

Article

# Deposition of PM<sub>2.5</sub> Sulfate in the Spring on Urban Forests in Beijing, China

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**Abstract:** Water-soluble ions such as sulfate may have great impacts on atmospheric pollution. To determine the deposition effect of PM<sub>2.5</sub> sulfates, the major PM<sub>2.5</sub> constituents, in the forest canopy in Beijing, China, an investigation was carried out in an urban forest, Olympic Forest Park, and a suburban forest, Jiufeng National Forest Park. We measured the vertical distributions of sulfate by using monitoring towers in the two forests at the same times in March and May 2013. Sulfate (SO<sub>4</sub><sup>2-</sup>) was predominant in all PM<sub>2.5</sub> water-soluble inorganic ions, with a proportion >40%. The vertical concentration of SO<sub>4</sub><sup>2-</sup> increased with height, and the average sulfate concentration in Olympic Forest Park was higher than that in Jiufeng National Forest Park. Results also revealed that meteorological conditions had significant impacts on both the sulfate concentration and the deposition velocity. In winter, the deposition of SO<sub>4</sub><sup>2-</sup> through the canopy was not obvious in the two forest parks, which was quite the opposite in spring. The deposition velocity in the daytime was higher than that in the nighttime in both Olympic Forest Park (0.9 ± 1.0 cm/s vs. 0.4 ± 0.3 cm/s) and Jiufeng National Forest Park (1.3 ± 1.2 cm/s vs. 0.8 ± 0.8 cm/s). While Jiufeng National Forest Park turned out to have a higher average sulfate deposition velocity than Olympic Forest Park.

**Keywords:** sulfate; deposition velocity; PM<sub>2.5</sub>; forest canopy

## 1. Introduction

PM<sub>2.5</sub> includes all particulate matter that has an aerodynamic diameter of 2.5 microns or smaller. PM<sub>2.5</sub> represents only a small percentage in the air, but is considered as one of main components in atmospheric pollution. It is the most important contributor to haze and results in damage to the surfaces of buildings. Moreover, PM<sub>2.5</sub> can carry harmful substances such as carcinogens, and can combine into molecules which are much more dangerous than single composition substances; these substances can accumulate in the respiratory system and cause diseases. Therefore, PM<sub>2.5</sub> has increasingly received attention in recent decades [1]. Water-soluble ions are important parts of PM<sub>2.5</sub> and have a great influence on atmospheric pollution [2]. Of all the water-soluble ions, sulfate ion (SO<sub>4</sub><sup>2-</sup>) is present in the largest proportion [3]. To date, studies on PM<sub>2.5</sub> sulfates have mainly focused on aspects related to concentrations, size distribution characteristics, source analysis, and seasonal and diurnal variations of PM<sub>2.5</sub> [4–6]. However, there are few data from field investigations of SO<sub>4</sub><sup>2-</sup> deposition velocity in China.

The process of deposition is an important way to remove particulate matter from the air, and the crown canopy is an extremely important boundary between the atmospheric environment and the forest ecosystem. Leaves, branches, buds, and bark strongly adsorb atmospheric particulate matter, thereby influencing particulate matter depositions [7]. To date, studies of deposition of PM<sub>2.5</sub> sulfate

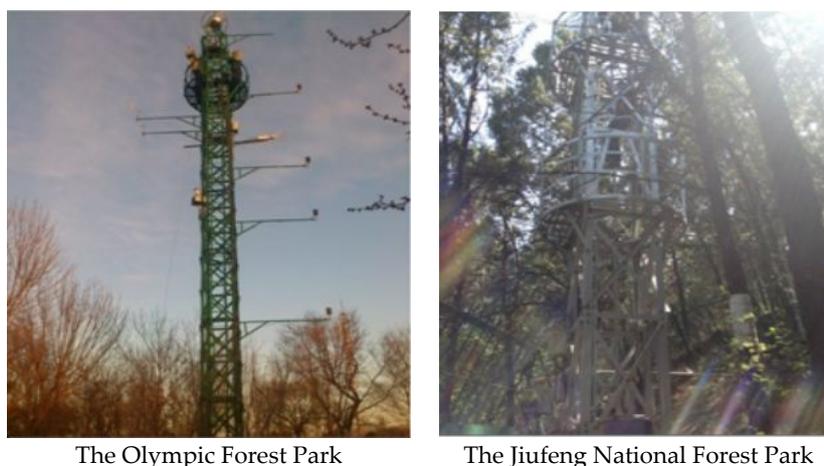
in forest systems have been mainly conducted in Europe and the United States [8–14], as well as some Asian countries other than China [15–17]. As the capital of China, which also happens to be deeply affected by haze, research on the deposition characteristics of PM<sub>2.5</sub> sulfate on forest systems in Beijing is of great importance and will help to determine the effect of these ecosystems on PM<sub>2.5</sub> sulfate removal in China.

## 2. Experimental Description and Methodology

### 2.1. Experimental Description

Beijing is located in the northeastern margin of the North China Plain. We selected for investigation a representative urban forest, Olympic Forest Park (40.258° N, 116.39° E) and a suburban forest, Jiufeng National Forest Park (40.06° N, 116.09° E). A portion of forest was selected in each park. There is a tower that is approximately 15 m tall in Olympic Forest Park (Figure 1), which served as the location where we placed three samplers; we placed one sampler on the monitoring tower at 15 m (out of the canopy), one at 9 m (the up side of the canopy), and one at 1.5 m (height of human respiratory) above the ground. The main plant species was *Populus tomentosa*, and there were bushes on the ground. On a tower with a height of approximately 15 m in Jiufeng National Forest Park, we also established three sampling points, at 15 m, 9 m, and 1.5 m above the ground surface. *Platyclusus orientalis* and *Pinus massoniana* Lamb were the main species.

The height of the trees was approximately 8 m around the tower in both sites. According to previous measurements at the site, the leaf area index (LAI) at the Jiufeng National Forest Park site was 3.8 in spring, and was 1.8 at the Olympic Forest Park site [18].



**Figure 1.** The experimental towers of Olympic Forest Park and Jiufeng National Forest Park.

### 2.2. Sample Collection

Investigations were conducted between March and May in 2013. Samples were collected five times a day by 6:00 a.m.–10:00 a.m., 10:00 a.m.–2:00 p.m., 2:00 p.m.–6:00 p.m., 6:00 p.m.–10:00 p.m., and 10:00 p.m.–6:00 a.m.. Each collecting process lasted for 4 h except the last one, which lasted for 8 h. A TH-150 sampling instrument equipped with a PM<sub>2.5</sub> cutter was used to collect the samples (TH-150A, Tianhong, Wuhan, China) with a flow rate of 100 L/min. The flow remained in stable condition during the sampling period. By comparing sampling filters, we decided to use quartz fiber filters (MK360, Munktell & Filtrak GmbH, Falun, Sweden) with 90 mm diameter because of their low background of inorganic ions, large specific surface area, and resistance to high temperatures. The filters were weighed before and after particulate collection using a balance (BT125D, Sartorius Co., Ltd., Beijing, China) with an accuracy of 0.00001 g. Ion concentrations of three blank films were lower than 2% of the lowest concentrations in the actual sample.

The atmospheric pressure weather instrument recorded meteorological parameters, including humidity and temperature (HMP45C, Campbell Scientific Inc., Logan, UT, USA), and wind velocity and direction (014A/024A, Met One Instruments Inc., Grants Pass, OR, USA). An ultrasonic anemometer (Wind Master, Gill Instruments, Lymington, UK) was used to attain Monin-Obukhov length and friction velocity. Before the collecting process, some preparatory steps were needed. Aluminum foil parceling membranes were placed in a muffle furnace and burning for 2 h under 400 °C, and then were left for 24 h. After that, the original weight of the membrane filters were recorded before being put to use. The membrane filters still needed another 24 h after the collection process, and were placed in a cold environment with a temperature of −4 °C and 75% relative humidity before they were weighed again to collect the quality and volume of PM<sub>2.5</sub>.

The water-soluble inorganic ions were extracted with deionized water and analyzed with an ion chromatograph (ICS-3000 with an DIONEX Ionpac As11-HC anion column, Thermo Scientific, Sunnyvale, CA, USA).

### 2.3. Calculation of Deposition Velocity

In this experiment, we calculated the deposition rate of fine particles through the tree canopy. Equations (1)–(3) were used to determine the  $d$  and  $Z_0$ .

$$U(z) = \frac{u^*}{k} \ln \frac{Z-d}{Z_0}, \quad (1)$$

in which  $U(z)$  ( $\text{m}\cdot\text{s}^{-1}$ ) is the average wind velocity;  $u^*$  ( $\text{m}\cdot\text{s}^{-1}$ ) is friction velocity which can be directly measured;  $k$  is the von Karman constant (0.41);  $d$  (m) is displacement height;  $Z_0$  is roughness length, which is used to model the horizontal mean wind speed near the ground and is equivalent to the height at which the wind speed theoretically becomes zero [19], according to Zhang et al. (2001) [20],  $Z_0$  was determined by considering different seasons and land use categories—in our study,  $Z_0$  was 0.75 at Olympic Forest Park and 0.8 at Jiufeng National Forest Park. The value of  $d$  can be calculated by iterative method [18] as:

$$f(d) = \frac{U(z_1) - U(z_2)}{U(z_1) - U(z_3)} = \frac{\ln(Z_1 - d) - \ln(Z_2 - d)}{\ln(Z_1 - d) - \ln(Z_3 - d)}, \quad (2)$$

$U(z_1)$ ,  $U(z_2)$  and  $U(z_3)$  are the wind velocity at height  $Z_1$ ,  $Z_2$ , and  $Z_3$ , respectively. In this study, we used 1.5 m, 9 m, and 15 m.

$$g(d) = d - \frac{f(d)}{f'(d)}, \quad (3)$$

$f(d)$  and  $g(d)$  are arbitrary functions used in the iterative process and  $f'(d)$  is the numerical derivative of  $f(d)$ . This equation set is used iteratively. First, an original value for  $d$  is assumed. Then, the value of  $g(d)$  is updated and used to determine the new value of  $d$ , then the updated  $d$  is substituted into Equations (2) and (3) to get a new  $g(d)$ . We assume the process has converged once the absolute value of the difference between the updated  $g(d)$  and the previous one is less than 0.001. The final value of  $d = g(d)$ .

We used the flux-gradient technique to calculate the deposition flux of PM<sub>2.5</sub> SO<sub>4</sub><sup>2-</sup>,  $F$  ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ) [8,16,21]. In Gradient method, the flux is derived from measurements of air concentrations at several heights above the receptor surface and from meteorological variables.  $F$  denotes deposition and was determined by Equation (4):

$$F = -u^*c^*, \quad (4)$$

where  $c^*$  ( $\mu\text{g}\cdot\text{m}^{-3}$ ) is the eddy concentration, expressed by the following equation:

$$c^* = \frac{k\Delta c}{\ln\left(\frac{Z_2-d}{Z_1-d}\right) - \Psi_h\left(\frac{Z_2-d}{L}\right) + \Psi_h\left(\frac{Z_1-d}{L}\right)}, \tag{5}$$

where  $Z_1$  and  $Z_2$  are the heights of 1.5 and 9 m;  $\Delta c$  is the concentration difference between heights of 1.5 m and 15 m, calculated by Equation (6);  $\Psi_h$  is the integrated stability correction function defined by Erisman and Draaijers (1997) [8], with its value obtained from Equations (7) and (8);  $L$  (m) is the Monin–Obukhov length;

$$\Delta c = c(z_3) - c(z_1), \tag{6}$$

$$\Psi_h\left(\frac{Z-d}{L}\right) = 2\ln\left(\frac{1+x}{2}\right) + \ln\left(\frac{1+x^2}{2}\right) - 2\arctan(x) + \frac{\pi}{2}, \tag{7}$$

$$x = \left[1 - 16\frac{(Z-d)}{L}\right]^{0.25}. \tag{8}$$

To sum up,  $F$  could be expressed as follows:

$$F = \frac{-ku^*[c(Z_3) - c(Z_1)]}{\ln\left(\frac{Z_2-d}{Z_1-d}\right) - \Psi_h\left(\frac{Z_2-d}{L}\right) + \Psi_h\left(\frac{Z_1-d}{L}\right)}, \tag{9}$$

$u^*$  was averaged every 15 min,  $L$  was the same as  $u^*$ ;  $F$  was averaged every 4 h. From Wesely and Hicks (1977) [22] we could obtain the deposition velocity, and  $V_d$  was determined using the following equation:

$$V_d = -F/C, \tag{10}$$

where  $C$  is the value of the concentration at 15 m height.

#### 2.4. Empirical Models

In order to compare measured data, three empirical models were chosen, which were proposed by Wesely and Hicks (1977) [22], Wesley et al. (1985) [12], and Ruijgrok et al. (1997) [23]. Although these three models are not entirely suitable for the situation, they are the most immediately applicable on account of being public spaces empirical models which consider wide open spaces. The model by Wesely et al. (1985) [12] is a dry deposition model over grass, whereas the Ruijgrok et al. (1997) [23] model is a dry deposition model over forest canopy. The Wesely and Hicks (1977) [22] model is a dry deposition model over all canopies.

(1) Wesley and Hicks (1977) [22]

$$V_d = \frac{1}{R_a + R_b + R_c}, \tag{11}$$

$$R_a = \frac{\left[\ln\left(\frac{z-d}{z_0}\right) - \Psi_h\left(\frac{z-d}{L}\right) + \Psi_h\left(\frac{z_0}{L}\right)\right]}{ku^*}, \tag{12}$$

$$R_b = \frac{2\left(\frac{Sc}{Pr}\right)^{\frac{2}{3}}}{ku^*}, \tag{13}$$

where the aerodynamic drag  $R_a$  is a value calculated by Garland (1978) [24],  $R_b$  is another atmospheric resistance reported by Hicks et al. (1987) [25],  $Pr$  is Prandtl number, and  $Sc$  is Schmidt number.  $R_c$  is forest canopy resistance and can be obtained based on theoretical considerations.

(2) Wesley et al. (1985) [12]

In this model, deposition velocities of the aerosol particles are expressed by the aerodynamic terms equation.  $V_{ds}$  in following equation is the surface deposition velocity.

$$V_d = 1 / (R_a + V_{ds}^{-1}). \quad (14)$$

It was fit to a grassland ecosystem in North America by Wesley et al. (1985) [12], where  $V_d$  is the forest surface deposition velocity, which can be determined by the following equation when the atmosphere is neutral or stable ( $L \geq 0$ ),

$$V_d = \frac{u^*}{500}, \quad (15)$$

when atmospheric conditions are unstable ( $L < 0$ ),

$$V_d = \frac{\frac{u^*}{500}}{(1 + \frac{300}{(-L)}^{2/3}) + 1}. \quad (16)$$

(3) Ruijgrok et al. (1997) [23]

The third model was proposed by Ruijgrok which was fit to a European forest. The general form for  $V_d$  is:

$$V_d = \frac{1}{\frac{1}{V_{ds}} + R_a} + V_g, \quad (17)$$

where  $V_{ds}$  is the surface deposition velocity, and  $V_g$  is the gravitational settling velocity. The  $V_{ds}$  for  $PM_{2.5}$  can be parameterized by the Equation (18):

$$V_{ds} = \frac{u^*{}^2}{u_h} E, \quad (18)$$

in which  $u_h$  is the wind speed at the canopy height (approximately 9 m), and  $E$  is the collection efficiency with which the canopy captures particles, as defined by Ruijgrok et al. (1997).

$$RH \leq 80, E = 0.05u^{*0.28}, \quad (19)$$

$$RH > 80, E = 0.05u^{*0.28} [1 + 0.18EXP(\frac{RH - 80}{20})], \quad (20)$$

$$RH \leq 80, V_g = 6.7 \times 10^{-3}, \quad (21)$$

$$RH > 80, V_g = 0.0067EXP(\frac{0.0066RH}{1.058 - RH}). \quad (22)$$

In the above equations,  $RH$  is the relative humidity.

### 3. Results and Discussion

#### 3.1. Meteorological Conditions

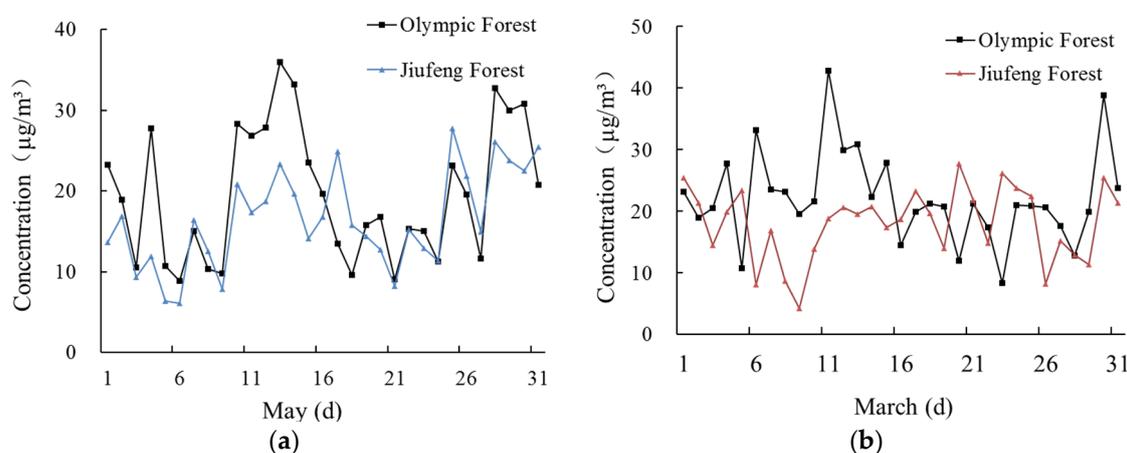
Meteorological conditions usually have significant effects on the diffusion and deposition of  $PM_{2.5}$  [26,27]. Beijing has a typical north temperate semi-humid continental monsoon climate (i.e., hot and rainy in summer, cold and dry in winter, with short spring and autumn with strong winds). Table 1 shows the average meteorological conditions in the sampling period. The general trends in the Olympic and Jiufeng parks with respect to weather conditions were very similar. The temperature in the daytime was higher than in the nighttime, and wind speeds showed a similar trend. The relative humidity was larger at night. Different meteorological conditions had different influences on the concentration and deposition rate of  $SO_4^{2-}$ .

**Table 1.** Meteorological conditions at two sampling sites during investigation period (mean  $\pm$  standard deviation).

	Olympic Forest Park				Jiufeng National Forest Park			
	March		May		March		May	
	Daytime	Nighttime	Daytime	Nighttime	Daytime	Nighttime	Daytime	Nighttime
Concentration of $\text{SO}_4^{2-}$ ( $\mu\text{g}/\text{m}^3$ )	29.8	15.0	26.8	15.0	22.5	14.7	21.3	13.7
Temperature ( $^{\circ}\text{C}$ )	$4.16 \pm 4.23$	$1.38 \pm 2.78$	$23.81 \pm 5.23$	$20.04 \pm 4.57$	$4.58 \pm 4.98$	$1.73 \pm 2.99$	$20.96 \pm 4.97$	$18.12 \pm 4.23$
Wind speed (m/s)	$1.12 \pm 0.5$	$0.86 \pm 0.43$	$1.06 \pm 0.64$	$0.79 \pm 0.49$	$0.97 \pm 0.49$	$0.7 \pm 0.38$	$1.28 \pm 0.73$	$0.96 \pm 0.51$
Relative Humidity (%)	$44 \pm 17$	$50 \pm 19$	$53 \pm 20$	$59 \pm 22$	$42 \pm 18$	$47 \pm 18$	$56 \pm 21$	$62 \pm 23$
Solar radiation (w)	$221 \pm 187$	$-1.24 \pm 1.3$	$312 \pm 251$	$0.94 \pm 1.6$	$208 \pm 199$	$-1.63 \pm 1.4$	$343 \pm 231$	$1.21 \pm 1.6$

### 3.2. Sulfate Concentrations and Vertical Gradients

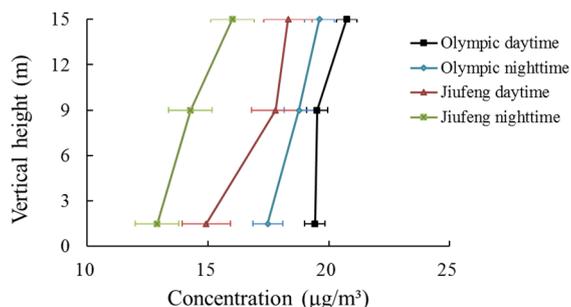
In March, the water-soluble total inorganic ion concentrations were  $56.9 \mu\text{g}/\text{m}^3$  in Olympic Forest Park, with  $\text{SO}_4^{2-}$  accounting for 39%; in comparison, ion concentration were  $44.7 \mu\text{g}/\text{m}^3$  in Jiufeng National Forest Park, with the proportion of  $\text{SO}_4^{2-}$  accounting for approximately 41%. While in May, these inorganic ions decreased to  $46.7 \mu\text{g}/\text{m}^3$  in Olympic Forest Park and  $35.8 \mu\text{g}/\text{m}^3$  in Jiufeng National Forest Park.  $\text{SO}_4^{2-}$  accounted for 42% and 47% of the ion concentrations in the Olympic and Jiufeng parks, respectively. Therefore,  $\text{SO}_4^{2-}$  was an important component of  $\text{PM}_{2.5}$  water-soluble inorganic ions. Figure 2 shows the concentration of  $\text{SO}_4^{2-}$  in March and May at the two sampling sites. It can be seen that regardless of the season, the concentration of  $\text{SO}_4^{2-}$  in the Olympic Park displayed more obvious fluctuations than that in Jiufeng Park. This phenomenon may be because Olympic Park is located in an urban area, whereas Jiufeng Park is located in a suburban area. The artificial disturbances in the urban area may cause the obvious fluctuations of  $\text{PM}_{2.5}$   $\text{SO}_4^{2-}$  concentrations in the Olympic Park.

**Figure 2.** The daily average concentrations of  $\text{SO}_4^{2-}$  at the height of 9 m in March and May in two sampling sites. (a) March 2013; (b) May 2013.

In order to study the effect of young leaves on dry deposition of  $\text{PM}_{2.5}$   $\text{SO}_4^{2-}$  in Beijing, we selected the early spring (i.e., May) as an example. The average concentrations of  $\text{SO}_4^{2-}$  measured at the various heights, sites, and times are shown in Figure 3. It can be seen that the concentration at 15 m was greater than that at 9 m, and concentrations of  $\text{SO}_4^{2-}$  appeared to decrease with height. This observation indicated a downward flux of the particulate sulfate (top down), which can be explained by the potential high absorption ability of the forests. As demonstrated in Figure 3, the average concentrations of  $\text{SO}_4^{2-}$  in Olympic Park in May were significantly higher than those in Jiufeng Park. This difference may be due to the geographical positions of the two sites. Olympic

Park is located closer to the central city than Jiufeng Park, which is in the suburbs. The number of residents and pollution sources around Jiufeng Park were relatively low, and the forest density was higher; hence, the concentration of  $PM_{2.5} SO_4^{2-}$  in atmosphere was lower than that in urban areas.

In addition, the concentrations of particulate sulfate were significantly higher in the daytime than in the nighttime at both experimental sites. This result was consistent with the experimental results of Matsuda et al. (2010) [16]. The gradient showed that  $SO_4^{2-}$  deposition actually happened within the forests, which revealed that the canopy had an effect on the deposition of  $SO_4^{2-}$ .



**Figure 3.** The average  $PM_{2.5} SO_4^{2-}$  concentration at the various heights and sites. The average  $PM_{2.5} SO_4^{2-}$  concentration at the heights of 1.5 m, 9 m, and 15 m during the day and night in May 2013 in Olympic Forest Park and Jiufeng National Forest Park. The error bars are the standard errors at the various heights.

### 3.3. Deposition Velocity of $PM_{2.5}$ Sulfate

We calculated the deposition velocities in May in Olympic Forest Park and Jiufeng National Forest Park, as shown in Table 2. Trees have no leaves in winter and therefore, had relatively small effects on particle deposition.  $PM_{2.5}$  concentrations in the vertical direction showed few differences, and the deposition velocities were close to zero or negative.

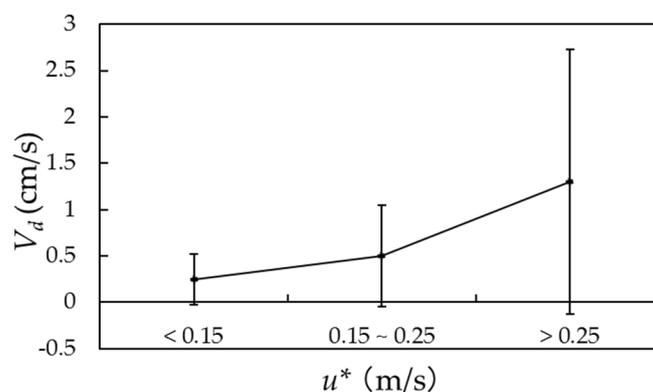
**Table 2.** Mean deposition velocities  $V_d$ , friction velocity  $u^*$  and Monine-Obukhov length  $L$  in the daytime (6:00 a.m.–18:00 p.m.) and nighttime (18:00 p.m.–6:00 a.m., morrow) during the study period (May 2013). All of the values are the mean  $\pm$  standard deviation.

	Olympic Forest Park		Jiufeng National Forest Park	
	Daytime	Nighttime	Daytime	Nighttime
$u^*$ (m/s)	$0.35 \pm 0.22$	$0.19 \pm 0.12$	$0.42 \pm 0.25$	$0.31 \pm 0.18$
$L$ (m)	$-0.18 \pm 9.7$	$27.97 \pm 14.3$	$-4.37 \pm 7.8$	$22.80 \pm 6.4$
$V_d$ (cm/s)	$0.9 \pm 1.0$	$0.4 \pm 0.3$	$1.3 \pm 1.2$	$0.8 \pm 0.8$

From Table 2 we can clearly see that deposition velocities were higher in Jiufeng Park than in Olympic Park. There may be three reasons: firstly, the LAI at the two sites were different. The LAI at Jiufeng Forest (3.8) was higher than that at Olympic Park (1.8). The greater the LAI, the more impaction and interception of fine particles may occur in the canopy. Secondly, different plant species have different effects on  $SO_4^{2-}$  retention. The more complex the leaf structure, the more conducive the leaf is to adsorbing particles. If blade roughness is high and mucus abundant, leaves adsorb fine particles more easily. The main species in Olympic Park was *Populus tomentosa*. In Jiufeng National Forest Park, the main species were *Platycladus orientalis* and *Pinus massoniana*. Because the leaf structure of *Platycladus orientalis* is more complex than that of *Populus tomentosa*, greater deposition occurred in Jiufeng Park [18]. Thirdly, the influence of meteorological conditions on fine particles may also have had an effect on the sulfate deposition. The wind speed was higher in Jiufeng Park than in Olympic Park. The higher the wind speed, the greater was the diffusion and migration velocity of

particles in Jiufeng Park. The humidity was greater in Jiufeng Park, and particulates adsorbed more water. When the particle volume increased, particulate matter fell more readily because of gravity. As solar radiation was the factor affecting the porosity of leaves, with intense radiation, the leaves removed more particles, so the deposition velocities were higher in the daytime than in the nighttime. This result was consistent with other results from previously established literature [16].

At both sites, the deposition rate increased during the day and was reduced at night. These results agreed with those of other studies [16,28]. The deposition of fine particles had a close relationship with aerodynamics. As shown in Figure 4, the deposition velocities ( $V_d$ ) increased with increasing friction velocities. When impaction is the only mechanism responsible for passing the viscous sublayer,  $V_d$  should increase according to a strong linear relationship with  $u^*$  [8]. The observed relationship suggests that a combination of deposition mechanisms are responsible for this dependency on  $u^*$ . The friction velocities were also affected by atmospheric stability [12,23,29]. If the environment experienced unstable conditions, the deposition velocities would correspondingly increase. Therefore, in the daytime, the friction rates ( $u^*$ ) reached a maximum value throughout the day, and the atmosphere experienced unstable conditions in the daytime. The deposition velocities in the day were greater than those in the night.



**Figure 4.** The relationship between deposition velocities  $V_d$  and friction velocities  $u^*$ .  $V_d$  is the mean value based on different ranges of  $u^*$  in May 2013 in both sites. The error bars are the standard errors of mean  $V_d$  values at each range of  $u^*$ .

#### 3.4. Comparison between Measured and Other Calculated $V_d$ by Model

We also obtained  $V_d$  by model calculation, as shown in Table 3. A very limited number of experiments on  $PM_{2.5}$  sulfate deposition have been performed over forests. For the function of  $SO_4^{2-}$  deposition in the forests, we computed  $V_d$  by the aerodynamic gradient method with a value higher than those in other reports.

For deciduous forests, the deposition velocities in Olympic Forest Park were close to the velocities measured by Matsuda et al. (2010) [16], with mean deposition velocity estimated to be 0.9 cm/s in the daytime and 0.3 cm/s in the nighttime. Hicks et al. (1989) [14] measured sulfate fluxes over a deciduous forest by eddy correlation, and they found that  $V_d$  peaked at 1.0 cm/s in the daytime and dropped to near 0.0 at night with a long-term average value of 0.6 cm/s.

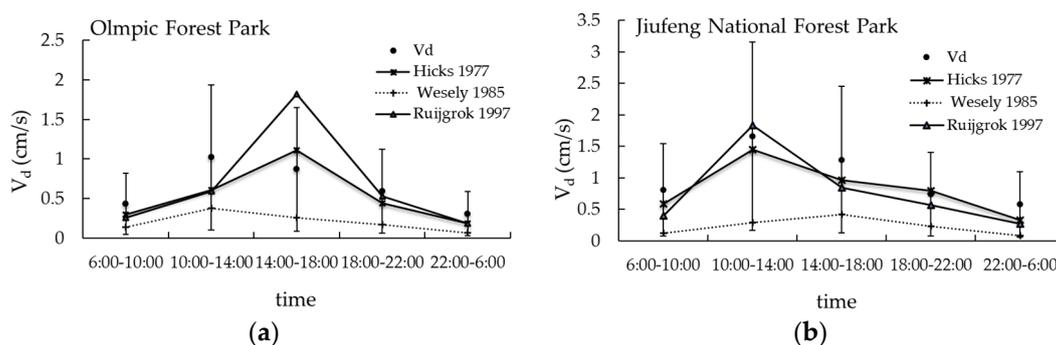
For coniferous forests, Wyers et al. (1997) [8] measured dry deposition velocity of sulfate over a coniferous canopy using the aerodynamic gradient technique, and they found that  $V_d$  ranged from near-zero under stable atmospheric conditions to 4.0 cm/s under unstable conditions, the average  $V_d$  was 0.7 cm/s. Hicks et al. (1982) [13] reported measurements over a Coniferous forest using an eddy correlation method for measuring total sulfur; the measurements indicated deposition velocities for particulate sulfur that averaged about 0.7 cm/s in the daytime. Similar values were reported by Wesely et al. (1985) [12] for a pine forest: the deposition velocity ranges from 0.9 cm/s for moderately unstable conditions to 0.5 cm/s for a neutral atmosphere.

**Table 3.** Comparison between measured  $V_d$  and other calculation model values.

Surface	Species	LAI	Sampling Time	Method	$V_d$ (cm/s)	Location	Reference
Deciduous forest	PM <sub>2.5</sub>	1.8	May 2013	Gradient method	Daytime $0.9 \pm 1.0$ , Nighttime $0.4 \pm 0.3$	Beijing Olympic, China	This work
Coniferous forest	Sulfate	3.8	May 2013		Daytime $1.3 \pm 1.2$ , Nighttime $0.8 \pm 0.8$	Beijing Jiufeng, China	
Deciduous forest	PM <sub>2.5</sub> Sulfate	5–7	Early summer (2 to 8 July) in 2009	Gradient method	Daytime $0.9 \pm 1.0$ , Nighttime $0.3 \pm 0.3$	Mt. Asama, Japan	[16]
Deciduous forest	Particulate sulfate	/	May 1983	Eddy correlation	Daytime 1.0, Nighttime 0, Mean 0.6	Oak Ridge, Tennessee	[14]
Coniferous forest	Sulfate	11	April, June/July, September and November/December 1993	Gradient method	Stable $\sim 0.0$ Unstable $< 4.0$ Mean $0.7 \pm 0.3$	The Netherlands	[8]
Pine forest	Particulate sulfur	/	June 1981	Eddy correlation	Moderately unstable $0.90 \pm 0.09$ Neutral $0.48 \pm 0.04$	America	[12]
Coniferous/Deciduous Forest	Sulfate	/	May 1990	Eddy correlation	All day mean 0.11	Asia	[30]
Coniferous forest	Particulate sulfur	/	July 1977	Eddy correlation	Daytime $0.5 \pm 1.0$ , Mean 0.7	North Carolina	[13]

3.5. Comparison between Measured and Parameterized  $V_d$

The comparison between the measured and three parameterized  $V_d$  is shown in Figure 5. The deposition velocities were calculated using the three models, and the error bars indicated the sampling errors in the experiment. It can be seen that the measured  $V_d$  was higher than the calculated values from the Ruijgrok et al. (1997) [23] model, the Wesely et al. (1985) [12] model, and the Hicks (1977) [22] model. The low deposition velocities in Olympic Park and the high deposition velocities in Jiufeng Park are consistent with the calculated results. However, the Hicks (1977) [22] model and the Ruijgrok et al. (1997) [23] model were more suitable for Beijing forests and could better reflect the influence of the forest on PM<sub>2.5</sub> sulfate deposition. The calculated results from the Wesely et al. (1985) [12] model were lower than those of the measured values. Therefore, the parameterizations of the Wesely and Hicks (1977) [22] and the Ruijgrok (1997) [23] could be applied to the calculation in the forests in our study and in forests in Beijing.



**Figure 5.** The daily variation of measured  $V_d$  and calculated  $V_d$  by using different parameters. (a) Olympic Forest Park; (b) Jiufeng National Forest Park.

4. Conclusions

The deposition of  $SO_4^{2-}$  in PM<sub>2.5</sub> above the forest was investigated in Beijing, China. In our study, the mean concentration of PM<sub>2.5</sub>  $SO_4^{2-}$  in May was  $19.7 \mu\text{g}/\text{m}^3$  in Olympic Forest Park and  $16.8 \mu\text{g}/\text{m}^3$  in Jiufeng National Forest Park. A comparison between the mean concentrations of  $SO_4^{2-}$

in March and May at the two experimental sites showed that the concentration in Olympic Park was higher than that in Jiufeng Park, and daytime concentrations higher than nighttime concentrations at both sites. Furthermore,  $\text{PM}_{2.5}$   $\text{SO}_4^{2-}$  concentrations decreased with height.

For the canopy layer deposition of  $\text{SO}_4^{2-}$ , deposition velocities in Jiufeng Forest Park were significantly higher than that in Olympic Park during the same time periods. This may be attributed to the greater friction velocity in Jiufeng National Forest Park. At both experimental sites,  $\text{PM}_{2.5}$  sulfate deposition velocities were significantly higher in the daytime than in the nighttime. In addition, our results suggest that the deposition velocities of  $\text{PM}_{2.5}$  sulfate were also influenced by the friction velocity ( $u^*$ ) (Figure 4), which was closely related to the aerodynamic conditions [12,23,29]. Thus, the deposition velocities of  $\text{PM}_{2.5}$  sulfate were also strongly affected by aerodynamic conditions.

The results of the comparisons between measured and parameterized  $V_d$  showed that the Wesely and Hicks (1977) and the Ruijgrok (1997) parameterizations could be applied to the forests in Beijing.

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