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Discussions

Aerosol Surface Area Concentration: a Governing Factor for New Particle Formation in Beijing

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Abstract. The predominating role of aerosol Fuchs surface area, A_{Fuchs}, in determining the occurrence of new particle formation (NPF) events in Beijing was elucidated in this study. Analysis was based on a field campaign from March 12th to April 6th, 2016, in Beijing, during which aerosol size distributions down to ~1 nm and sulfuric acid concentration were simultaneously monitored. The 26 days were classified into 11 typical NPF days, 2 undefined days, and 13 non-event days. A dimensionless factor, L_Γ, characterizing the relative ratio of the coagulation scavenging rate over the condensational growth rate and predicting whether or not a NPF event would occur (Kuang et al., 2010), was applied. The three parameters determining L_Γ are sulfuric acid concentration, the growth enhancement factor characterizing contribution of other gaseous precursors to particle growth, Γ, and A_{Fuchs}. Different from other atmospheric environment such as in Boulder and Hyytiälä, the variations of daily maximum sulfuric acid concentration and Γ in Beijing are in a narrow range with geometric standard deviations of 1.40 and 1.31, respectively. Positive correlation was found between estimated new particle formation rate, $J_{1.5}$, and sulfuric acid concentration with a mean fitted exponent of 2.4. However, sulfuric acid concentration on NPF days is not significantly higher than that on non-event days. Instead, A_{Fuchs} varies greatly among days in Beijing with a geometric standard deviation of 2.56, while it is relatively stable at other locations such as Tecamac, Atlanta, and Boulder. Good correlation was found between A_{Fuchs} and L_Γ in Beijing ($R^2 = 0.88$). It appears that the abundance of gaseous precursors such as sulfuric acid in Beijing is high enough to have nucleation, however, it is A_{Fuchs} that determines the occurrence of NPF event in Beijing. 10 in 11 NPF events occurred when A_{Fuchs} is smaller than 200 $\mu m^2/cm^3$, and the NPF event was suppressed due to coagulation scavenging when A_{Fuchs} is larger than 200 $\mu m^2/cm^3$. Measured A_{Fuchs} is in good correlation with $PM_{2.5}$ mass concentration ($R^2 = 0.85$) since A_{Fuchs} in Beijing is mainly determined by particles in the size range of 50 – 500 nm that also contribute to $PM_{2.5}$ mass concentration.

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1 Introduction

New particle formation (NPF) is closely related to atmospheric environment and human life. It is a common atmospheric phenomenon, which has been observed all over the world (Kulmala et al., 2004). High concentration of ultrafine particles is formed intensively during a NPF event. It has been illustrated through both theoretical modelling and field observation that these ultrafine particles can grow up to cloud condensation nuclei size (Kuang et al., 2009; Spracklen et al., 2008), and thus affect climate (IPCC, 2013). The increased number concentration of ultrafine particles also raises concerns on human health (HEI, 2013).

New particles are formed by nucleation from gaseous precursors such as sulfuric acid, ammonia, and organics. Newly formed particles either grow up by condensation or are lost by coagulation with other particles (McMurry, 1983). Aerosol Fuchs surface area, A_{Fuchs}, is a parameter that describes the coagulation scavenging effect quantitatively. In addition to gaseous precursors participating in nucleation and subsequent condensational growth, it has been a consensus that the occurrence of NPF event is also limited by A_{Fuchs}, because the survival possibility of nucleated particles is suppressed when the coagulation scavenging effect is significant (Weber et al., 1997; Kerminen et al., 2001; Kuang et al., 2012). Reported average A_{Fuchs} (or in the form of condensation sink) on NPF days was found to be lower than that on non-event days at several locations (Dal Maso et al., 2005; Gong et al., 2010; Qi et al., 2015).

A dimensionless criterion, L_{Γ}, was proposed to characterize the ratio of particle scavenging loss rate over condensational growth rate, and to predict the occurrence of NPF event in diverse atmospheric environment (Kuang et al., 2010). By definition, L_{Γ} is determined by three factors, i.e., sulfuric acid concentration, the growth enhancement factor representing contribution of other gaseous precursors in addition to sulfuric acid, Γ, and A_{Fuchs}. Sulfuric acid has a drastic diurnal variation because of radiation, and the increase in sulfuric acid concentration after the sunrise can lead to nucleation. A_{Fuchs} is often characterized in a narrow range at locations such as Tecamac, Atlanta, Boulder, and Hyytiälä (Kuang et al., 2010), while sulfuric acid concentration among days may differ significantly at locations such as Atlanta and Hyytiälä (Eisele et al., 2006; Petäjä et al., 2009) and it often governs nucleation and subsequent growth in the sulfur-rich atmosphere such as in Atlanta (McMurry et al., 2005). The growth enhancement factor, Γ, may vary in a wide range at locations such as Hyytiälä and may also fluctuate in a relative narrow range at other locations such as Tecamac and Boulder.

Aerosol concentration in Beijing is usually much higher than that in clean environments. The annual average $PM_{2.5}$ mass concentration in 2016 was 73 $\mu g/m^3$ (reported by Beijing Municipal Environmental Protection Bureau), and the average A_{Fuchs} measured in Beijing by this study was 381.5 $\mu m^2/cm^3$, which is approximately a magnitude higher than those measured in clean environments such as in Hyytiälä (Dal Maso et al., 2002). Different from comparatively slow accumulation and depletion process of aerosol concentration in clean environments, A_{Fuchs} in Beijing may change rapidly because of transport or accumulation of pollutants.

Sulfuric acid concentration is needed to estimate L_{Γ}, and direct measurement of particle size distribution down to ~1 nm will help to better quantify NPF events. Although sulfuric acid has been measured around the world (Erupe et al., 2010), and analysis based on sub-3 nm size distribution have been conducted sporadically since the development of diethylene glycol scanning mobility particle spectrometer (DEG SMPS, Jiang et al., 2011a; Jiang et al., 2011b; Kuang et al., 2012) and particle size magnifier (PSM, Vanhanen et al., 2011; Kulmala et al., 2013), there are limited data on atmospheric sulfuric acid concentration and directly measured sub-3 particle size distributions in China. A campaign in Beijing during 2008 Olympic Games characterized atmospheric sulfuric acid concentration and its correlation with new particle formation rate (Yue et al., 2010). The exponent in the correlation of formation rate, J_3, with sulfuric acid was found to be 2.3, and the exponent for correlating derived $J_{1.5}$ with sulfuric acid was 2.7 (Wang et al., 2011), which were different from the exponents between 1 and 2 often reported in other places around the world (Riipinen et al., 2007; Sihto et al., 2006; Kuang et al., 2008). Sub-3 nm particle size distribution has not been reported previously in China except for 1-3 nm particle number concentration in Shanghai in Winter 2013 inferred by a PSM (Xiao et al., 2015). Due to the limitation of observation data, although good correlation was found between new particle formation rate and sulfuric acid concentration in Beijing and the ratio of sulfuric acid concentration over A_{Fuchs} was found to positively correlate with number concentration of 3-6 nm particles (Wang et al., 2011), the roles of sulfuric acid concentration and A_{Fuchs} in determining the occurrence of NPF event have not been quantitatively illustrated.

In this study, we aimed to examine the roles of A_{Fuchs} and sulfuric acid in determining whether a NPF event will occur on a particular day in Beijing. Data analysis was based on simultaneous measurement of particle size distributions down to ~1 nm and sulfuric acid. Correlation between particle formation rate, $J_{1.5}$, and sulfuric acid concentration was examined. L_{Γ} was used to predict the occurrence of NPF events, and relative daily variations of the three parameters determining L_{Γ}, i.e., sulfuric acid concentration, Γ, and A_{Fuchs}, were compared. A nominal value of A_{Fuchs} was suggested to predict the occurrence NPF events in Beijing, and the relationship between $PM_{2.5}$ mass concentration and NPF events was also examined.

2 Experiments

A field campaign studying NPF in Beijing was carried out from Mar. 7th to Apr. 7th, 2016. The campaign site was located on the campus of Tsinghua University, and descriptions of this site can be found elsewhere (Cai & Jiang, 2017; He et al., 2001). A home-made DEG SMPS was used to measure sub-5 nm particle size distribution and a particle size distribution system (including a TSI aerodynamic particle sizer and two parallel SMPSs, equipped with a TSI nanoDMA and a TSI

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long DMA, respectively) was used to measure size distributions of particles from 3 nm to 10 μm (Liu et al., 2016). A specially designed miniature cylindrical differential mobility analyser (mini- cyDMA) for effective classification of sub-3 nm aerosol was equipped with the DEG SMPS (Cai et al., 2017). A cyclone was used at the sampling inlet to remove particles larger than 10 μm. The sampled aerosol was subsequently dried by a silica-gel diffusion drier. The diameter change due to drying was neglected when calculating A_{Fuchs} since the mean daytime relative humidity during the campaign period was ~25%. Diffusion losses, charging efficiency, penetration efficiencies through DMAs, detection efficiencies of particle counters, and multi-charging effect were considered during data inversion. Particle density was assumed to be 1.6 g/cm^3 according to local observation results (Hu et al., 2012).

Sulfuric acid was measured by a modified high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS, Aerodyne Research Inc.). Instead of using radioactive ion source, a self-made corona discharge (CD) ion source was utilized with the HR-TOF-CIMS. The CD ion source was design to be able to operate from a few Torr up to near atmospheric pressure and has been successfully implemented in ambient amine (Zheng et al., 2015a) and formaldehyde measurements (Ma et al., 2016). In this work, nitrate reagent ions were used to measure gaseous sulfuric acid (Zheng et al., 2010). The detailed ion chemistry to generate nitrate ions and the sulfuric acid calibration procedures have been detailed by Zheng et al. (2015b). Ambient sulfuric acid concentration in Beijing has been reported only once in a field campaign conducted in 2008 (Zheng et al., 2011; Wang et al., 2011). Comparing to previous work, sulfuric acid concentration reported in this study displayed similar diurnal variations, but with relatively lower daily maximum values. This might due to the relatively weak solar radiation intensity encountered in this springtime observation than the previous summertime campaign. To verify the precision of sulfuric acid measurement, the instrument was calibrated daily at night and background checks were performed for ~3 minutes each hour during daytime.

A meteorological station (Davis 6250) was located ~10 m away from the sampling inlet at a comparatively open position, measuring temperature, relative humidity, wind speed, wind direction, and precipitation. $PM_{2.5}$ mass concentration measured in the nearest national monitoring station (Wanliu station, ~5 km away on the southwest of our campaign site) was also used for analysis. Backward trajectories were obtained from online HYSPLIT server of national oceanic and atmospheric administration (NOAA).

3 Theory

Nucleation is only the first step of new particle formation. Gaseous precursors form clusters by random collision and bound together by Van der Waals force and/or chemical bond, and these clusters become particles if they are more likely to grow by condensation rather than evaporate. However, particles formed by nucleation may be scavenged through coagulation with larger particles before they grow large enough to be detected. Nucleation only refers to the process that stable molecular clusters formed spontaneously from gaseous precursors, while new particle formation also requires subsequent condensational growth of freshly nucleated particles. That is, the occurrence of nucleation is mainly determined by gaseous precursors (e.g., sulfuric acid and organics) in atmospheric environment, while new particle formation is also influenced by the coagulation scavenging effect of pre-existing aerosols. Possibility exists that nucleation occurs while NPF events are not observed because of the short lifetime of nucleated particles due to the coagulation scavenging. In fact, nucleation can also be suppressed when aerosol concentration is high, since vapours and clusters may also be scavenged through diffusion onto aerosol surface.

Aerosol Fuchs surface area, A_{Fuchs}, is a representing parameter of coagulation scavenging based on kinetic theory, and it is corrected for particles whose size fall in the transition between free molecular regime and continuum regime (Davis et al., 1980; McMurry, 1983). The formula assuming unity coagulation efficiency (fraction of effective collisions) is shown in Eq. (1),

$$A_{\mathrm{Fuchs}} = \frac{4\pi}{3}\int_{d_{\min}}^{\infty} {d_p}^2 \cdot \left(\frac{Kn + Kn^2}{1 + 1.71Kn + 1.33Kn^2}\right) \cdot n \cdot \mathrm{d}d_p , \tag{1}$$

where d_p is particle diameter, d_{min} is the minimum particle diameter in theory and the measured minimum one in practice, Kn is Knudsen number and n is particle size distribution function, $\mathrm{d}N/\mathrm{d}d_p$. Condensation sink and coagulation sink can also describe how rapidly gaseous precursors and particles will be scavenged by pre-existing aerosol, respectively (Kerminen et al., 2001; Kulmala et al., 2001). Since condensation sink is proportional to A_{Fuchs} (McMurry et al., 2005) and coagulation sink can be approximately converted to condensation sink using a simple formula (Lehtinen et al., 2007), only A_{Fuchs} is used in this study to describe the coagulation scavenging effect and condensation sink reported in previous studies is referred in the form of A_{Fuchs}. The diffusion coefficient of sulfuric acid is assumed to be 0.117 $\mathrm{cm^{-2}s^{-1}}$ (Gong et al., 2010) when converting condensation sink into A_{Fuchs}.

A dimensionless criterion, L_Γ, have been proposed to predict the occurrence of NPF events (Kuang et al., 2010). It is defined as,

$$L_\Gamma = \frac{\bar{c} \cdot A_{\mathrm{Fuchs}}}{4\beta_{11} N_1} \cdot \frac{1}{\Gamma} , \tag{2}$$

where $\bar{c}$ is the mean thermal speed of sulfuric acid which can be calculated from molecular kinetic theory; β_{11} is the coagulation coefficient between sulfuric acid monomers which can be calculated using Eq. 13.56 in Seinfeld & Pandis (2006); N_1 is the number concentration of sulfuric acid; and Γ is a growth enhancement factor and is defined as,

$$\Gamma = \frac{2GR}{v_1 N_{\mathrm{m}} \bar{c}} \tag{3}$$

GR is the observed mean growth rate, v_1 is the corresponding volume of sulfuric acid monomer and it is estimated to be 1.7×10^{-28} $\mathrm{m^3}$ (approximately the volume of a hydrated sulfuric acid molecule, Kuang et al., 2010) in this study, and N_{m} is

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the maximum number concentration of sulfuric acid during the whole period of a NPF event. Since other gaseous precursors in addition to sulfuric acid might also contribute to condensational growth of particles formed by nucleation (O'Dowd et al., 2002; Ristovski et al., 2010), while only concentration of sulfuric acid is used in Eq. (2), the ratio of measured growth rate over the growth rate assuming condensation of sulfuric acid (Weber et al., 1997), i.e., Γ, is used for correction. It should be clarified that L_Γ in Eq. (2) is defined similar to that in McMurry et al (2005) but slightly different from that in Kuang et al (2010), since L_Γ in this study are time-resolved values rather than event specific ones. Theoretically, Γ can also be time and size-resolved if using time and size-resolved GR and real-time concentration of sulfuric acid (Kuang et al., 2012), however, Γ during each NPF event is assumed to be constant in Eq. (3) because the validity of the improved model has not been tested. Note that the absolute concentration of sulfuric acid does not participate in calculation and thus has no influence on the results and conclusions reported in this study.

A new balance formula to estimate new particle formation rate was proposed recently (Cai & Jiang, 2017) and is given below,

$$J_k = \frac{\mathrm{d}N_{[d_k,d_u)}}{\mathrm{d}t} + \sum_{d_g=d_k}^{d_{u-1}} \sum_{d_i=d_{\min}}^{+\infty} \beta_{(i,g)} N_{[d_i,d_{i+1})} N_{[d_g,d_{g+1})} - \frac{1}{2} \sum_{d_g=d_k}^{d_{u-1}} \sum_{\substack{d_i^3+d_{j+1}^3=d_g^3 \\ d_{i+1}^3+d_j^3=d_g^3 \\ d_i,d_j \ge d_{\min}}} \beta_{(i,j)} N_{[d_i,d_{i+1})} N_{[d_j,d_{j+1})} + n_u \cdot GR_u \quad , \tag{4}$$

where J_k is the formation rate of particles at size d_k, $N_{[d_k,d_u)}$ is the total number concentration of particles from d_k to d_u (not included), d_u is the upper bound of the size range for calculation (25 nm in this study), $d_{\min}$ is the size of minimum cluster in theory and the lower limit of measuring instrument in practice (1.3 nm in this study). The second and third terms in the right hand side of Eq. (4) are the coagulation sink term (*CoagSnk*) and the coagulation source term (*CoagSrc*), respectively. The difference between *CoagSnk* and *CoagSrc* is net *CoagSnk*, which represents the net rate of particles from d_k to d_u lost by coagulation scavenging. The last term is supposed to be negligible according to the determination criterions for d_u. dN/dt, which is the essential parameter representing the occurrence of NPF events, is actually the balance result of J_k, and net *CoagSnk*.

4 Results and Discussion

Total 26 days from Mar. 12th to Apr. 6th were classified by the occurrence of daytime NPF event. A typical NPF day is defined by intuitive features that distinct and persisting increasing of sub-3 nm particle concentration and subsequent growth of these nucleated particles. A day is classified as a non-event day if neither of these two features was observed. As shown in Fig. 1, 11 days are typical NPF days, 13 days are non-event days, and the rest two days were classified as undefined days. On these undefined days, i.e., Mar. 19th and Mar. 30th, the increase of sub-3 nm particle concentration and subsequent growth were both observed, however, sub-3 nm aerosol concentration was comparatively low and evolution of particle size distributions was not continuous. NPF events mainly occurred when wind came from northwest of Beijing, and the air mass mainly arrived at Beijing from southwest on non-event days (as summarized in Table 1). This is because air mass coming from north usually experiences less influence from urban pollution, i.e., A_{Fuchs} is likely to be lower than that on days dominated by southwest wind.

The dimensionless criterion, L_Γ, predicts NPF occurrence well in most days if unity was chosen as the threshold value. L_Γ is the ratio of the rate at which particles are lost by coagulation over the growth rate. Larger L_Γ indicates higher possibilities of nucleated particles to be scavenged by coagulation before they can continue to grow. Growth rates on non-event days were assumed to 2.4 nm/h, which was the mean value of observed growth rates on NPF days (ranging from 1.2 nm/h to 3.3 nm/h). A threshold value of L_Γ can not be theoretically predicted but can be empirically estimated. 0.7 was suggested as the threshold value by Kuang et al. (2010), however, unity suggested by McMurry et al. (2005) seemed to work better for NPF events observed in this campaign. Again, the nominal value of unity is only an empirical division of NPF days and non-events days. In this campaign, median and mean value of L_Γ on NPF days were 0.55 and 0.71, respectively, comparing to 3.05 and 3.45 on non-event days, respectively. However, some exceptions were also observed. For instance, on the two undefined days, L_Γ were 1.40 and 0.64, respectively, and weak nucleation was observed. Estimated L_Γ on Mar. 18th (an NPF event day) was 1.75, while a comparatively weak but still distinct NPF event was observed. Despite these few exceptions, L_Γ works well in most cases in this campaign and were verified in other places as well (Kuang et al., 2010). Following discussions will be focused on the contribution of different factors, i.e., sulfuric acid concentration, Γ, and $A_{\text{Fuchs.}}$

4.1 The Role of Gaseous Precursors

Positive correlation was found between estimated new particle formation rate, $J_{1.5}$, and sulfuric acid concentration during most NPF periods. On NPF days, the increase of sub-3 nm particle concentration was accompanied with the increase of sulfuric acid concentration (as shown in Fig. 2). $J_{1.5}$ and sulfuric acid monomer concentration was only correlated during NPF periods considering the possible sensitivity of the fitted parameters to the fitting time period (Kuang et al., 2008), and the mean coefficient of determination during NPF periods in this campaign, R^2, was 0.53. The exponents in the correlation of the $J_{1.5}$ and sulfuric acid monomer concentration ranged from 1.5 to 4.0 in the 10 days with a mean value of 2.4 (Mar. 29th is not included because of insignificant correlation), which is in consensus with reported mean exponent of 2.3 using J_3 in Beijing (Wang et al., 2011). However, this result is quite different from those exponents no larger than 2 measured in North America and Europe (Kuang et al., 2008; Riipinen et al., 2007; Sihto et al., 2006), indicating activation or kinetic nucleation alone can not explain the main nucleation mechanism on some days in this campaign.

Although correlation between sulfuric acid and particle formation was significant, sulfuric acid appeared not to be the determining factor for whether a NPF event would occur, judging by the behaviour of sulfuric acid concentration. As illustrated by time series of sulfuric acid concentration in Fig. 2, significant diurnal variation was observed every day. However, the difference of daily maximum sulfuric acid concentration was small. The daily variations of sulfuric acid concentration were significantly smaller than those of A_{Fuchs}. For instance, the geometrical standard deviation and relative standard deviation of maximum sulfuric acid concentration on each day were 1.40 and 0.34, respectively, while those of daily averaged A_{Fuchs} were 2.56 and 0.82, respectively. Sulfuric acid concentration during NPF periods was not significantly higher than that between 8:00 - 16:00 on non-event days (p=1). In addition, comparatively high concentration of sulfuric acid, e.g., on Apr. 4th - 6th, did not necessarily lead to NPF events.

The influence of growth enhancement factor, Γ, on the occurrence of NPF also needs to be addressed because sulfuric acid alone may not explain the observed condensation growth. Estimated Γ values were normalized by dividing geometric mean value during the campaign to compare with those in previous studies (Kuang et al., 2010): MILAGRO in Tecamac (Iida et al., 2008); ANARChE (McMurry et al., 2005) in Atlanta; Boulder (Iida et al., 2006); QUEST II (Sihto et al., 2006), QUEST IV (Riipinen, et al., 2007), and EUCCARI (Manninen et al., 2009) at the SMEAR II station in Hyytiälä. It should be clarified that the relative value of Γ can improve the comparability by overcoming some uncertainties in measuring sulfuric acid concentration by different studies. Fig. 4 indicates that Γ observed in this study distributes in a relatively narrow range, similar to those observed in Tecamac, Atlanta, and Boulder, while different from the wide-spreading characteristics observed in Hyytiälä. Geometric standard deviations of Γ were 1.31, 1.75, 2.23, 1.87, 1.62, 2.77, and 2.87 in this campaign, MILAGRO, ANARChE, Boulder, QUEST II, QUEST IV, and EUCCARI, respectively. The daily variations of Γ in this work were smaller than those observed in other places. They were also smaller than the daily variations of A_{Fuchs} measured in this campaign. Considering the small daily variations of both sulfuric acid concentration and Γ, it was reasonable to conclude that the abundance of sulfuric acid in Beijing during the campaign period was sufficiently high for nucleation to occur but the occurrence of NPF events appeared to be governed by A_{Fuchs}.

4.2 Relationship between A_{Fuchs} and NPF Event

Relatively smaller A_{Fuchs} were found during most of the NPF days, while sulfuric acid concentrations on NPF days were not significantly higher than that on non-event days. NPF events mainly occurred when A_{Fuchs} was smaller than 200 $\mu m^2/cm^3$, and non-event days mainly corresponded to real-time A_{Fuchs} larger than 200 $\mu m^2/cm^3$ and average A_{Fuchs} larger than 350 $\mu m^2/cm^3$ (Fig. 5). The value of 200 $\mu m^2/cm^3$ appeared to be an empirical division between NPF days and non-event days. If A_{Fuchs} was lower than this value, NPF event tended to occur, otherwise the occurrence of NPF event was suppressed because of the predominant coagulation scavenging effect.

The variation of L_Γ in Beijing was governed by A_{Fuchs}. The measured L_Γ and A_{Fuchs} were in good correlation with a coefficient of determination, R^2, of 0.88, and the relative error of fitted L_Γ using A_{Fuchs} was 11.4% compared to the measured ones (Fig. 6(a)). It should be clarified that GR on non-event days in this campaign were assumed to be the same

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(2.4 nm/h, average of fitted values on NPF days), however, the correlation between L_Γ and A_{Fuchs} on NPF days alone showed a R^2 of 0.89. A_{Fuchs} of 200 μm^2/cm^3 corresponded to a L_Γ of approximately unity in this campaign. Since L_Γ has been verified as a proper nucleation criterion in diverse atmospheric environment, it is reasonable to conclude that A_{Fuchs} was the determining factor of the occurrence of NPF events in Beijing during the campaign period.

The A_{Fuchs} dominated characteristic of NPF events in Beijing showed a different pattern from those at other locations. L_Γ and A_{Fuchs} in most other places do not correlate well (as shown in Fig. 6(b)) indicating that A_{Fuchs} alone could not predict the occurrence of NPF events at these locations. Governing factors for the occurrence of NPF events at different locations are illustrated in Fig. 10. At locations such as in Atlanta and Hyytiälä, A_{Fuchs} was observed to fluctuate within relatively narrow ranges, while concentration of gaseous precursors participating in nucleation differed significantly. The variations of L_Γ at these locations were mainly the consequence of relatively large variations in the concentrations of gaseous precursors. However, the contribution of gaseous precursors to L_Γ was relatively stable in Beijing, while the variation of L_Γ was mainly caused by varying A_{Fuchs}.

The predominant role of A_{Fuchs} in Beijing can also be explained by using the balance formula shown in Eq. (4). It is dN/dt rather than formation rate, J, that directly reflects whether a NPF event has occurred or not, and dN/dt is the balance result of formation rate and net *CoagSnk* (*CoagSnk* − *CoagSrc*). Different from L_Γ which is the ratio of particle loss rate over growth rate, the ratio of net *CoagSnk* over J represents how many nucleated particles are lost to coagulation scavenging, while the surviving particles are reflected as the increment of particle number concentration in nucleation mode. Nucleation mode (1-25 nm) was used in this study to estimate dN/dt caused by nucleation because newly formed particles seldom grew beyond 25 nm in the evaluated time period. Surviving possibilities of nucleated particles can also be inferred using growth rate and A_{Fuchs} (Weber et al., 1997; Kerminen & Kulmala, 2002; Kuang et al., 2012), however, we consider the ratio of net *CoagSnk* over J to be more accurate because it is based on measured particle size distributions. Note that theoretically the ratio of new *CoagSnk* over J can be larger than unity, corresponding to a negative dN/dt. However, for better description of the occurrence of NPF event rather than the whole process including termination, only NPF period when dN/dt was positive is considered here. On average, 70.0% of particles formed by nucleation were lost due to coagulation scavenging on NPF days (as shown in Fig. 8), indicating high coagulation loss in Beijing even on NPF days. When A_{Fuchs} was much higher, most nucleated particles were lost to coagulation scavenging rather than growing to larger sizes such that few NPF events were observed. Theoretically, NPF event can occur everyday in Beijing if one can simply remove pre-existing aerosols while keeping other atmospheric compositions the same.

It should be clarified that although with much less possibility, NPF events may also occur when A_{Fuchs} was larger than 200 μm^2/cm^3 in Beijing. In this campaign, a distinct NPF event was observed with a comparatively high A_{Fuchs} (on Mar. 18$^{\mathrm{th}}$) of 329 μm^2/cm^3, which was significantly higher than the suggested threshold value of 200 μm^2/cm^3. As indicated by the content of Table 1, this exception was caused by the failure of L_Γ rather than A_{Fuchs} alone. The comparatively low number concentration of sub-3 nm particles together with the moderate particle formation rate indicated that the NPF event was suppressed. In addition, NPF events previously reported in Beijing occurred when A_{Fuchs} was relatively high (Wu et al., 2007; Wang et al., 2013; Wang et al., 2017) with a maximum A_{Fuchs} value of ~555 $\mu m^2/cm^3$ (Kulmala et al., 2016). The A_{Fuchs} reported in these studies might be overestimated because daily average rather than average over NPF event period only was used. For instance, A_{Fuchs} in Beijing during non-event period can be significantly higher and it may change rapidly because of transport or subsequent growth of nucleated particles. Nevertheless, A_{Fuchs} can be considered as the major determining factor of the occurrence of NPF events in Beijing, while admitting that exceptions can occasionally occur at a medium L_Γ larger than unity, corresponding to A_{Fuchs} larger than 200 $\mu m^2/cm^3$.

4.3 A case Study of 3 Days

Three continuous days including two NPF days and one non-event day are shown in Fig. 9 to further illustrate the roles of A_{Fuchs} and sulfuric acid (together with other gaseous precursors) in affecting the occurrence of NPF events in Beijing. On Apr. 2nd, A_{Fuchs} maintained at a relative low level and NPF event occurred after sunrise together with the increase in sulfuric acid concentration, and ended in the afternoon when sulfuric acid concentration decreased to a low level. The whole NPF event began at approximately 7:30 and ended at approximately 14:30, which was also the typical time period for other NPF days. However, on Apr. 3rd, wind direction changed from northwest into southwest at noon, sulfuric acid concentration decreased, and A_{Fuchs} increased rapidly because of transport of particles from south, causing the increase in L_Γ. The ongoing NPF event was interrupted and no newly nucleated particles was observed even though sulfuric acid concentration increased later. On Apr. 4th, A_{Fuchs} was at a high level, causing L_Γ to be always larger than unity. Sulfuric acid concentration on Apr. 4th was higher than those on Apr. 2nd and 3rd, however, no NPF event was observed. Therefore, even though the abundance of gaseous precursors in Beijing often seemed to be high enough for nucleation to happen, whether or not an NPF event to occur was mainly governed by A_{Fuchs}.

4.4 Predicting NPF Days Using $PM_{2.5}$ Mass Concentration

A rough but simple parameter, i.e., $PM_{2.5}$ mass concentration, can also be applied to predict whether an NPF event can happen in Beijing. Theoretically, the exponent in the relationship between A_{Fuchs} and particle diameter is between 1 and 2 depending on particle size (as shown in Eq. (1)), while particle mass is proportional to the 3rd power of particle diameter. Hence the correlation between A_{Fuchs} and mass concentration can be determined by particle size distributions. Accumulation mode particles ranged from 50 nm to 500 nm was the major contribution to A_{Fuchs} in Beijing, and normalized size distribution of accumulation mode particles were relative stable at different A_{Fuchs} levels (as shown in Fig. 11). On NPF days when A_{Fuchs} were relatively low, nucleation mode particles formed by nucleation and subsequent growth also contributed to A_{Fuchs}, however, A_{Fuchs} was still governed by accumulation mode particles. Thus, A_{Fuchs} should show better correlation with particle mass concentration rather than number concentration. Figure 10 indicates that there is a good correlation between A_{Fuchs} and $PM_{2.5}$ mass concentration in Beijing with a R^2 of 0.85, although the correlation at low A_{Fuchs} level is not as good as that at high A_{Fuchs} level because of influence of particles formed by nucleation. Measured $PM_{2.5}$ mass concentration in the 26 days ranged from 3 to 420 $\mu g/m^3$, which was wide enough to represent both relative clean days and severe polluted days in Beijing. $PM_{2.5}$ mass concentrations during NPF periods were mostly smaller than 30 $\mu g/m^3$ except for the case of Mar. 18th and it was higher than 30 $\mu g/m^3$ between 8:00 and 16:00 on non-event days. Note that the threshold of 30 $\mu g/m^3$ may not be valid for the whole year since it was based on field measurement in March and early April and the concentration of gaseous precursors perhaps varied with season because of different radiation intensity and emissions.

The criterion using $PM_{2.5}$ mass concentration was applied to predict NPF events measured at the same site in Beijing in April and May, 2014. Among 38 days in that campaign, 11 typical NPF events were identified. Average $PM_{2.5}$ mass concentration during NPF period was lower than 30 $\mu g/m^3$ in 9 NPF events, while that in the rest two days was 49.8 and 40.5 $\mu g/m^3$, respectively. In another campaign in Beijing during January 2016, 12 in 14 NPF events were observed to occur when daily mean $PM_{2.5}$ mass concentration was less than 30 $\mu g/m^3$ (the maximum value on NPF days was 43 $\mu g/m^3$), and $PM_{2.5}$ mass concentration on 16 non-event days were all larger than 40 $\mu g/m^3$ (Jayaratne et al., 2017).

Conclusions

Factors governing the occurrence of NPF events in Beijing were examined using data from a field campaign during Mar. 12th to Apr. 6th, 2016. In these 26 days, 11 typical NPF event days were observed. The rest were 2 undefined days and 13 non-event days. New particle formation rate, $J_{1.5}$, was in positive correlation with sulfuric acid concentration with a fitted mean exponent of 2.4, however, sulfuric acid concentration on NPF days was not significantly higher than that on non-event days. A dimensionless criterion proposed by Kuang et al. (2010), L_Γ, was found to be applicable to predict NPF event in most days. Theoretically, L_Γ was determined by sulfuric acid concentration, the enhancement factor, Γ, and Fuchs surface area, A_{Fuchs}, together. However, A_{Fuchs} alone was found to be in good correlation with L_Γ (R^2 = 0.88) in Beijing. Different from NPF events observed at other locations such as Hyytiälä, the variations of daily maximum sulfuric acid concentration and the enhancement factor in Beijing were in a narrow range with geometric standard deviations of 1.40 and 1.31, respectively, while A_{Fuchs} varied significantly among days with a geometric standard deviation of 2.56. It was inferred that the concentrations of gaseous precursors such as sulfuric acid in Beijing were high enough to cause nucleation, while it was A_{Fuchs} that ultimately determined whether a NPF event would occur or not in Beijing. In this work, we proposed that an A_{Fuchs} of 200 $\mu m^2/cm^3$ can be used as the empirical threshold value, below which NPF events were

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highly likely to occur in Beijing. However, NPF events would be suppressed when A_{Fuchs} was higher than this threshold value. The A_{Fuchs} dominated characteristic of NPF events in Beijing was different from those at other locations such as Atlanta, Boulder, and Hyytiälä. Since A_{Fuchs} in Beijing was mainly governed by accumulation mode particles (50 to 500 nm) and in this size range the normalized $\mathrm{d}A_{\mathrm{Fuchs}}/\mathrm{dlog}d_p$ was relatively stable at different A_{Fuchs} levels, measured A_{Fuchs} was in good correlation with $PM_{2.5}$ mass concentration (R^2 = 0.85). Accordingly, $PM_{2.5}$ mass concentration may also serve as a rough and simple parameter to predict the occurrence of NPF events in Beijing. An empirical threshold value of 30 μg/m^3 was proposed based on data from this field campaign and was found to work well for other field campaigns in Beijing as well.

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Table 1: Summary of parameterized descriptions for each campaign day.

Date (mm/dd)	Classification	Max $J_{1.5}$ ($cm^{-3}\ s^{-1}$)	N_{1-3}^{*}	A_{Fuchs}^{*}	L_{Γ}^{*}	Wind direction*

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			(#/cm^3)	(μm^2/cm^3)		
03/12	Non-event	–	0	919.5	3.63	SW
03/13	NPF	156.0	26347.5	119.7	0.71	NW
03/14	Non-event	–	0	632.7	3.05	NW
03/15	Non-event	–	0	733.9	3.73	SW
03/16	Non-event	–	0	796.2	4.15	WSW
03/17	Non-event	–	0	1140.1	9.04	WSW
03/18	NPF	33.8	741.2	329.0	1.75	WNW
03/19	Undefined	Weak**	1643.67	240.8	1.40	SE
03/20	Non-event	–	137.9	348.8	1.74	NNW
03/21	Non-event	–	0	512.0	2.76	SSW
03/22	Non-event	–	0	457.6	2.58	E
03/23	NPF	30.1	3846.3	76.1	0.57	NNW
03/24	NPF	46.8	5576.7	145.2	0.76	NNW
03/25	NPF	57.0	4637.7	126.7	0.52	NNE
03/26	NPF	41.5	9640.9	100.4	0.71	N
03/27	NPF	31.2	2806.2	90.6	0.44	NW
03/28	Non-event	–	0	508.1	2.86	W
03/29	NPF	32.3	2449.8	121.0	0.69	NW
03/30	Undefined	17.7	2885.7	88.8	0.64	NW
03/31	Non-event	–	0	767.0	4.21	SW
04/01	NPF	50.9	5477	51.7	0.22	WNW
04/02	NPF	46.9	10002	63.1	0.31	NW
04/03	NPF	21.6	10962.9	105.7	0.24	NW
04/04	Non-event	–	442	398.2	3.09	SW
04/05	Non-event	–	185	391.2	2.33	NW
04/06	Non-event	–	0	365.5	1.71	SW

***: Indicated by 12-hour backward trajectory (starting at noon, 500 m in altitude). **: Difficult to estimate.**

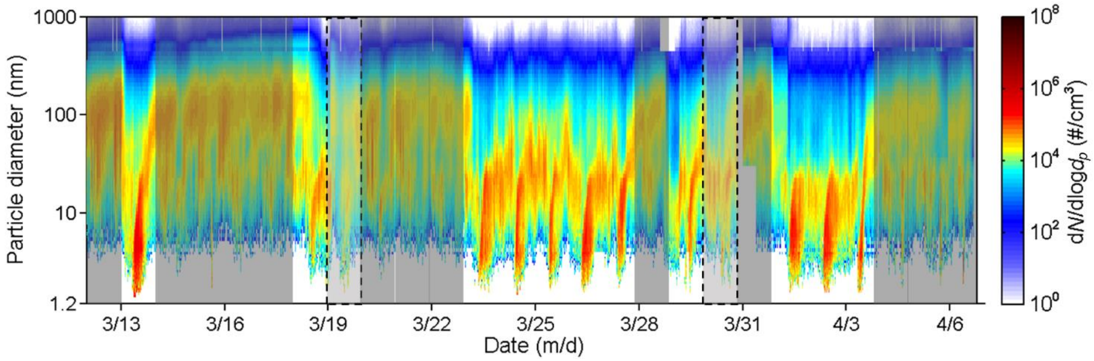

Figure 1 Contour of measured particle size distribution during Mar. 12th to Apr. 6th. Identified thirteen non-event days are shadowed by grey colour. Two undefined days are shadowed by lighter grey boxes with dashed lines as the edges.

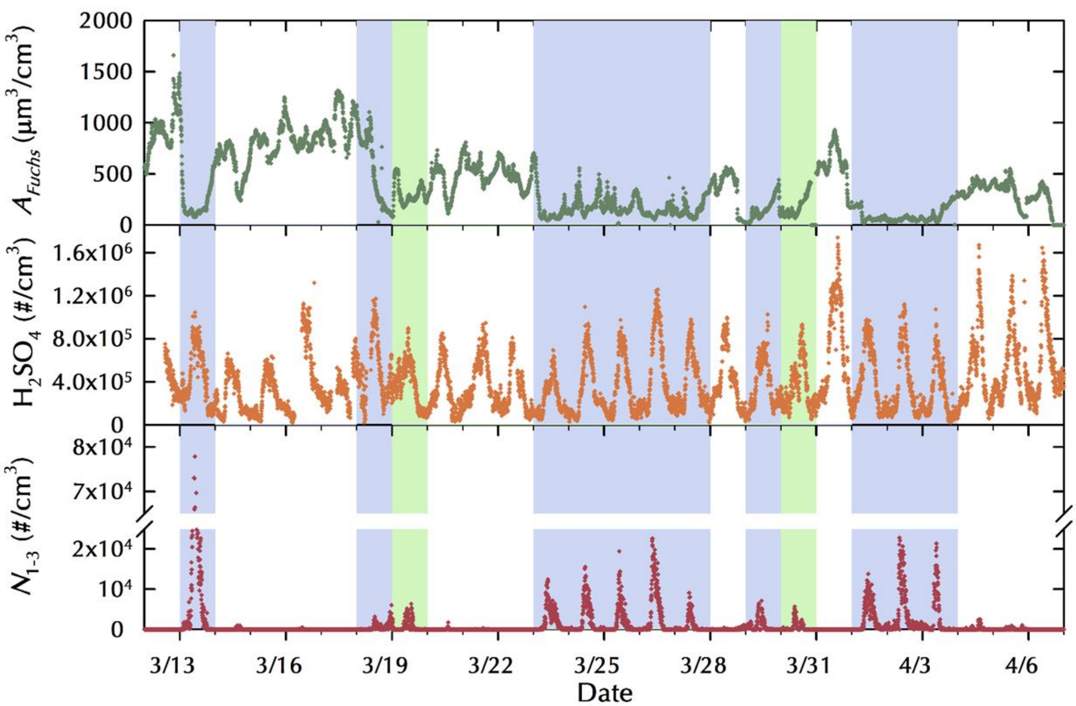

Figure 2: Time series for Fuchs surface area (A_{Fuchs}), sulfuric acid concentration, and number concentration of 1-3 nm particles. Typical NPF days and undefined days are shadowed by light blue and light green background, respectively.

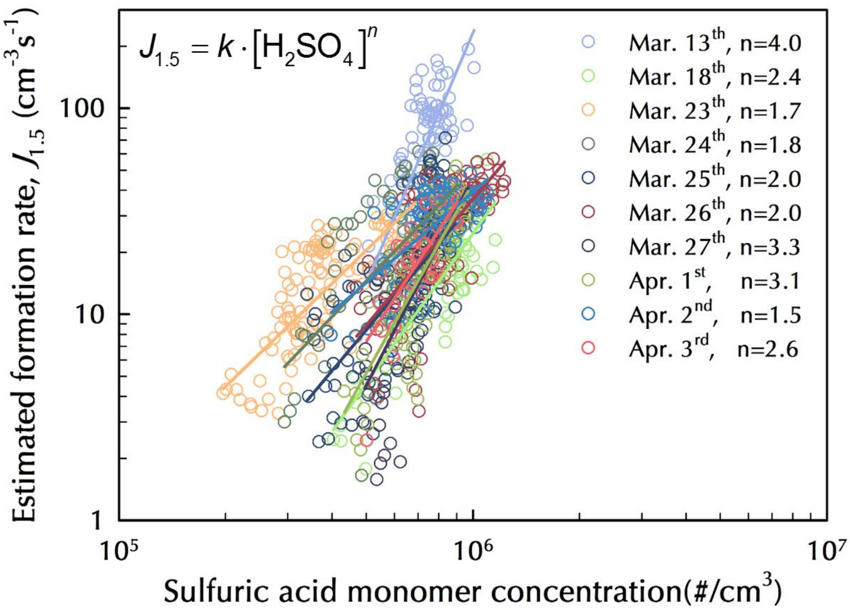

Figure 3: Correlations between estimated new particle formation rate, $J_{1.5}$, and number concentration of sulfuric acid monomer during NPF period on each NPF day. Regression line of $J_{1.5}$ versus sulfuric acid monomer concentration is exponentially fitted, where n is the exponent. Data on Mar. 29th is not included because the correlation between $J_{1.5}$ and sulfuric acid monomer concentration was not significant (p = 0.34).

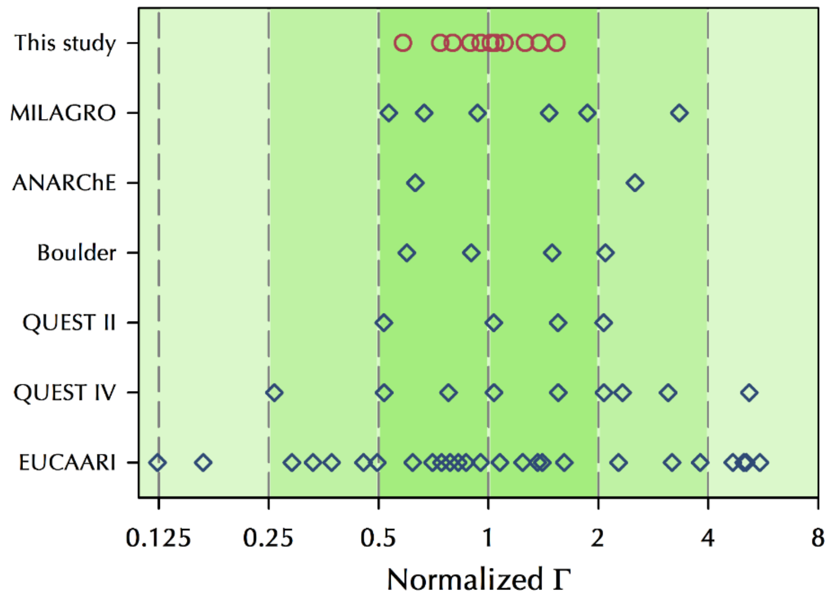

Figure 4: Normalized growth enhancement factor, Γ, in this campaign and previous ones. Γ is normalized by the geometric mean value in each campaign.

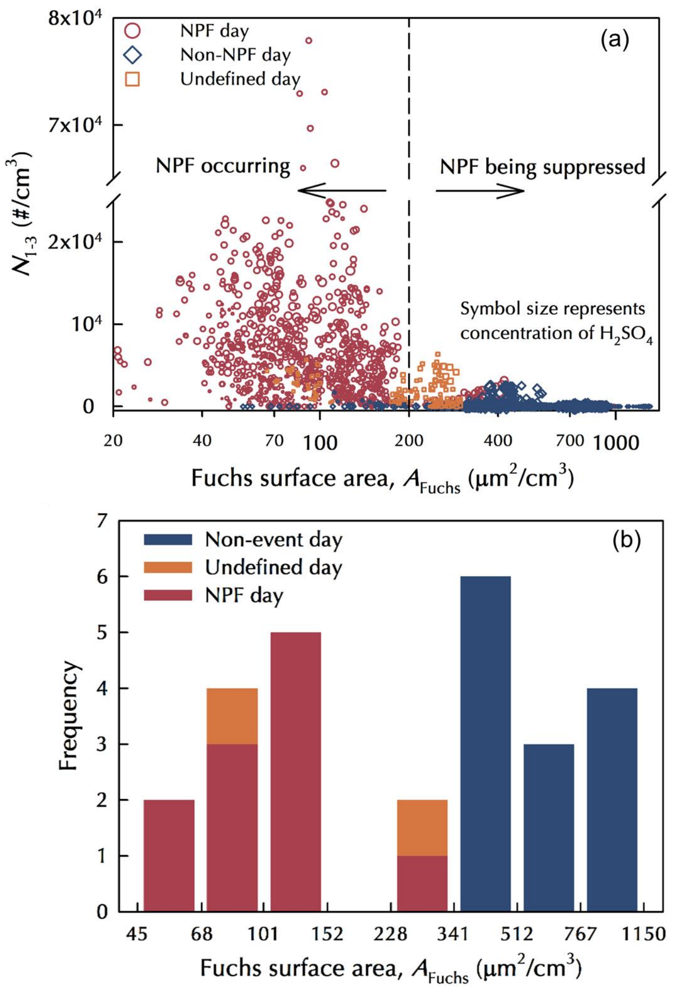

Figure 5: (a) Relationship between Fuchs surface area and number concentration of 1-3 nm particles, N_{1-3}. Relative concentration of measured sulfuric acid is represented by symbol size, i.e., the higher the relative concentration, the bigger the symbol size . Data points are 5-minute-resolved. (b) Histogram of frequency of observed NPF days, undefined days and non-event days sorting by daily average Fuchs surface area. On typical NPF days and undefined days, A_{Fuchs} was averaged during NPF period. On non-event days, it was averaged between 8:00 and 16:00. Values of A_{Fuchs} were binned in logarithmic scale ranging from 45 to 1150.

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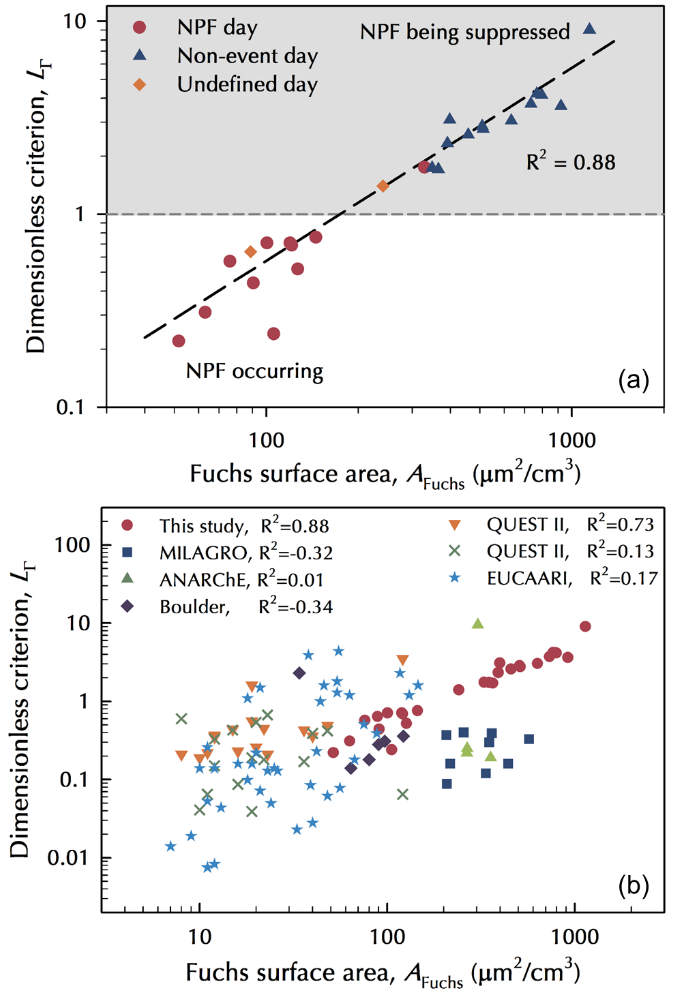

Figure 6: (a) Correlation between L_Γ and A_{Fuchs} (data from Table 1) in this campaign. NPF days, non-event days, and undefined days are shown by different symbols, while regression is base on all observation days. (b) Correlation between L_Γ and A_{Fuchs} in previous studies and this campaign.

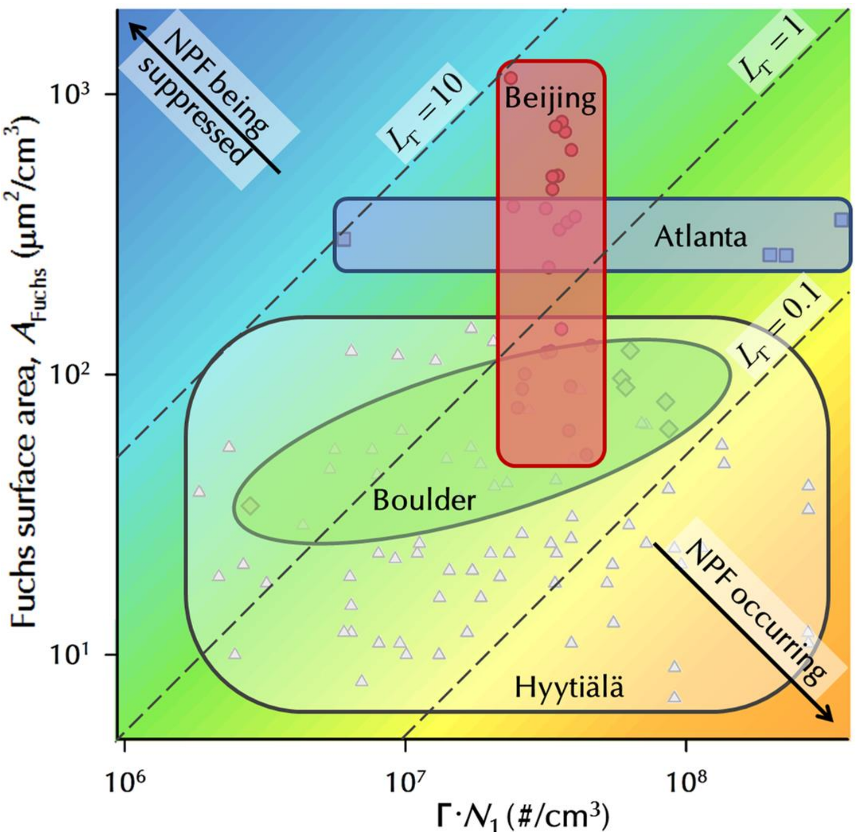

Figure 7: Schematic of governing factors for L_Γ at different locations. Concentration of growth relevant gaseous precursors is represented by $\Gamma \cdot N_1$, where Γ is the growth enhancement factor and N_1 is number concentration of sulfuric acid. Background colour represents the value of L_Γ. Observed data at each locations are shown in different symbols (circle: Beijing; square: Atlanta; diamond: Boulder; triangle: Hyytiälä), while the ellipse and the boxes are artificially drawn to illustrate the ranges of data points at different locations. Tecamac was not included because of lacking data on non-event days. Both axes are in log scale.

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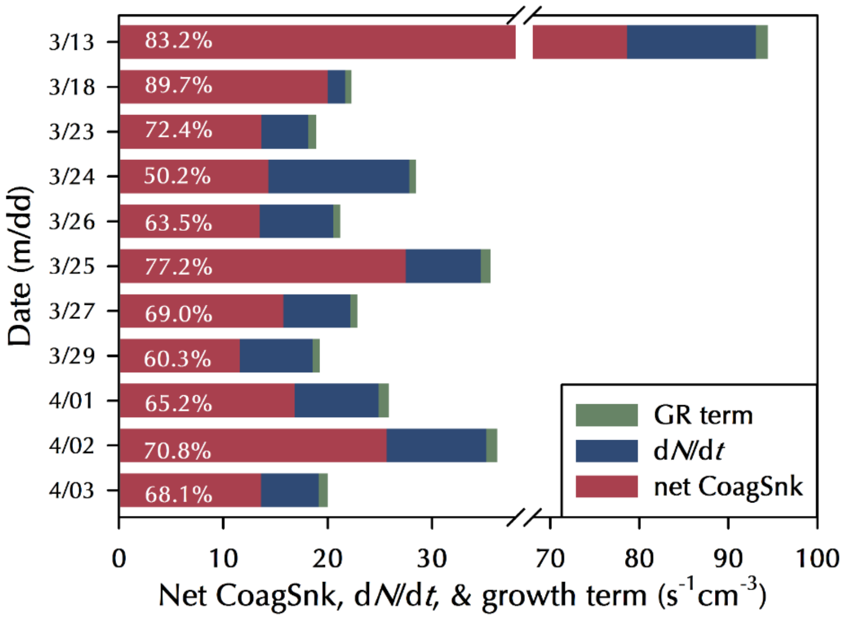

Figure 8: Average contribution of net CoagSnk, d*N*/d*t*, and condensational growth term (GR term) to the estimated new particle formation rate, $J_{1.5}$, on identified typical NPF days. The percentage presented in each column is the relative ratio of net CoagSnk compared to $J_{1.5}$ in that NPF day. Note that only the time period when d*N*/d*t* is positive during a NPF event was taken in to account when calculating average contribution.

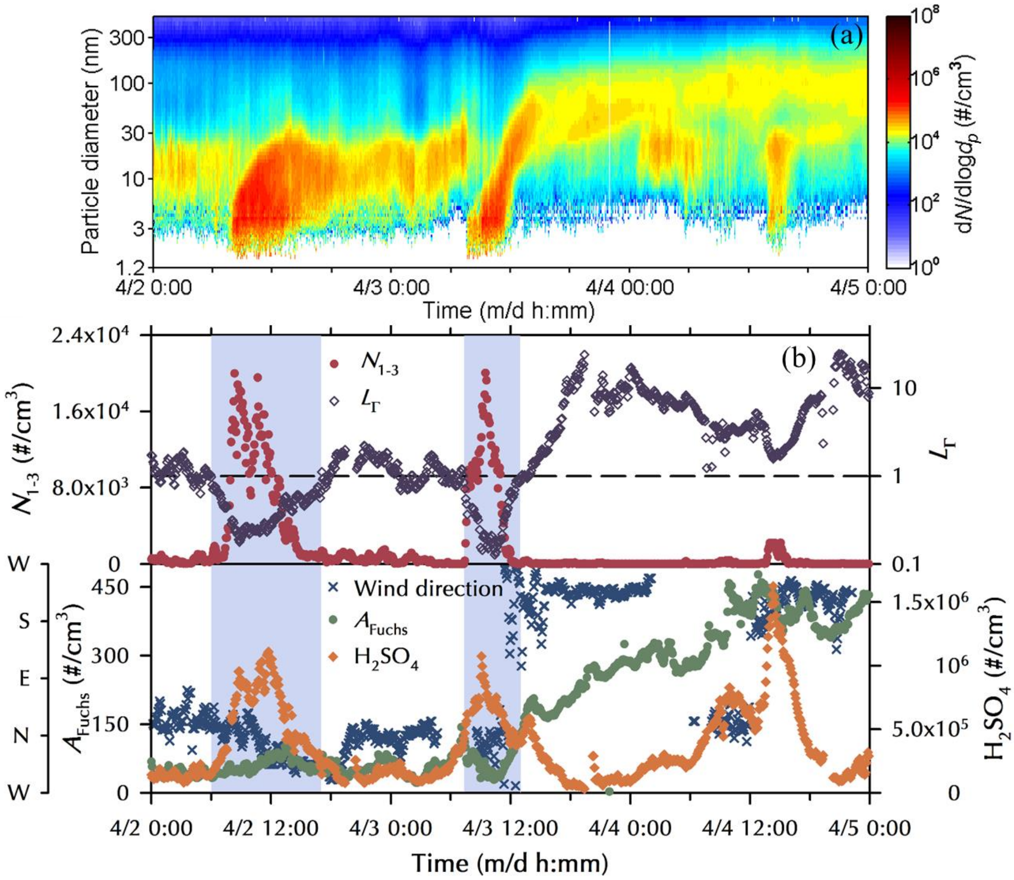

Figure 9: (a) Contour of measured particle size distribution on Apr. 2nd, 3rd, and 4th. (b) Representative parameters on these three NPF days. Time period when L_Γ was smaller than 1.0 is shadowed by light blue background. Wind direction data is obtained from local meteorological station and it is not shown when the wind speed was close to zero.

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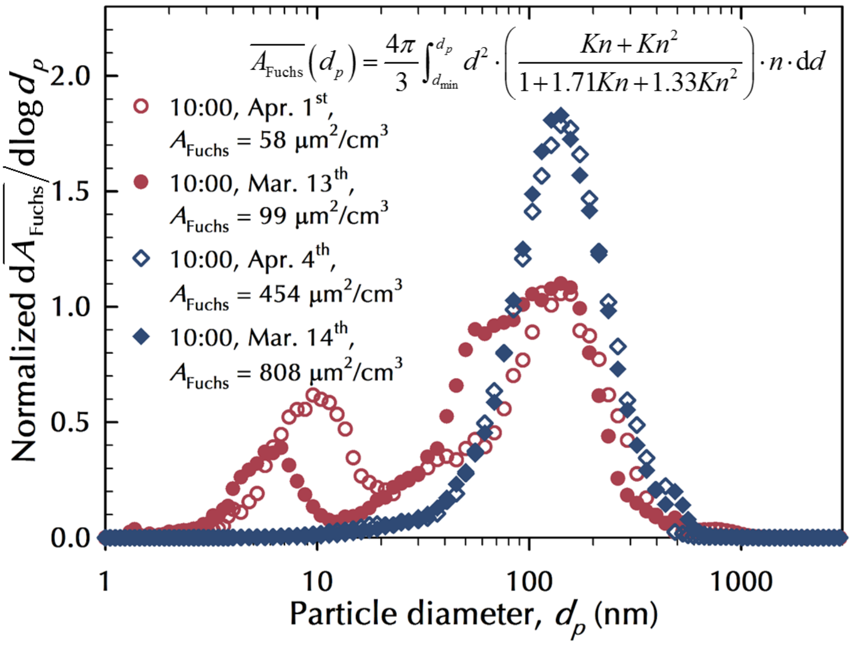

Figure 10: Normalized distribution of cumulative Fuchs surface area, $\overline{A_{\text{Fuchs}}}$, as a function of particle diameter, d_p, on two NPF days (red circle) and two non-event days (blue diamond). $\overline{A_{\text{Fuchs}}}$ is equal to A_{Fuchs} when d_p is approaching positive infinity. $\mathrm{d}\overline{A_{\text{Fuchs}}}/\mathrm{d}\log d_p$ is normalized by dividing A_{Fuchs}.

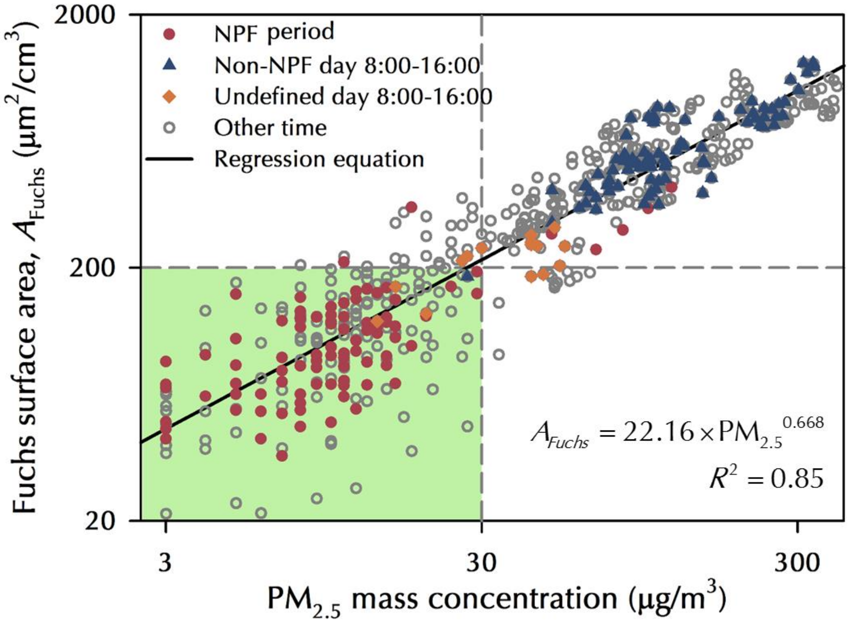

Figure 11: Relationship between hourly averaged A_{Fuchs} and $PM_{2.5}$ mass concentration in Beijing. Data during the time period when A_{Fuchs} changed rapidly is not included to avoid potential influence caused by the distance between Wanliu station and our campaign site. NPF period, daytime (8:00-16:00) on non-event days and undefined days, and other time is represented by different symbols, while the regression of A_{Fuchs} versus $PM_{2.5}$ mass concentration is based on all these data. The proposed criterion for NPF event, i.e., A_{Fuchs} smaller than 200 $\mu m^2/cm^3$ which approximately corresponds to $PM_{2.5}$ mass concentration smaller than 30 $\mu g/cm^3$, is shadowed by light green.