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Coagulation effect of aero submicron particles on plant leaves: Measuring methods and potential mechanisms[☆]

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ABSTRACT

Aero submicron particles (d < 1 μm) have attracted widely attention due to their difficulty in removal from the air and serious threat to human health. Leaves are considered as important organs to purify particulate matter and alleviate air pollution. However, the current research mainly focuses on the removal capacity of particulate matter by urban plants at different scales, there are relatively few studies on the change of particle diameter at the air-leaf interface during this process. This study is one of the first to propose the existence of coagulation effect of aero submicron particles on the leaves, and a sweep-resuspension method and X-ray microscope were used to measure such size changes of two typical subtropical broad-leaf plants. The results showed that the size of submicron particles increased significantly during the migration from atmosphere to leaf surface: the average particle size increased from 0.48 μm at emission to 3.40 μm on the leaf surface, while the proportion of submicron particles decreased from 95% to less than 20%. The sweep-resuspension method was easy to implement, the data was easy to obtain, and the cost was low, therefore it could be widely used in the determination of the coagulation effect. The coagulation effect was also inferred as an important mechanism used by plants to reduce particulate matter. In the process of particulate removal: coagulation effect and dry deposition are actually two steps that occur simultaneously and interact. This finding refined the understanding of particulate removal processing, and laid a foundation for further research on factors affecting coagulation, which can be helpful for optimizing tree species selection and plant arrangement.

1. Introduction

Atmospheric particulate matter, a primary air pollutant in the city (Shi et al., 2018; Voliotis and Samara, 2018) has been a key focus of research in the field of urban environment (Janhäll, 2015). The dispersion of particulate matter in the atmosphere can significantly reduce visibility, which is the cause of haze, and particulate matter can enter the respiratory tract of the human body, increasing the risk of diseases of the cardiopulmonary system and causing significant harm to health (Samek et al., 2018; Hofman et al., 2013).

Depending on their aerodynamic diameter, atmospheric particulates can be classified into micron-sized particles (diameter > 1 μm), submicron particles (0.1–1 μm), and ultrafine particles (diameter < 0.1 μm). The quantity concentration of PM_1 is higher than other particle sizes (Zhou et al., 2018). In terms of mass concentration, PM_1 is also the most important part of fine particles. The $PM_1/PM_{2.5}$ ratio can be over 70% (Gomišček et al., 2004; Qiao et al., 2016). The smaller the size of particles, the larger the light absorption coefficient, resulting in lower atmospheric visibility (Chow et al., 2002). However, the characteristics of submicron particles means they are not as easy to disperse as ultrafine particles and have a smaller gravitational sedimentation velocity than

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micron-sized particles (Zhu et al., 2018), which have difficulty settling naturally in the atmosphere. Therefore, it is extremely important to pay attention to the transmission and purification of submicron particles in the air.

Although it has been recently pointed out that the impact of urban plants on air pollution is very complex (Eisenman et al., 2019; Viippola et al., 2018; Janhäll, 2015; Setälä et al., 2013), most studies still believe that they play important roles in the removal of different kinds of particulate matter and ultimately can effectively mitigate and control such pollution (Du et al., 2019; Selmi et al., 2016; Xu et al., 2019; García de Jalón et al., 2019; Ji and Zhao, 2018). It is generally accepted that dry deposition is the primary mechanism of particulate removal (Giardina et al., 2019), a process that involves particles colliding with or contacting the leaves and then staying on the contact surface to escape the atmosphere (Beckett et al., 1998; Du et al., 2019). As part of this process, a large size particle is generally intercepted and held by the action of gravity and inertia to the leaves and branches. The submicron particles primarily reach the leaf surface through Brownian motion, and then wrap around the airflow and disperse along the boundary layer between the leaf and the atmosphere (Grantz et al., 2003) before adhering to the leaf surface (Mitchell et al., 2010).

A large number of studies have been carried out on the dry deposition rates of different plants and scales and their influencing factors. Beckett et al. (2000), Freer-Smith et al. (2004), Pullman (2009), Sæbø et al. (2012), Przybysz et al. (2014) and Chen et al. (2016) used different atmospheric simulants measured the dry deposition velocity of various tree species. Hofman et al. (2016) studied the effect of canopy morphology on dry deposition velocity. Räsänen et al. (2013) and Leonard et al. (2016) explored the effects of leaf surface microstructures, especially leaf fluff. Przybysz et al. (2014) and Zhang et al. (2019) explored the effect of rainfall on dry deposition velocity. Pellerin et al. (2017) and Giardina et al. (2019) developed various models for predicting dry deposition velocity.

Although it has been proposed that different particle size played different roles in pacticulate removal, there are few studies on systematic measurement and description (Viippola et al., 2018; Janhäll, 2015; Setälä et al., 2013). What's more, changes in the size of particulate matter, especially submicron particulate matter, has been of less concern to researchers. During particulate removal, the airflow carrying the particles surrounds the leaf. And its movement in the boundary layer differs from that prior to approaching the leaf. For example, the airflow will form a velocity gradient and turbulence (Molina-Aiz et al., 2006) that affects the particles (Pullman, 2009). The original motion law is then broken, and the particles collide, adhere, and agglomerate in the disturbed air (Wu et al., 2002). Therefore, when the submicron particulate matters migrate from the atmosphere to the leaf, the phenomenon of concentration at a large particle size, also called the coagulation effect, occurs. Such coagulation means the submicron particles are more efficiently retained on the leaf and effectively removed from the atmospheric environment. Thus, the coagulation effect at the atmosphere–leaf interface is also an important mechanism of particulate removal.

However, confirming and measuring this effect, especially in relation to particle size, remains difficult. The most common methods used are scanning electron microscopy (SEM) (Margiotta et al., 2015; Yan et al., 2016; Song et al., 2015; Kocić et al., 2014) and washing-different pore size filter (Dzierzanowski et al., 2011; Song et al., 2015). However, the SEM can only observe the surface of the leaf and increases the randomness of the results due to its small field of view. Different magnifications will also affect the number, area, traits, and other information about the particles (Lin et al., 2018). The other method also has problems such as retention of small particles after saturation of the filter membrane, and defects in which the water-soluble component cannot be separated. A more effective method of measurement is therefore needed to characterize the coagulation effect.

The objective of this paper was to confirm the existence of coagulation effect by measuring the diameter change of submicron particle migrating from the atmosphere to the leaf surface. Therefore, we chose *Cinnamomum camphora* and *Osmanthus fragrans* as experimental plants, developed two methods, sweep-resuspension and X-ray microscopy, and calculated the average particle size and proportion of each particle size segment to characterize the degree of aggregation of submicron particles.

Furthermore, we attempted to explore the potential mechanisms behind coagulation, and refined the understanding of particulate removal process. And it could also lay a foundation for further research on factors affecting coagulation, which helps to optimize tree species selection and plant arrangement.

2. Materials and methods

2.1. Sample collection

The sampling site in this experiment was the plant specimen garden of the Minhang Campus, Shanghai Jiao Tong University (see Fig. 1). Shanghai is located at the mouth of the Yangtze River and has a typical subtropical monsoon climate. The average annual precipitation is 1098 mm. The typical forest type is evergreen broad-leaf forest. The soil pH is between 8.0 and 9.0, and the organic matter content is moderate. As common greening plants in Shanghai, *C. camphora* and *O. fragrans* were selected as the experimental species, representing typical trees and shrubs respectively. The sampling requirements were as follows: 3 adjacent plants were selected for each sample species chosen to performed 6 replicates; mature leaf samples were collected from the outer crown; the height was approximately 2/3 of the tree; the growth condition was good; the growth posture was similar. The leaf area of each group was controlled at approximately 400–600 cm^2, and there was minimal overlap between the leaves. To reduce the influence of time on the characteristics of the leaf, samples were collected on the same day and brought back to the laboratory immediately after collection. These were then soaked in water for 3 min, after which the surface of the leaf was washed once with flowing water and then 2–3 times with deionized water. The sample was then inserted into the flower mud and dried quickly in the fume cupboard. The experiment began after the moisture had completely evaporated.

2.2. Simulated particulate removal of plants in smog chamber

Particulate removal by leaf was simulated in a self-made aerosol smog chamber. NaCl was selected as the simulated atmospheric particle due to its stable chemical properties and a particle size that aligned with the experimental requirements. The average particle size was 0.48 μm, of which the submicron proportion was more than 95% when emitted. When evenly dispersed by a fan in the smog chamber, the average particle size was 0.79 μm and the submicron proportion exceeded 77%. Most of the simulated particles were certain to have been submicron particles prior to contact with plants.

The self-made aerosol smog chamber was a stainless-steel cylinder with a radius of 40 cm and a height of 80 cm. An aerosol generator equipped with a drying tube was placed at the bottom of the smog chamber and the flow rate controlled to stabilize the concentration of particulate matter in a certain range. The fan above the generator produced a stirred updraft and formed a more

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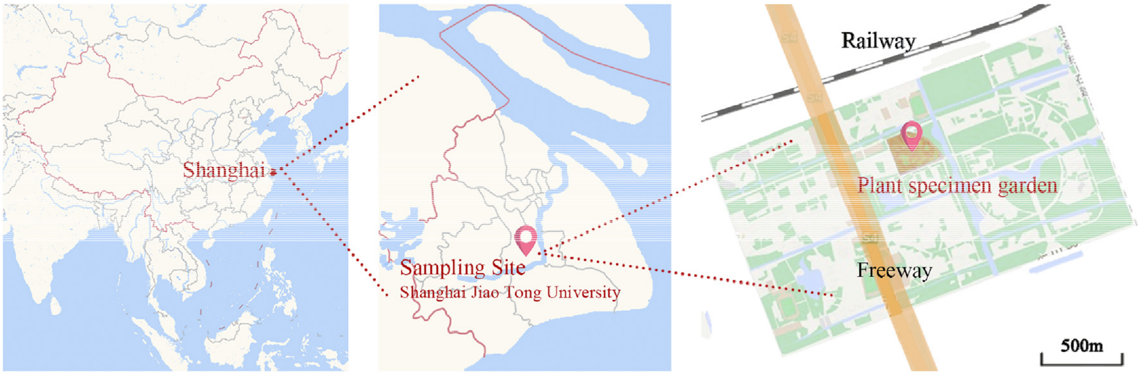

Fig. 1. Study area and sampling sites.

complex path when passing through the leaves in the middle (Hwang et al., 2011). This meant that leaves were exposed to an omni-directional aerosol flow. The particle size spectrometer (GRIMM 11-R, German) recorded the quantity and mass concentration of particles in the atmosphere of the chamber every 6 s in 30 particle size intervals in the range of 0.2—30 μm.

Particulate removal was divided into four steps: 1) N_2 was added into the smog chamber to reduce the PM_1 concentration to less than 5 μg/m^3; 2) The heating device and fan were turned on to control the environmental conditions as follows: temperature 25 °C, humidity 40%—50%, wind speed 2 m/s; 3) The washed leaf samples were placed into the chamber to keep them as natural as possible; 4) The particle size spectrometer was connected and the aerosol generator with NaCl saturated solution turned on to maintain the mass concentration of PM_1 at approximately 200 μg/m^3. The particulate removal test time was 30 min.

Each sample was divided into two groups after that. One group was determined by sweeping method and the other group was determined by X-ray microscopy.

2.3. Determination of particle size on leaves using the sweep-resuspension method

This method was implemented in a sweep-resuspension smog chamber, the structure of which is shown in Fig. 2. By cleaning the leaf with a brush, the retained particles were resuspended back into the air. It was therefore possible to measure the concentration of particles of different sizes in the air to determine the condition of particles retained on the leaf.

The chamber was a stainless-steel cylinder with a diameter of 60 cm and a length of 150 cm, which was cleaned using N_2 before the test. The sweeping operation was conducted using the rubber gloves sealed on the chamber to ensure the tightness inside. The fan in the smog chamber helped ensure the resuspended particles were evenly distributed. The particle size spectrometer recorded the quantity and mass concentration of particles in the atmosphere of the chamber every 6 s in a total of 30 particle size intervals in the range of 0.2—30 μm.

The sweep-resuspension method comprised 6 steps: 1) The concentration of PM_1 in the sweeping smog chamber was reduced below 5 μg/m^3 by adding N_2. The background concentration $N_{0(0.2\text{-}30)}$ and the mass concentration $M_{0(0.2\text{-}30)}$ of each particle size were then recorded; 2) The dusty plant leaves were placed on the operating table in the sweeping smog chamber and the particles on the leaf surface were gently brushed. The fan was then turned on, following which the particles dispersed in the air of the chamber quickly and evenly; 3) The quantity and mass concentration of each particle size was recorded 10 times by a particle size spectrometer before and after reaching the peak value. The average values $N_{1(0.2\text{-}30)}$ and $M_{1(0.2\text{-}30)}$ were calculated; 4) The formulas for calculating quantity (LN_x) and mass (LM_x) of particles per unit leaf surface are as follows: Eqns (1) and (2):

$$LN_x = \frac{\left(N_{1(0.2-30)} - N_{0(0.2-30)}\right)\cdot V}{LA} \tag{1}$$

$$LM_x = \frac{\left(M_{1(0.2-30)} - M_{0(0.2-30)}\right)\cdot V}{LA} \tag{2}$$

where x is the particle size, $x \in [0.2, 30]$, V is the smog chamber volume, and LA is the sample leaf area.

5) The above steps were repeated six times to obtain six parallel groups of LN_x and LM_x. Their mean values ($\overline{LN}_x$ and $\overline{LM}_x$) were used to plot the quantity and mass distribution curves of particulate matter on the leaves. 6) The average particle diameter (D_C) on the leaf surface can be obtained by integrating the fitting curve of each

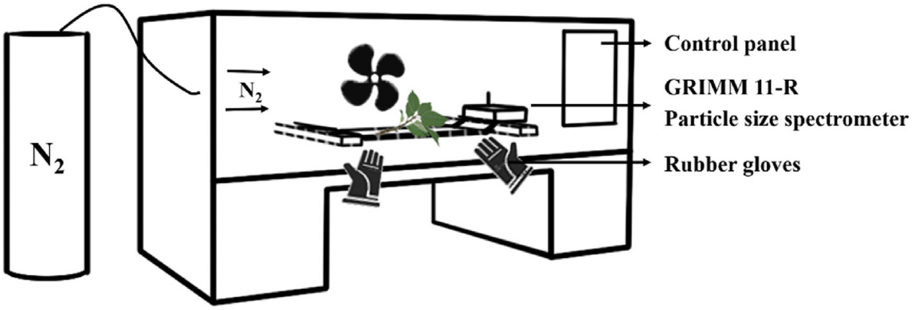

Fig. 2. Sweep-resuspension smog chamber.

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particle size as equation (3). The proportion of each particle size can be obtained by subsection integral. Similarly, this step is repeated six time.

$$D_C = \frac{\int_{0.2}^{30} x \cdot LN_x dx}{\int_{0.2}^{30} LN_x dx} \tag{3}$$

where x is the particle size and LN_x represents the corresponding quantity of the particle size.

2.4. Determination of particle size on leaves using X-ray microscopy

The X-ray microscope has the characteristics of high precision, a wide field of view, and three-dimensional imaging. In this experiment, the X-ray microscope (Xradia 520 Versa, Zeiss) was used to scan the dusty plant leaves directly. The main steps were as follows: 1) Select a leaf randomly from each sample and cut a small piece (approximately 2 mm × 4 mm) under a dissecting microscope; 2) The leaf pieces were wrapped with a sealing film to keep the leaves moist and prevent them from deforming during scanning; 3) The bottom of the leaf was fixed on the special sample clip of the X-ray microscope and 3D scanning was performed; 4) The scanned file was imported into Dragonfly image processing and 3D reconstruction software (ORS, 2.0.0.140), within which the 3D scanning image (Fig. 3) was established. As shown in the figure, debugging the imaging parameters enables the various structures of the leaf (the red part of the picture) to be clearly seen and the particles on the leaf segmented (the white part of the picture, mainly distributed on the surface).

Using this matching software, not only the size of the particle could be measured manually using the ruler tool, but also it was possible to derive volume Vi and surface area Si of each particle based on the gray value. Thus, it can further calculate the average particle diameter and distribution of the respective particle size segments for each sample. Similarly, this step is repeated six time. Through imaging observation, we found that the accumulation of particles on the leaf surface was mainly in the lateral expansion, and the whole was an irregular cylindrical shape. Therefore, we calculated the particle size Di of each particle according to formula Eqn (4).

$$V_i = \pi \cdot r_i^2 \cdot h_i$$

$$S_i = 2\pi \cdot r_i \cdot h_i + 2 \cdot r_i^2 \cdot h_i$$

$$D_i = \sqrt{\left[(2r_i)^2 + h_i^2\right]} \tag{4}$$

where r_i represents the bottom radius of cylinder-like particles, and h_i represents the height of cylinder-like particles. Three groups of solutions of r_i and h_i were calculated using volume V_i and surface area S_i. According to the practical significance, a set of realistic solutions could then be reserved and D_i calculated.

3. Results

3.1. Particle size distribution on the leaf surface using the sweep-resuspension method

Following simulated particulate removal and sweep-resuspension, the particle size distribution of *O. fragrans* and *C. camphora* leaves is as shown in Fig. 4.

Fig. 4 shows the mass concentration and quantity concentration of simulated particles during emission and following long-term dispersion in the smog chamber as well as the mass and quantity of particles retained per unit leaf area of *O. fragrans* and *C. camphora*. To clearly show the distribution, the quantity distribution figure only included 0–10 μm as most of the particles were concentrated below 10 μm.

The mass distribution curve of particles with different sizes showed that the distribution of particles on the surface of leaves moved to a larger particle size than that in the smog chamber. The particles retained on leaves reached a peak at 5, 10, and 20 μm.

The quantity distribution curve also showed that the particle size was less than 1 μm when emitted. Then after being dispersed evenly in the smog chamber by the fan, the submicron particles still accounted for the vast majority of the particles. Conversely, most of the particles on the surface of *O. fragrans* and *C. camphora* leaves were micron particles, with an obvious increase in the quantity of particles in the range of 1–5 μm. The two particle size distribution curves showed that the particles combined with each other making the size increased on leaves and that the coagulation effect indeed occurred in the process of particulate removal.

The average particle size and the proportion of each particle size segment were obtained by calculating the number of particles with each particle size. The results are as follows.

Fig. 5 (a) shows the proportion of each particle size segment in different media, which included: the proportion at the time of emission, after long-term dispersion, and on *O. fragrans* and *C. camphora* leaves. Fig. 5 (b) shows the corresponding average particle size. The coagulation effect of particles could be clearly seen from the proportion of submicron particles and the average

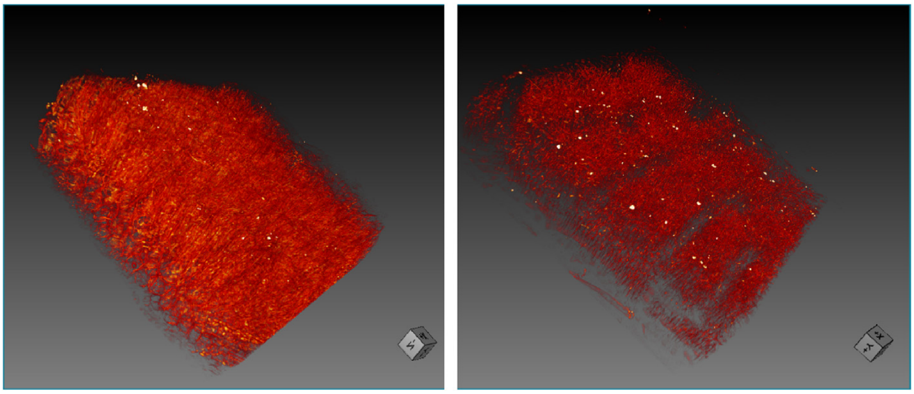

Fig. 3. X-ray microscope scan picture. (a) *Osmanthus fragrans*; (b) *Cinnamomum camphora*.

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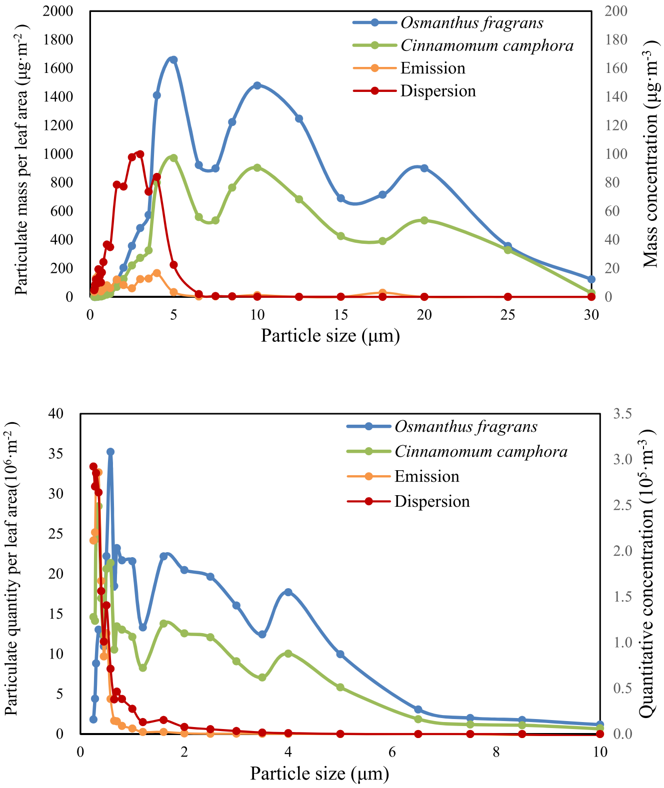

Fig. 4. Size of each particle in each medium (based on the sweep-resuspension method).

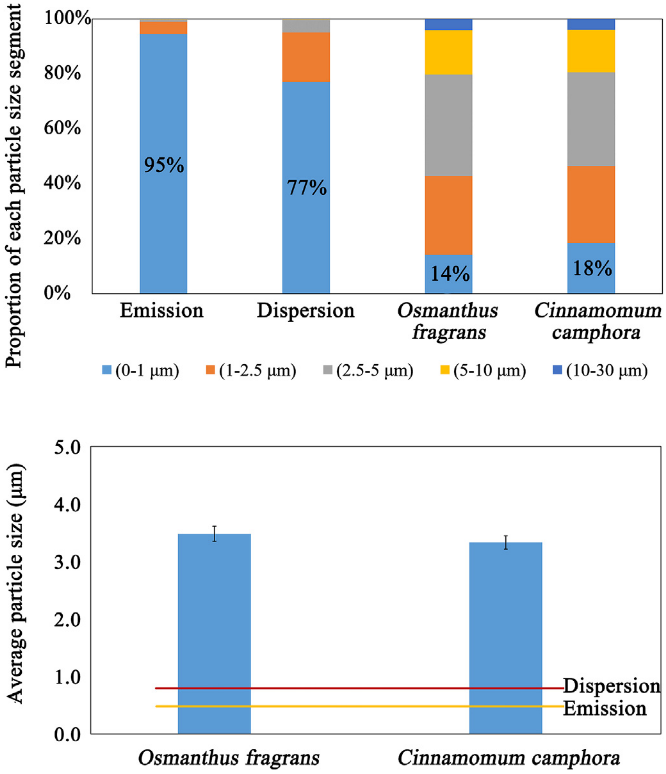

Fig. 5. Indexes of coagulation in each medium (based on sweep-resuspension method). (a) Proportion of each particle size segment; (b) Average particle size.

particle size.

When simulated particles were emitted, the proportion of submicron particles reached as high as 95%. After a long period of dispersion, the proportion remained high at 77%. This indicated that the accumulation of submicron particles in the smog chamber was trace and that the particles remained in a submicron state before they contacted the leaves.

On the surface of the leaves, the proportion of submicron particles was only 14%–18%. Furthermore, approximately 28%–29% and 34%–37% of the particles fell in the range of 1–2.5 μm and 2.5–5 μm, respectively, the latter of which was the main particle size section on the leaf surface. This indicated that during the migration from air to leaf surface, the size of particles increased and the proportion of submicron particles clearly decreased.

The average particle size also increased significantly. The average particle size was 0.48 μm at emission, increasing slightly to 0.77 μm after dispersion. However, it increased to 3.48 μm on the *O. fragrans* surface and 3.33 μm on the *C. camphora* surface, 4–5 times larger than that before contact.

The above results showed that particulate removal by plants was not a pure reduction in terms of the mass of particles. In the process of migrating from the atmosphere to the leaves, the small size particles would gather together so that the particle size retained on the leaf surface was larger than that in the air, that is, the coagulation effect occurred.

Sweeping and resuspending the particles on leaves, measuring the particle size concentration using a particle size spectrometer, and then calculating average particle size and the proportion for each particle size section, helped elucidate the change in particle size and better quantified the coagulation effect.

3.2. *Particle size distribution on the leaf surface by X-ray microscopy*

Following particulate removal, X-ray microscope scanning and Dragonfly software calculating, the average particle size and the proportion are shown in Fig. 6. Due to the resolution limitations of the X-ray microscope, it was impossible to capture submicron particles completely. According to the results of the previous sweep-resuspension method, most of the particles on the leaf surface were micron particles; therefore, we only conducted a statistical analysis on the micron scale.

Based on the proportion of each particle size segment, particles in the range 1–2.5 μm and 2.5–5 μm respectively accounted for 82% and 18%, when emitted; thus, the former was the main particle size. However, on the leaf surface, the proportion of both segments was approximately 40%. Furthermore, almost 20% particles were above 5 μm in size. Therefore, the quantity of small particles reduced while the quantity of large particles significantly increased.

The average particle size on the *O. fragrans* surface was 3.70 μm and on the *C. camphora* surface was 3.80 μm, 8–9 times higher than that of emission and 5 times higher than that after dispersion. Because particles below the resolution accuracy were not included, the average particle size would be larger than this in real life, but still within a reasonable range. The above results also demonstrate the existence of the coagulation effect.

4. Discussion

4.1. *Comparison of two methods for quantifying the effect of coagulation*

In the previous section, particle size on the leaves of the same batch of samples was measured using a sweep-resuspension method and X-ray microscope. The former was an indirect

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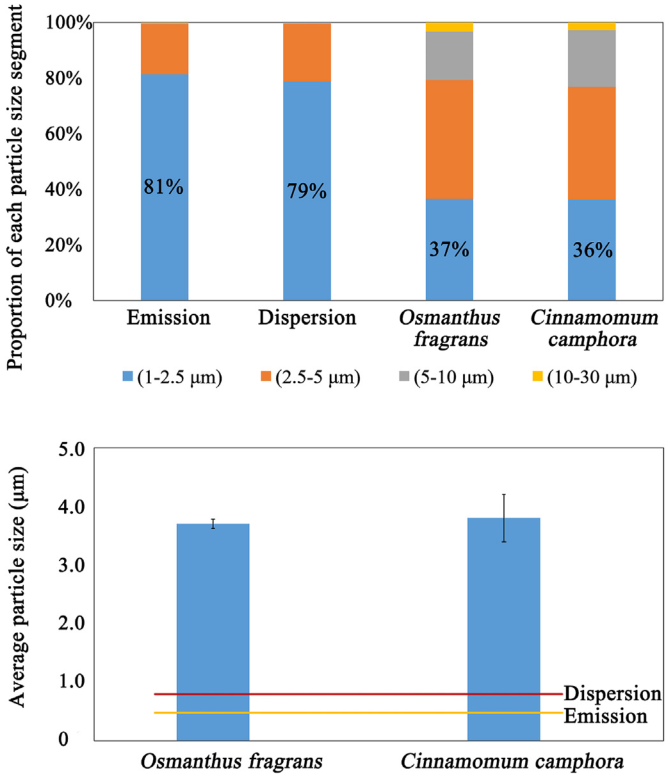

Fig. 6. Indexes of coagulation in each medium (based on X-ray microscopy). (a) Proportion of each particle size segment; (b) Average particle size.

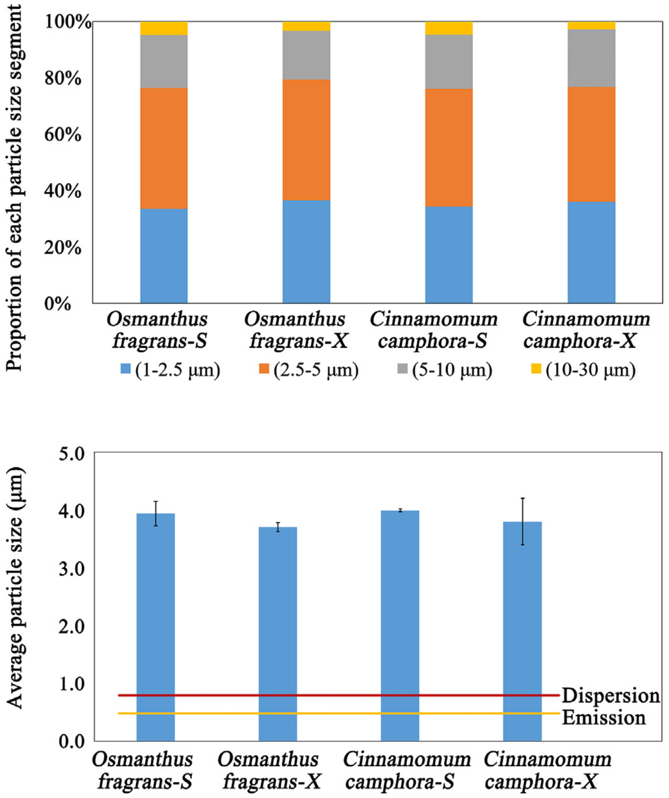

Fig. 7. Indexes of coagulation under two methods. (a) Proportion of each particle size segment; (b) Average particle size S stands for sweep-resuspension; X stands for X-ray microscope.

method. It converted the foliar particles into atmospheric particles by resuspension and simplifies the previous problem of direct measurement to a common measurement method. The principle underlying the particle size spectrometer was to obtain different particle sizes from the different light scattering angles of particles to the laser. The X-ray microscope used a more advanced microscope and system to scan the leaf surface and obtain a three-dimensional structure of the entire scanning domain. The whole process of measurement was considerable, the results are more intuitive and accurate, and it has high reliability.

Due to the resolution limitations of the X-ray microscope, the results obtained using the sweep method were counted and recalculated only at the micron level to facilitate a comparison between the two methods. The results are as follows (see Fig. 7):

As shown in the proportion of each particle size segment, the distribution of the four groups was similar. Particles in the range 1–2.5 μm and 2.5–5 μm accounted for 34%–37% and 41%–43% respectively. The latter was much higher than that at the time of emission and before contacting the leaf.

The difference between average particle size was also small. The particle size obtained using the sweep-resuspension method was approximately 3.9 μm and that obtained using the X-ray microscope was in the range 3.7–3.8 μm. Under both methods, the results for *O. fragrans* were slightly smaller than those of *C. camphora*. Combining the two indexes, the results using the two methods were very close.

We therefore conducted an independent sample *t*-test on the average particle size and the proportion of main segments of the particles on two kinds of plant leaves. The results are as follows (see Table 1):

The results show that the highest significance level of the three indexes was 0.977, the lowest was 0.073, and all six items were higher than 0.05. Therefore, there was no significant difference between the results obtained by the sweep-resuspension and X-ray microscope methods. This indicated that the results were scientific and reliable and that both methods could be used in the characterization of the coagulation effect.

Through our analysis, we found that the sweep-resuspension cleverly solved the problem of traditional direct measurement, which made the measurement of particle size easy to implement. Furthermore, counting every 6 s effectively eliminated error, improved the accuracy of measurement, and made the process of obtaining the data efficient and straightforward. However, we were concerned that the sweeping process may have an impact on the particles, causing some to change their morphology when they were suspended back in the atmosphere from the leaves, thus affecting the results of the determination. However, a comparison of the two methods showed that such an effect was acceptable.

As the control method for this experiment, the X-ray microscope observation method has high reliability. Compared with the traditional scanning electron microscope method, the X-ray microscope could realize three-dimensional imaging with high precision and a larger field of vision. Combined with the Dragonfly software, data on each particle in all the structures of the leaf could be accurately obtained, which meant the observation was more intuitive and the calculation of particle size was more comprehensive and objective. Moreover, the three-dimensional spatial distribution of particles on the surface layer of the leaf could be fully understood from a 3D image, facilitating further exploration of the mechanism of particulate removal. However, resolution limitations meant it was impossible to capture submicron particles completely. And the cost was high and the scanning time was lengthy; therefore, this method was not suitable for the batch treatment of samples.

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Table 1
Differences in the results of two measurement methods.

Species		*Osmanthus fragrans*	*Cinnamomum camphora*
Average particle size	S	3.935 ± 0.211	3.991 ± 0.026
	X	3.699 ± 0.077	3.796 ± 0.402
	Sig.	0.073	0.364
Proportion of (1–2.5 μm)	S	0.336 ± 0.035	0.344 ± 0.025
	X	0.365 ± 0.047	0.363 ± 0.103
	Sig.	0.232	0.663
Proportion of (2.5–5 μm)	S	0.429 ± 0.027	0.419 ± 0.021
	X	0.429 ± 0.026	0.406 ± 0.052
	Sig.	0.977	0.622

S stands for sweep-resuspension; X stands for X-ray microscope.

The two methods developed in this paper to quantify the coagulation effect were greatly improved compared with the previous particle size determination methods. Given that there is no ideal method for the determination of particle size, the sweep-resuspension method and the X-ray microscope observation method can be considered the best choice for measuring particle size. Using these two methods, the concentration of each particle size can be measured, and the average particle size and the proportion of each particle size section can be calculated. This can help us to intuitively understand the change in submicron particles in the process of particulate removal and realize the quantification of the coagulation effect.

4.2. Speculation on the mechanism of coagulation of particles on leaves

In the previous section, we used two methods to confirm the coagulation effect of submicron particles in the process of particulate removal by plants. The process of atmospheric particles being retained by plant leaves was different from natural sedimentation. When particles migrate from the atmosphere to the leaf surface, they were more concentrated and the particle size increased. However, existing research did not offer any description of this particle size change, and there was no research on the coagulation effect of submicron particles.

During particulate removal, the airflow in the boundary layer was different from that in the atmosphere. Most previous studies suggested that plants caused resistance to fluid, resulting in a velocity gradient and vortex current (Molina-Aiz et al., 2006). Some scholars believed that the airflow would hit the leaf more violently (Wu et al., 2002). Other scholars believed that wind speed would slow down near the leaves to form a quieter interface (Lovett, 1994; Pandis et al., 1995). However, irrespective of the type of change, smaller size particles in the atmosphere would be disturbed by the change in airflow as the airflow approaches the leaves to the boundary layer. Therefore, we contended that, in such a boundary layer, particles would collide, adhere, reunite, and exhibit a coagulation effect due to disturbance.

The coagulation effect increased the particle size, so it could accelerate the dry deposition. Meanwhile particles that have been retained on the leaves by dry deposition were also affected by the characteristics of the leaves, which drove the small particles to continue coagulating on the surface of the large particle. Therefore, dry deposition and coagulation for submicron particles were actually two steps that occurred simultaneously and interacted in the process of particulate removal, which made submicron particles to be more efficiently retained on the leaves and removed from the atmospheric environment. Because coagulation effect affected the particulate removal capacity of different tree species, in the vicinity of coal-fired sources, metallurgical chemical sources, roads and other pollution sources, where the content of submicron particles is higher, the greening tree species with stronger coagulation effect could be selected, and more scientific plant arrangement could be carried out.

4.3. Possible inducing factors of coagulation effect

The change in the boundary layer microenvironment caused by the characteristics of leaves altered the movement law of particles and allowed them to collide with each other, which was the main cause of the coagulation effect. Therefore, environmental conditions and leaf functional trait will greatly affect the degree of particle size increase. In the previous paper, we strictly limited these two aspects to made the average particle diameter and proportion of each particle size reliable, which indirectly shows that these factors have an effect on coagulation.

Firstly, we proposed the following possibilities of coagulation from the external environmental conditions:

(1) Steam phase transition coagulation: Transpiration increased the humidity near the leaves and may even form a water film on the pore walls (Burkhardt, 2010). The submicron particles acted as a condensation nucleus to adsorb steam and increase the particle size. They also increased adhesion due to the formation of a liquid bridge to promote agglomeration (Pullman, 2009; Zhang et al., 2018). Studies have shown that after the transpiration rate of the leaves was accelerated, the removal efficiency of fine particles was much larger than that of PM_{10} (Ryu et al., 2019), which supported this hypothesis.

(2) Wind coagulation: Wind strengthened airflow disturbance and increased the frequency of collisions between particles. The leaf surface was an extremely uneven and smooth interface. Its gully, villi, and other microstructures would change the wind speed and direction of the leaf surface, which supported the coagulation of particles.

(3) Thermal diffusion coagulation: The physiological activity of the leaf changed the temperature in the microenvironment. When there was a temperature gradient in the flow field, the frequency of collisions on the high temperature side increased and particles tended to move toward the low temperature side (Romay et al., 1998; Williams, 1986). The more vigorous the physiological activity of the plant, the more intense the convective heat transfer, and the greater the probability of collision between particles. Additionally, the higher the temperature, the faster the overall movement speed of particles (Kej and Zachariah, 2001).

From leaf functional traits, as described in the previous 2.4, X-ray microscopy images show that particulate matter mainly concentrates on the surface, which probably related to the wax on the leaf surface. Adding a polymer organic agglomeration agent was a common dust removal method (Chen et al., 2015). The waxy layer of

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the leaves was mainly composed of extra-long chain fatty acids and their derivatives, as well as other trace secondary metabolites (Popek et al., 2013) that were likely to promote the coagulation of submicron particles.

For the specific impact of the above potential mechanisms, further in-depth experimentation is required. That will be helpful to understand the mechanism of the coagulation effect and control the pollution of submicron particles.

5. Conclusions

In this paper, we took *C. camphora* and *O. fragrans* as examples and measured particle size distribution on the leaf surface. We found that when submicron particles migrated from the atmosphere to the leaf surface, they reunited with each other so that the particle size on the leaf surface was much larger. This result proved that the coagulation effect occurred during particulate removal. And a characterization system of coagulation was established. The average particle size and proportion of each different particle size segments can be used to characterize coagulation effect. And both sweep-resuspension method and X-ray microscope were scientific and effective methods for measuring the size of leaf particles to get that two indexes. And we proposed that coagulation and dry deposition were two steps that occurred simultaneously and interacted. Coagulation effect was also one of the important mechanisms plants used to remove atmospheric particulate matter. But the inducing and influencing factors of the submicron coagulation effect we mentioned need further in-depth experimentation to check.

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Appendix A. Supplementary data

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