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Physicochemical characteristics of ambient particles settling upon leaf surfaces of urban plants in Beijing

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Abstract: Particulate pollution is a serious health problem throughout the world, exacerbating a wide range of respiratory and vascular illnesses in urban areas. Urban plants play an important role in reducing particulate pollution. Physicochemical characteristics of ambient particles settling upon leaf surfaces of eleven roadside plants at four sites of Beijing were studies. Results showed that density of particles on the leaf surfaces greatly varied with plant species and traffic condition. *Fraxinus chinensis*, *Sophora japonica*, *Ailanthus altissima*, *Syringa oblata* and *Prunus persica* had larger densities of particles among the tall species. Due to resuspension of road dust, the densities of particles of *Euonymus japonicus* and *Parthenocissus quinquefolia* with low sampling height were 2—35 times to other taller tree species. For test plant species, micro-roughness of leaf surfaces and density of particles showed a close correlation. In general, the larger micro-roughness of leaf surfaces is, the larger density of particles is. Particles settling upon leaf surfaces were dominantly PM_{10} (particulate matter less than 10 μm in aerodynamic diameter; 98.4%) and $PM_{2.5}$ (particulate matter less than 2.5 μm in aerodynamic diameter; 64.2%) which were closely relative to human health. Constant elements of particles were C, O, K, Ca, Si, Al, Mg, Na, Fe, S, Cl and minerals with higher content were SiO_2, $CaCO_3$, $CaMg(CO_3)_2$, NaCl and $2CaSO_4 \cdot H_2O$, SiO_2. $CaCO_3$ and $CaMg(CO_3)_2$ mainly came from resuspension of road dust. $2CaSO_4 \cdot H_2O$ was produced by the reaction between $CaCO_3$ derived from earth dust or industrial emission and SO_2, H_2SO_4 or sulfate. NaCl was derived from sea salt.

Keywords: density of particles; particle size distribution; element composition; micro-configuration of leaf epidermis; mineral composition; particles; urban plants

Introduction

Particulate pollution is a serious problem with the potential to cause the most severe and damaging health effects currently in industrial and urban areas of both developed countries and those in transition. Particles are either primary, emitted directly from power stations, motor vehicles, cement factories, etc., or secondary, formed in the atmosphere through reactions of other pollutants such as SO_2, NO_X, ammonia and VOCs (DoE, 1995). The combination of high population density and rapid industrialization in China has inevitably led to an increase in emissions. Coal burning particles are recognized as a major source of particles in China (He *et al.*, 2001). Automobile exhaust particles are becoming an important source of particles with the increase of vehicle population. For example, the vehicle population in Beijing exceeds 2.4 million vehicles in August 2005, nearly two times to that in 1999. In addition, dust storms invading Beijing in March and April are another source of particles (Liu *et al.*, 1981; Gao *et al.*, 2002). The types of illness reportedly exacerbated by particulate pollution have mainly been those affecting the cardiovascular and respiratory systems (Ostro *et al.*, 1991; Pope *et al.*, 1995; Powe and Willis, 2004). There have been a number of important medical studies that have linked high concentrations of PM_{10} (particulate matter less than 10 μm in aerodynamic diameter) with adverse human health effects, and more recently attention has moved to the finer $PM_{2.5}$ (particulate matter less than 2.5 μm in aerodynamic diameter), since smaller particles may penetrate further into the respiratory system (Koenig *et al.*, 1993; Pekkanen *et al.*, 1997).

Plants in urban areas may improve air quality by the removal of gaseous pollutants and of particles (Beckett *et al.*, 1998; McPherson *et al.*, 1998). As a result of their larger leaf areas and the turbulent air movements created by their structure, trees take up more pollutants, including particulates (PM_{10}), than shorter vegetation (Fowler *et al.*, 1999; Beckett *et al.*, 2000a). Pollutant removal from the atmosphere is by wet deposition in rain, snow and mist (particularly windblown aerosols), or by dry deposition. Particles, whether organic species or aqueous and present as aerosols (ammonium sulphate, sulphuric acid, etc.), are deposited via four processes: sedimentation under gravity, diffusion (i.e. by Brownain motion) or by turbulent transfer resulting in impaction and interception (Chamberlain and Little, 1981). Size is the main characteristic which determines the behavior of particles in the atmosphere and it is expressed as aerodynamic diameter (D_p).

Recent studies have tested for particulate absorption through sampling leaves and examining the residue washed from sampling leaves (Lovett and Lindberg, 1992; Freer-Smith *et al.*, 1997; Beckett *et al.*, 2000b; Freer-Smith *et al.*, 2005). Significant variation in particulate deposition was observed partly

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due to the ambient pollution at the sites, and partly due to significant same site species differences, indicating that pollution absorption varies between tree species. It is clear that species choice, planting design and location relative to pollution source are critical in determining the effectiveness of particle capture by trees (Beckett *et al.*, 1998). However, relatively little data is available on particle removal by plants or physicochemical characteristics of particles settling upon leaf surfaces in China. Densities of particles settling upon leaf surfaces of plant species can guide species choice to maximize particle removal from urban air. Size distribution of particles settling upon leaf surfaces can illuminate the role that urban plants play in removing PM_{10} and element and mineral analyses benefit to determine likely sources of particles.

Our objectives were to (1) assess densities of particles settling upon leaf surfaces of selected roadside plants and observe variation in density of particles with plant species and traffic condition; (2) examine the influence of micro-roughness of leaf surfaces on density of particles; (3) determine size distribution of particles settling upon leaf surfaces, since PM_{10} and $PM_{2.5}$ have a major influence on the risk to human health; (4) carry out element and mineral analyses so that the composition and source of particles could be determined.

1 Materials and methods

Four sampling sites were selected in Beijing, Yangjiazhuang between the five-ring road and the six-ring road in the northwest direction, Beijing Normal University near the northern three-ring road, Fuchengmen and Fuxingmen both on the western two-ring road (Fig.1). Total eleven plant species were chosen, eight deciduous tree species (*Populus tomentosa, Populus canadensis, Salix matsudana, Juglans regia, Fraxinus chinensis, Prunus persica, Ailanthus altissima* and *Sophora japonica*), one deciduous shrub species (*Syringa oblata*), one evergreen shrub species (*Euonymus japonicus*) and one climber species (*Parthenocissus quinquefolia*). They all grow on the roadside. For the convenience of fieldwork, sampling heights of the deciduous trees and the deciduous shrub were about 2 m, and those of the evergreen shrub and the climber were about 1—1.5 m. Leaf samples were collected from 10—20 plants of each species in late August 2003, after a period of 10 d without rain. The number of leaves collected for each species varied from 100 to 400 so that the total leaf area of each sample was approximately equal.

Leaves were washed in distilled water with a 3-cm wide, no-hair-loss brush. The wash solution was transferred into the pre-weighted conical flask, and then was completely vaporized on the hot plate. The

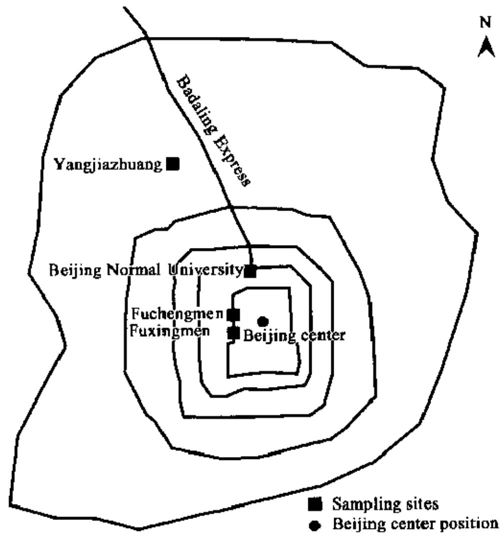

Fig.1 Sketch map of sampling sites

drying particles with the conical flask were immediately weighed using an electrical mono-pan balance with a 0.01 g precision. After a leaf washed was naturally dry in the shady and ventilated space, the area of each leaf was measured using a Li-2000 leaf area instrument. Density of particles settling upon leaf surfaces was calculated using the equation $W = (w_2-w_1)/A$, where W is density of particles (g/m^2), w_1 is initial weight of conical flask, w_2 is final weight of conical flask with particles, and A is total area of leaves.

Scanning electron micrographs of micro-configurations of upper and lower leaf surfaces of eleven plant species were taken using a Philips XL30 Environmental Scanning Microscopy (ESEM). Constant element composition of leaf surfaces was measured using the electron probe of ESEM in the same time. The longest dimension of the particle, regarded as the size of the particle, was recorded for each particle in the quarter area of the scanning electron micrographs using the Photoshop software, with measurement to the nearest 0.44 μm being possible.

The samples of particles collected from leaf surfaces were analyzed using a Philips X' pert Pro MPD X-ray diffraction instruction (XRD) to determine mineral compositions. Qualitative analysis was at 40 kV and 40 mA to produce Cu-Kα radiation and scanning rates of 0.05° 2θ min^{-1} from 5° to 90°. Quantitative analysis adopted the "Number-K method" using Si as reference matter at 40 kV and 40 mA to produce Cu-Kα radiation and scanning rates of 0.05° 2θ min^{-1} from 8° to 35°.

2 Results and discussion

2.1 Densities of particles settling upon leaf surfaces of eleven plant species

Fig.2 shows that density of particles settling upon leaf surfaces varies with plant species and traffic conditions of sampling sites. The plants with low sampling height, such as *Euonymus japonicus* and *Parthenocissus quinquefolia*, have larger densities of particles settling upon leaf surfaces than other taller plants with high sampling height. As automobile exhaust including particles and gaseous and resuspended road dust are at ground level, lower leaves are directly exposed to the sources and hence have larger densities of particles settling upon leaf surfaces. The densities of particles of *Euonymus japonicus* and *Parthenocissus quinquefolia* are 20.80 g/m^2 and 15.11 g/m^2, respectively. For the tall plants, *Fraxinus chinensis* has the maximum and *Populus Canadensis* has the minimum density of particles. Densities of particles of *Fraxinus chinensis* facing road and back to road are 9.21 g/m^2 and 6.40 g/m^2, respectively. Density of particles of *Populus Canadensis* is 0.78 g/m^2. The trend of density of particles among the tall species is *Fraxinus chinensis* >*Sophora japonica* >*Ailanthus altissima* >*Syringa oblata* >*Prunus persica* > *Populus tomentosa* > *Juglans regia* > *Salix matsudana* > *Populus canadensis*.

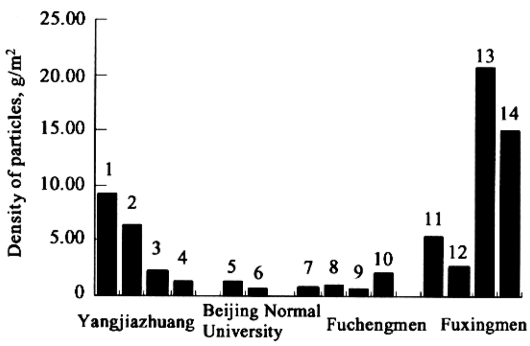

Fig.2 Densities of particles settling upon leaf surfaces of eleven plant species at four sites in Beijing

1. *Fraxinus chinensis* (facing road); 2. *Fraxinus chinensis* (back to road); 3. *Syringa oblata*; 4. *Populus tomentosa*; 5. *Juglans regia*; 6. *Populus Canadensis*; 7. *Populus Canadensis*; 8. *Salix matsudana* (main road); 9. *Salix matsudana* (secondary road); 10. *Prunus persica*; 11. *Sophora japonica*; 12. *Ailanthus altissima*; 13. *Euonymus japonicus*; 14. *Parthenocissus quinquefolia*

The influence of traffic condition on density of particles can be clearly demonstrated from the densities of particles of the same plant species at various traffic flow sites. For instance, density of particles of facing road leaves of *Fraxinus chinensis* is larger than that of leaves back to road. Density of particles of *Populus Canadensis* in Beijing Normal University is smaller than that in Fuchengmen and those are 0.61 g/m^2 and 0.78 g/m^2, respectively. Density of particles of *Salix matsudana* on the main road is 1.02 g/m^2, and that on the secondary road is 0.67 g/m^2.

2.2 Micro-configurations of leaf surfaces

Scanning electron micrographs show the micro-configurations of upper and lower leaf surfaces of eleven plants (Fig.3). Stomata of most plants are on the upper leaf surfaces except *Populus Canadensis* and

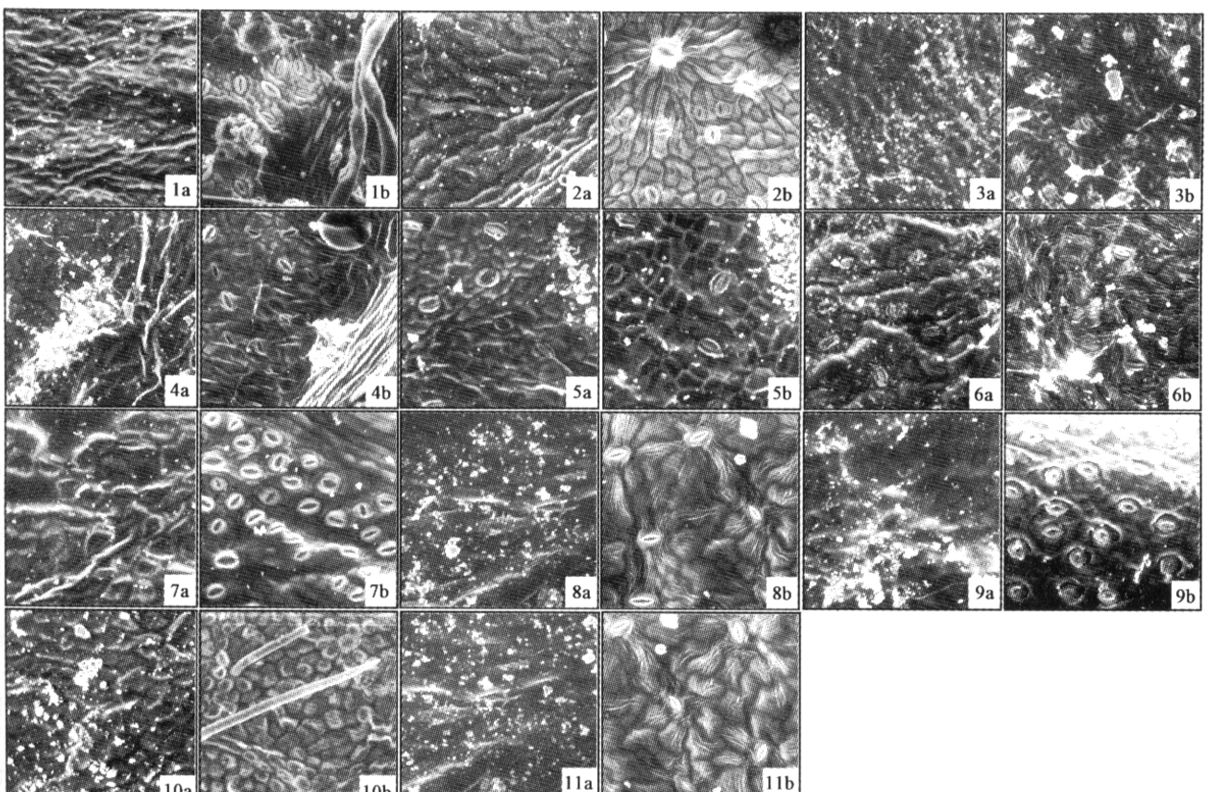

Fig.3 Scanning electron micrographs of micro-configurations of upper and lower leaf surfaces of eleven plant species

1. *Fraxinus chinensis*; 2. *Syringa oblata*; 3. *Populus tomentosa*; 4. *Juglans regia*; 5. *Populus Canadensis*; 6. *Salix matsudana*; 7. *Prunus persica*; 8. *Sophora japonica*; 9. *Ailanthus altissima*; 10. *Euonymus japonicus*; 11. *Parthenocissus quinquefolia*; a. upper leaf surface; b. lower leaf surface; ×350

Salix matsudana. Hairs are only present on the lower leaf surface of *Euonymus japonicus*. Leaf veins can be clearly seen from the micrographs of the adaxial leaf epidermis of *Syringa oblata*, *Juglans regia* and *Prunus persica*. The fall between heave and groove of epidermal cells and the density of micro-configurations such as heave, groove, cell and vein determine the micro-roughness of leaf surfaces. Test plant species show a good correlation between micro-roughness of leaf surfaces and density of particles settling upon leaf surfaces. The larger micro-roughness of leaf surfaces is, the larger density of particles is. For example, *Fraxinus chinensis*' upper leaf surface presents the densest and deepest strip groove which benefits to capture and hold particles, and hence corresponds to the largest density of particles settling upon leaf surfaces among the tall plants. Moreover, there are deeper strip grooves on the upper leaf epidermis of *Syringa oblata* and *Prunus persica*, with relatively larger densities of particles.

2.3 Size distribution of particles settling upon leaf surfaces

Table 1 shows the total number of measured particles settling upon upper and lower leaf surfaces of eleven plant species, proportions of PM_{10}, $PM_{2.5}$, $PM_{2.5}/PM_{10}$ and statistical analysis of particle size. The total number of particles measured is 1847, with 1531 particles on upper leaf surfaces and 316 particles on lower leaf surfaces in the same areas, suggesting that plants mainly capture particles by upper leaf surfaces.

Table 1 Total number of measured particles settling upon upper and lower leaf surfaces of eleven plant species, proportions of PM_{10}, $PM_{2.5}$, $PM_{2.5}/PM_{10}$ and statistical analysis of particle size

	Total number of measured particles	Minimal particle size, μm	Maximal particle size, μm	Mean particle size, μm	Standard deviation, μm	Percentage of PM_{10}, %	Percentage of $PM_{2.5}$, %	Percentage of $PM_{2.5}/PM_{10}$, %
Upper leaf surface	1531	0.73	22.66	2.75	2.36	98.4	64.2	65.2
Lower leaf surface	316	0.73	26.17	3.53	3.17	96.2	50.6	52.6

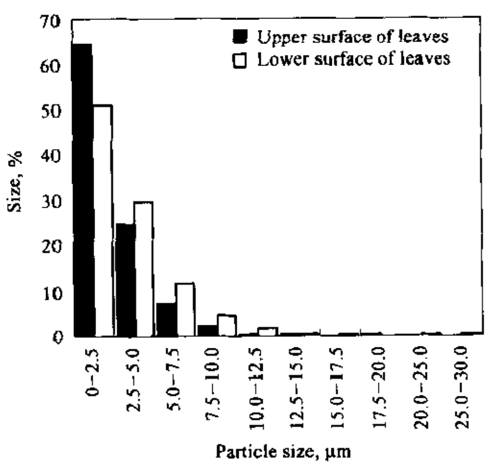

Fig.4 Size distribution of particles settling upon upper and lower surfaces of leaves of eleven plant species

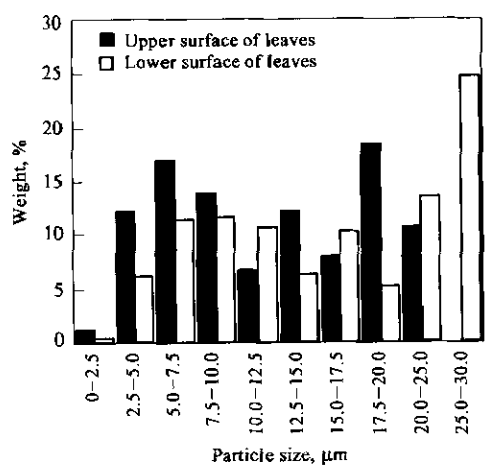

Fig.5 Weight distribution of particles settling upon upper and lower surfaces of eleven plant species in some size interval, which were gained from particle size distribution

Particles settling upon upper leaf surfaces were dominantly PM_{10} (98.4%) and $PM_{2.5}$ (64.2%) which were closely relative to human health. The average, maximal and minimal sizes of particles settling upon upper leaf surfaces are 2.75 μm, 22.66 μm and 0.73 μm, respectively. Particle size distribution is shown in Fig.4.

Supposing that the density of each particle settling upon leaf surfaces is equal, we can get the weight distribution of particles in some size interval derived from particle size distribution (Fig.5). The weight percentage of PM_{10} and $PM_{2.5}$ settling upon upper leaf surfaces makes up 44.0% and 1.2% , respectively. The weight percentage of $PM_{2.5}$ accounts for 2.7% of that of PM_{10}. To the air of Beijing, average weight percentages of PM_{10}/TSP (total suspended particle), $PM_{2.5}$/TSP and $PM_{2.5}/PM_{10}$ are 55%, 29% and 52.7% (He *et al.*, 2002), respectively. These data indicate that PM_{10} can be captured by plants more effectively than $PM_{2.5}$, which results in that $PM_{2.5}$ is difficult to settle under gravity due to too small aerodynamic diameter and that $PM_{2.5}$ captured by leaf surfaces is prone to resuspending.

2.4 Constant elements composition of particles settling upon leaf surfaces

Mean constant element composition of the leaf surfaces of the eleven plant species measured by ESEM is shown in Fig.6. There are eleven constant elements which are C, O, K, Ca, Si, Al, Mg, Na, Fe, S, Cl. The total content of C (73.11%) and O (19.26%) counts for 92.37%, as they are the main elements of

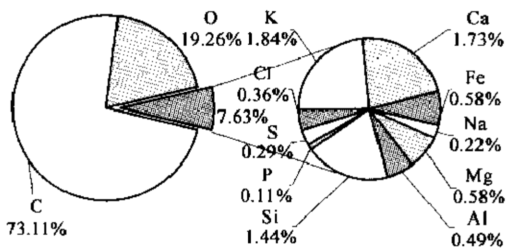

Fig.6 Mean constant element composition of leaf surfaces of eleven plant species measured by ESEM

leaf tissues. Moreover, C and O are the main elements of particles in many forms, such as SiO_2, CO_3^{2-}, SO_4^{2-} and organic matter. The contents of K, Ca and Si are higher.

2.5 Main minerals contents of particles settling upon leaf surfaces

The results of qualitative analysis of particles settling upon leaf surfaces by XRD showed that peak values of SiO_2, $CaCO_3$, $CaMg(CO_3)_2$, NaCl, $2CaSO_4 \cdot H_2O$, (Na,Ca)Al(Si, $Al)_3O_8$ and clay minerals were higher. Table 2 shows the contents of SiO_2, $CaCO_3$, $CaMg(CO_3)_2$, NaCl and $2CaSO_4 \cdot H_2O$ of particles settling upon leaf surfaces of eleven plants at four sites in Beijing by the "Number-K method". SiO_2 is presented in the highest content in all the plants except *Populus canadensis* in Fuchengmen. $CaCO_3$ in the contents is next to the SiO_2, except *Parthenocissus quinquefolia*. Mineral composition of particles varied with plant species and sampling sites. For *Euonymus japonicus* and *Parthenocissus quinquefolia* with low sampling height, NaCl and $2CaSO_4 \cdot H_2O$ could not be

Table 2 Main mineral contents of particles settling upon leaf surfaces of eleven plant species at four sites in Beijing (%)

Species	Sampling site	SiO_2	$CaCO_3$	$CaMg(CO_3)_2$	NaCl	$2CaSO_4 \cdot H_2O$	Total	Remark
Fraxinus chinensis	Yangjiazhuang	21.51	15.08	6.92	0.67	1.33	45.51	Facing road
Fraxinus chinensis	Yangjiazhuang	23.74	13.00	6.01	2.45	3.90	49.10	Back to road
Syringa oblata	Yangjiazhuang	23.96	6.91	7.38	0.00	0.00	38.25	
Populus tomentosa	Yangjiazhuang	19.17	7.47	4.10	0.42	0.00	31.16	
Juglans regi	Beijing Normal University	5.62	1.45	1.08	1.33	1.78	11.26	
Populus canadensis	Beijing Normal University	9.70	9.35	1.71	4.79	6.60	32.15	
Populus canadensis	Fuchengmen	12.15	13.90	4.13	4.37	4.56	39.11	
Salix matsudana	Fuchengmen	11.62	6.72	3.41	5.06	11.76	38.57	Main road
Salix matsudana	Fuchengmen	11.77	10.74	1.56	2.41	3.63	30.11	Secondary road
Prunus persica	Fuchengmen	19.26	9.04	6.64	0.69	5.46	41.09	
Sophora japonica	Fuxingmen	14.36	8.04	6.32	2.08	5.56	36.36	
Ailanthus altissima	Fuxingmen	15.57	8.05	7.00	1.13	0.00	31.75	
Euonymus japonicus	Fuxingmen	28.32	17.22	7.33	0.00	0.00	52.87	
Parthenocissus quinquefolia	Fuxingmen	29.59	10.96	15.52	0.00	0.00	56.07	

detected and the total contents of SiO_2, $CaCO_3$ and CaMg $(CO_3)_2$ arrived to 52.87% and 56.07% , respectively. The total contents of the five minerals of *Fraxinus chinensis* facing road and back to road are 45.51% and 49.10% , next to those of *Euonymus japonicus* and *Parthenocissus quinquefolia*. The total mineral content of *Juglans regi* (11.26%) is the lowest.

As the major components of sand, SiO_2, $CaCO_3$ and $CaMg(CO_3)_2$ settling upon leaf surfaces are mainly derived from resuspension of road dust. Related with SO_2 emission closely, $2CaSO_4 \cdot H_2O$ is produced by the reaction between $CaCO_3$ derived form earth dust or industrial emission and SO_2, H_2SO_4 or sulfate. The research on the source of PM_{10} in California concluded that Na and Cl marked maritime sources, Si marked geological sources, and C marked anthropogenic combustion sources (Chow, 1996). Other studies also reported that Na and S are related with sea aerosol (Lee *et al.*, 1994). Therefore, NaCl settling upon leaf surfaces under the study is deemed to come from sea salt.

The results of element and mineral analyses of particles settling upon leaf surfaces suggest that a large proportion of particles are organic in origin. Further investigations need be conducted for detail information about this.

3 Conclusions

Density of particles settling upon leaf surfaces greatly varied with plant species and traffic condition. The trend of density of particles among the tall species is *Fraxinus chinensis* > *Sophora japonica* > *Ailanthus altissima* > *Syringa oblata* >*Prunus persica* > *Populus tomentosa* >*Juglans regia* > *Salix matsudana* > *Populus canadensis*. *Fraxinus chinensis*, *Sophora japonica*, *Ailanthus altissima*, *Syringa oblata* and *Prunus persica* had larger densities of particles. Due to resuspension of road dust, the densities of particles of *Euonymus japonicus* and *Parthenocissus quinquefolia* with low sampling height were 2—35 times to other taller tree species. For test plant species, micro-roughness of leaf surfaces and density of particles show a close correlation. In general, the larger micro-roughness of leaf surfaces is, the larger density of particles is. Particles setting upon leaf surfaces were dominantly PM_{10} (98.4 %) and $PM_{2.5}$ (64.2 %) which were closely relative to human health. Therefore, plants in the urban area can play an important role in removing PM_{10} and $PM_{2.5}$. Constant elements of particles are C, O, K, Ca, Si, Al, Mg, Na, Fe, S, Cl and minerals with higher content are SiO_2, $CaCO_3$, $CaMg(CO_3)_2$, NaCl and $2CaSO_4 \cdot H_2O$. SiO_2, $CaCO_3$ and $CaMg(CO_3)_2$ mainly come from resuspension of road dust. $2CaSO_4 \cdot H_2O$ is produced by the reaction between $CaCO_3$ derived from earth dust or industrial emission and SO_2, H_2SO_4 or sulfate. NaCl is derived from the sea salt.

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