.73 a</td>
<td>24.84 ± 10.63 b</td>
</tr>
<tr>
<td>Pinus bungeana</td>
<td>2.94 ± 1.86 a</td>
<td>24.36 ± 10.71 b</td>
</tr>
<tr>
<td>Platycladus orientalis</td>
<td>2.90 ± 1.59 a</td>
<td>24.79 ± 9.16 b</td>
</tr>
<tr>
<td>Pinus tabulaeformis</td>
<td>1.64 ± 0.71 a</td>
<td>14.64 ± 6.58 b</td>
</tr>
<tr>
<td><strong>average</strong></td>
<td>2.95</td>
<td>27.55</td>
</tr>
</tbody>
</table>

Planting J. formosana may also have a high efficiency in PM accumulation.

In our study, we only measured the mass of insoluble particles in three size fractions (0.2–2.5 µm, 2.5–10 µm, and 10–100 µm). The soluble particles were not analyzed because it was impossible to distinguish them in the size fraction. Furthermore, it was difficult to extract the PM dissolved in the large quantity of water produced from the washing method. In addition, during the procedure, the soluble ions of the leaf may leak out and cause a deviation of the results. According to Chen et al. (2005) and Zhang et al. (2007), the percentage of the total water-soluble ions of the total suspend particles was less than 9% in the RCEES. So the results were slightly undervalued the effects of plants on PM deposition. There may be a deviation in the estimation of the PM deposited by the whole plant. The samples were collected at the height of 1.5 m and we did consider the variance in the canopy height. Therefore, improvements are necessary for a future study. In addition, the high efficiency in PM removal means more damage to the growth.

### 4. Conclusion
Urban plants play important roles in mitigating urban airborne PM. Fine PM (at least up to 2 µm) can get into the stomatal cavity. The leaf-deposited PM mainly comprised C, O, Si, Fe, and Ca, indicating that the PM was mainly from natural source around the RCEES. The number of particles per leaf cm² was 1.95 × 10⁷. The mass concentration was 148.44 µg/cm² on the leaf surfaces of evergreen species in Beijing. Fine PM (less than 2.5 µm) only accounted for 2.09% of the total mass PM, but the number of fine PM was large and accounted for 96% of the total PM number on the leaf surface. J. formosana was the most effective at mitigating airborne PM at the leaf scale, and P. bungeana had the most PM deposited at the tree scale. Because of the large leaf area, pine trees accumulated more PM than cypress trees. Therefore, in the high PM concentration areas, the planting of more pine trees should be considered. We estimated the difference between the PM depositions on the five evergreen species. We provided basic and accurate data for the evaluation of PM accumulated by urban plants, which is especially important for PM2.5 mitigating in Beijing.

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### Appendix A. Supplementary data
Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.01.032.

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