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Investigation of the connections between atmospheric new particle formation and organics at an urban site of Beijing

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Abstract

The role of low-volatility organic vapors in atmospheric new particle formation has been studied based on a data set of 17 nucleation events observed during the CAREBeijing 2008 campaign. The particle formation rates show good correlations with sulfuric acid and organic vapors implying that both play an important role in the atmospheric new particle formation. High correlation coefficients are observed in all investigated nucleation mechanisms. The best fit ($R = 0.73$, slope = 1.1) between the observed and modelled particle formation rates is achieved with the homogenous nucleation theory of sulfuric acid (both homomolecularly and hetermolecularly) with separate coefficients in $J = K_{\mathrm{SA1}}[\mathrm{H_2SO_4}]^2 + K_{\mathrm{SA2}}[\mathrm{H_2SO_4}][\mathrm{Org}]$. The contributions of the sulfuric acid and the organics involving terms have been 43 % and 57 %, respectively. In addition, the higher particle formation rates are observed on polluted nucleation days, indicating the organic vapors should be involved in the new particle formation process in the polluted urban environment of Beijing with high background aerosol loading.

1 Introduction

New particle formation (NPF) in the atmosphere through nucleation of gas phase species and continuous condensational growth is a crucial secondary transformation process (Kulmala, 2003; Zhang et al., 2011). The freshly formed particles can grow into sizes where they can act as cloud condensation nuclei (CCN) and in this way influence cloud and climate-relevant properties. Model results show that nucleation is an important source of the total particle number concentration and CCN concentration on the global scale (Merikanto et al., 2009). Field observations also reveal the increasing CCN number concentrations originate from new particle formation (Kuang et al., 2009; Yue et al., 2011). Detailed knowledge on the formation mechanisms of new particles and the properties of their subsequent growth will lead to a better understanding on the various effects of atmospheric aerosols.

NPF events have been observed in a variety of environments, including the remote atmosphere of the polar region, above and inside forests, coastal areas, rural and polluted urban regions (Kulmala et al., 2004; Holmes, 2007; Kulmala and Kerminen, 2008). Gaseous sulfuric acid has been identified as a key component in the nucleation process because of its low vapor pressure at typical atmospheric temperatures (Berndt et al., 2005; Sipila et al., 2010). Most studies reveal the relationship between observed nucleation rates and ambient gaseous sulfuric acid concentrations with the exponents in the range 1–2 (Sihto et al., 2006; Riipinen et al., 2007; Kuang et al., 2008; Nieminen et al., 2009; Paasonen et al., 2009, 2010). These exponent values are predicted with activation (exponent 1) and kinetic (exponent 2) nucleation theories (McMurry and Friedlander, 1979; Kulmala et al., 2006). Meanwhile, higher power values in Beijing have been reported recently (Wang et al., 2011), which may imply that thermodynamic processes seem to work better than the activation and kinetic nucleation theories or that sulfuric acid is the vapor mainly causing the very initial growth of particles (Paasonen et al., 2012).

Observation results, however, show large differences in the nucleation coefficients of kinetic nucleation in diverse ambient environments. The values vary in several orders of magnitude (Chen et al., 2012). The variability of the nucleation coefficients in different environments may be influenced by co-nucleation species such as low-volatility organic vapors (Paasonen et al., 2010). Recent results from laboratory studies and field observations imply that organic vapors participate in the nucleation process (Laaksonen et al., 2008; Zhang et al., 2009; Kerminen et al., 2010; Metzger et al., 2010). However, the identities of the specific organic species possibly directly involved in the atmospheric nucleation process are still not known.

A long term study on NPF in the urban of Beijing has been conducted since 2004 at Peking University (Wehner et al., 2004; Wu et al., 2007). Recent results suggest that sulfuric acid plays a dominant role in the nucleation process (Yue et al., 2010; Wang et al., 2011). In this paper, we apply the methods described by Paasonen et al. (2010) and present an analysis of the relationship between particle formation rates and precursor concentrations, taking into account the possible participation of organic vapors, which has not been discussed before. The role of organics in the nucleation process is evaluated and two typical nucleation event cases in the urban atmosphere of Beijing are discussed.

2 Measurements

2.1 Experimental method

The measurements were performed on the campus of Peking University (39.99° N, 116.31° E), which is located in the northwestern urban area of Beijing. The sampling site is located on the sixth floor of an academic building (about 20 m above the ground level). The local emissions are major contributed by the surrounding traffic. Detailed descriptions of the measurement site and surrounding environment can be found in Wu et al. (2008). Simultaneous measurements of particle number size distributions and gaseous sulfuric acid concentrations were conducted as part of the Campaign of Air Quality Research in Beijing and Surrounding areas in 2008 (CAREBeijing 2008) from 12 July to 25 September.

Number size distributions of atmospheric particles from 3 to 900 nm (mobility diameter) and ambient sulfuric acid concentrations were measured with TDMPS (Twin Differential Mobility Particle Sizer) system and AP-ID-CIMS (atmospheric pressure ion drift – chemical ionization mass spectrometry), respectively. Detailed information on the instrumentations is given in previous publications (Birmili et al., 1999; Yue et al., 2010; Zheng et al., 2011). The 17 NPF event days investigated in this study are exactly the same as in the research by Wang et al. (2011), however, the data set of particle number size distribution is reevaluated including the additional corretion for internal losses of TDMPS as described in Wiedensohler et al. (2012).

2.2 Data analysis

2.2.1 Particle formation rate J_3

The time evolution of the formation rate J_3 is calculated with the procedure described by Kulmala et al. (2012), recommended by Wang et al. (2011) and Vuollekoski et al. (2012):

$$J_3 = \frac{dN_{3-6}}{dt} + \mathrm{CoagS}_4 \cdot N_{3-6} + \frac{1}{2\,\mathrm{nm}}\mathrm{GR}_6 \cdot N_{5-7} \tag{1}$$

Here, N_{3-6} refers to the particle number concentration in the size range 3–6 nm (covers the five lowest channels of the TDMPS) which are considered as the freshly nucleated particles. The value of GR_6 is assumed equal to the growth rate of the nucleation mode (GR_{3-7} in this study). CoagS_4 is the coagulation sink for the 4 nm particles which is calculated directly from the measured particle number size distribution (Kulmala et al., 2001). Hence, the right hand side of the Eq. (1) includes the measured change of the particle concentration per time interval (first term), the loss by coagulation scavenging (second term) and the growth out of the specific size range at 6 nm (third term).

2.2.2 Particle growth rate (GR) contributed by sulfuric acid

The growth rate of newly formed particles (GR_{3-7}) is estimated based on the particle number size distributions. The determination of the growth rate is made with the method presented by Lehtinen and Kulmala (2003). In this study, the method developed recently by Nieminen et al. (2010) is applied to calculate the vapor concentration required for growth rate of 1 nm h^{-1} in certain particle size ranges:

$$C_{\mathrm{GR}=1\,\mathrm{nm\,h^{-1}}} = \frac{2\rho_v d_v}{\gamma m_v \Delta t} \cdot \sqrt{\frac{\pi m_v}{8kT}} \cdot \left[\frac{2x_1+1}{x_1(x_1+1)} - \frac{2x_0+1}{x_0(x_0+1)} + 2\ln\left(\frac{x_1(x_0+1)}{x_0(x_1+1)}\right)\right] \tag{2}$$

here x_0 and x_1 are the ratios of the vapour molecule diameter (d_v) to the initial and final particle diameter (3 nm and 7 nm in this study), respectively. The mass (m_v) and density (ρ_v) of sulfuric acid applied in this study are 135 amu and 1650 kg m^{-3}, respectively corresponding to hydrated sulfuric acid molecules (Kurten et al., 2007). However, the calculated $C_{\mathrm{GR}=1\,\mathrm{nm\,h^{-1}},\mathrm{H_2SO_4}}$ may be an underestimate because it is assumed that every sulfuric acid molecule colliding with the particle is attached to it which is not necessarily the case. Further descriptions of Eq. (2) can be found in Nieminen et al. (2010).

Then the growth rate contributed by sulfuric acid during the time period used for the determination of GR_{3-7} is calculated directly as:

$$\mathrm{GR}_{\mathrm{H_2SO_4}} = [\mathrm{H_2SO_4}]_{\mathrm{det}} / C_{\mathrm{GR}=1\,\mathrm{nm\,h^{-1}},\mathrm{H_2SO_4}} \quad (3)$$

where $[\mathrm{H_2SO_4}]_{\mathrm{det}}$ is the median value from the measured sulfuric acid concentration during the timeframe for the determination of GR_{3-7}.

2.2.3 Estimating concentration of low-volatility organic vapors

The sulfuric acid concentrations could not explain the observed growth rates of newly formed particles implying that the growth of aerosol particles is affected by other vapors (Boy et al., 2005; Fiedler et al., 2005; Kuang et al., 2010; Riipinen et al., 2011). Donahue et al., (2011) point out that organic condensation to freshly nucleated particles (below 10 nm) contributes substantially to their growth. Meanwhile, previous field observations (O'Dowd et al., 2002; Laaksonen et al., 2008; Riipinen et al., 2012) show the significant contribution of organic compounds to the growth of freshly formed particles which indicates that organic molecules play a crucial role in atmospheric new particle formation . However, the specific organic species in the nucleation and growth are still unclear. Therefore, we have to estimate their properties such as molecular formula, density and concentrations indirectly. For this, we use the following method presented by Paasonen et al. (2010).

We assume that a large gap between the observed growth rates and that due to sulfuric acid condensation is totally contributed by organic vapors, i.e.:

$$\mathrm{GR}_{\mathrm{Org}} = \mathrm{GR}_{\mathrm{det}} - \mathrm{GR}_{\mathrm{H_2SO_4}} \quad (4)$$

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Apparently the determination of the GR_{Org} may cause an uncertainty and further influence the calculation of organic vapor concentration, the uncerntainty analysis is presented in Sect. 3.3.

Field observations show evidence for the role of oxidation products of monoterpenes (MTOP) in the nucleation and growth processes (Laaksonen et al., 2008). Here we assume the properties of these organic vapors as MTOP with the chemical formula $C_{10}H_{16}O_2$ (Taipale et al., 2008). The corresponding molecular mass is 168 amu and the density is $1200\,\mathrm{kg\,m^{-3}}$ (Kannosto et al., 2008; Hallquist et al., 2009). Using Eq. (2) we calculate the potential organic vapor concentration $C_{GR=1\,\mathrm{nm\,h^{-1}},Org}$ leading to $1\,\mathrm{nm\,h^{-1}}$ growth, and further the GR_{Org} could be estimated with:

$$[Org]_{det} = GR_{Org} \cdot C_{GR=1\,\mathrm{nm\,h^{-1}},Org} \quad (5)$$

With the above calculations we can derive one value of the organic vapor concentration per day during the timeframe for determination of GR_{3-7}. The diurnal variations of organic vapor concentrations depend on both, their source (the oxidation rate of precursors) and sink (condensation on the preexisting particels). Because the concentrations of the precursors could not be achieved, we assume that the nucleation organic vapor concentration is determined by the concentration of hydroxyl radical (OH) and the condensation sink (CS). We approximate that the organic vapors condensaing on the newly formed particles are produced via OH oxidation neglecting the other oxidation pathway such as ozonelysis in the daytime (Hao et al., 2009). Even though this assumption may not hold exactly, the diurnal cycle of OH is stronger than that of ozone, which may not have significant infulence on the diurnal variation of organic vapors. Here global radiation (GlobRad) is used to make up the lack of the measured OH concentrations because it represents a good correlation with the UVB radiation which is the driving force of ozone photolysis to produce OH radicals. CS is refered to sink of organic vapors which could be obtained from particle number size distribution measurement. Hence, the estimated concentration of organic vapor could be express as:

$$[\mathrm{Org}](t) = [\mathrm{Org}]_{\mathrm{det}} \cdot \frac{\mathrm{GlobRad}(t)/\mathrm{GlobRad}_{\mathrm{det}}}{\mathrm{CS}(t)/\mathrm{CS}_{\mathrm{det}}} \tag{6}$$

where t means the certain time and subscript "det" refer to the median value during the timeframe of determination of the growth rate. However, it should be clarify that when we calculate the correlation between the nucleation rates and the precursor vapor concentrations, we only choose the data in the timeframe when strong nucleation event happening.

2.2.4 Nucleation mechanisms

The limitation of activation and kinetic nucleation mechanisms for the Beijing case have been discussed in a paper published by Wang et al. (2011). However these two mechanisms only consider sulfuric acid. In this study, we assume that those organic molecules which are responsible for the growth of the smallest particles are also involved in the nucleation process.

The following two mechanisms consider the organic species instead of sulfuric acid into the nucleation process via cluster activation:

$$J = A_{\mathrm{Org}}[\mathrm{Org}] \tag{7}$$

or assume both the sulfuric acid and organic vapor can activate clusters:

$$J = A_s([\mathrm{H_2SO_4}] + [\mathrm{Org}]) \tag{8}$$

Here, A_{Org} and A_s are the activation coefficients (in unit s^{-1}).

Meanwhile we can use organics instead of sulfuric acid in kinetic nucleation mechanism and can write:

$$J = K_{\mathrm{Org}}[\mathrm{Org}]^2 \tag{9}$$

Also if we only use one organic replacing the sulfuric acid which means the homogenous heteromolecular nucleation between sulfuric and organic vapor, the nucleation mechanism could be expressed as:

$$J = K_{\text{het}}[\text{H}_2\text{SO}_4][\text{Org}] \tag{10}$$

If we consider the homogenous homomolecular nucleation of sulfuric acid and organic vapor to the heteromolecular nucleation, we obtain:

$$J = K_{\text{SA}}\left([\text{H}_2\text{SO}_4]^2 + [\text{H}_2\text{SO}_4][\text{Org}]\right) \tag{11}$$

$$J = K_S\left([\text{H}_2\text{SO}_4]^2 + [\text{H}_2\text{SO}_4][\text{Org}] + [\text{Org}]^2\right) \tag{12}$$

where all the cofficients K refer to kinetic type nucleation in unit $\text{cm}^3\,\text{s}^{-1}$.

In addition to the nucleation mechanisms with one coefficient, as discribed above, we discuss those mechanisms contain two terms (Eqs. 8 and 11) with separate nucleation coefficients. Then the nucleation mechanisms are rearranged as:

$$J = A_{s1}[\text{H}_2\text{SO}_4] + A_{s2}[\text{Org}] \tag{13}$$

and

$$J = K_{\text{SA1}}[\text{H}_2\text{SO}_4{}^2 + K_{\text{SA1}}[\text{H}_2\text{SO}_4][\text{Org}] \tag{14}$$

The coefficients above are obtained by minimizing the sum of the squares of the differences between the observed and modelled nucleation rates in every data point.

Both the method to estimate the organic vapor concentration and proposed mechanisms have been discussed in detail in previous study which have been proved justified and reasonable. We refer the reader to Paasonen et al. (2010) for detailed material. Meanwhile, we should clarify that the correlation between formation rates (J_3) and vapor concentrations could only reflect the roles of vapors in atmospheric new particle formation, including the nucleation process and the initial growth of critical clusters from nucleation size to 3 nm.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◂◂ | ▸▸
◂ | ▸
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

3 Results and discussion

3.1 Growth rate and organic vapor concentrations

The sulfuric acid concentration $C_{\mathrm{GR}=1\,\mathrm{nm\,h^{-1}},\mathrm{H_2SO_4}}$ needed for 1 nm h^{-1} growth varies between $1.1 \times 10^7\,\mathrm{cm^{-3}}$ and $1.5 \times 10^7\,\mathrm{cm^{-3}}$ due to the different ambient conditions. The parameter Γ, which is defined as the ratio between the observed growth rate and the growth rate related to sulfuric acid, is shown in Fig. 1. The values vary from 6 to 44, which are consistent with previous studies (Stolzenburg et al., 2005; Wehner et al., 2005; Kuang et al., 2010). Hence, the contributions of gaseous sulfuric acid to growth rate are in the range of 2 % to 16 %, with the mean value of 5 %. Since only a minor fraction of the observed, the huge different between the observed growth rate and that which is explained by sulfuric acid indicates the important role of organics in the growth of newly formed particles.

The median organic vapor concentration calculated by the method presented in Sect. 2.2 is 5.7×10^7 molecules cm^{-3} for the whole data set. This value is higher than estimated results for Hyytiälä (1.6×10^7 molecules cm^{-3}), Melpitz (1.6×10^7 molecules cm^{-3}) and Hohenpeissenberg (HPB) (4.8×10^7 molecules cm^{-3}). They are however lower than that observed for San Pietro Capofiume (SPC) (6.3×10^7 molecules cm^{-3}) (Paasonen et al., 2010). The daily maximum concentrations are in the range of $4.6–42.2 \times 10^7$ molecules cm^{-3} with a mean value of $1.5 \pm 1.0 \times 10^8$ molecules cm^{-3}.

3.2 Correlation between particle formation rate J_3 and vapor concentration in different nucleation mechanisms

3.2.1 Organic vapor nucleation

Strong correlations ($R = 0.67$) between the particle formation rate J_3 and organic vapor concentration is observed in Beijing site (see Fig. 2). The same correlation coefficient

R in activation nucleation and kinetic nucleation is due to that R is calculated by the logarithmic values of the observed and modeled particle formation rate, then the exponent of the vapor concentration does not effect on R. $V_{90/10}$ is the ratio of 90th and 10th percentiles of the specific nucleation coefficient, which is calculated through the division between observed nucleation rate and the applied parametrization. The variation of $V_{90/10}$ reflects the dispersion of the nucleation coefficient. For example, the $V_{90/10}$ equal to 10 means 80 % of the specific nucleation coefficients are located within one order of magnitude. However, the variation $V_{90/10}$ is sensible to the order of the vapor concentration. Hence, the slightly higher $V_{90/10}$ values for the mechanisms involving the second order vapor concentration (exponent 2 or term $[H_2SO_4][Org]$) are found compared with those related to first order mechanisms. The values of $V_{90/10}$ are 10 and 25 in organic activation and kinetic nucleation mechanisms, respectively (the 10th and 90 percentilts of coefficients in different nucleation mechanisms are also shown in Fig. 2). The median values of the nucleation coefficients in organic vapor activation and kinetic nucleation mechanisms are $4.4 \times 10^{-8}\,s^{-1}$ and $6.6 \times 10^{-16}\,cm^3\,s^{-1}$, respectively.

The comparisons of the correlation coefficient R with other sites in the nucleation mechanisms only involving one species are shown in Table 1. At the comparison sites, only one of the two studied precursors correlates with the particle formation rate: sulfuric acid at Hyytiälä, Melpitz, SPC and organic vapor at HPB. Instead, at Beijing site, J_3 correlates well, both with the sulfuric acid and organic vapor concentrations. The correlation coefficients are 0.66 and 0.67, respectively. This phenomenon implies that the sulfuric acid and low-volatility organic vapors are both have great contribution in the atmospheric new particle formation for Beijing case, compared with the other sites, which are dominated by a single precursor.

3.2.2 Nucleation of sulfuric acid and organic vapor

Since both the sulfuric acid and organic vapor play crucial roles in the new particle formation process at the Beijing site, fair correlation coefficients in the nucleation mechanisms involving both species are achieved as expected (see Table 2). The correlation

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
|◀ | ▶|
◀ | ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

coefficients vary from 0.67 to 0.73, which are higher in all proposed nucleation mechanisms compared with the other sites (Paasonen et al., 2010). Highest correlation coefficient ($R = 0.73$) for the entire data set is achieved with the model involving the sum of sulfuric acid homogenous heteromolecular nucleation and homogenous homomolecular nucleation, $J = K_{\mathrm{SA}}([\mathrm{H_2SO_4}]^2 + [\mathrm{H_2SO_4}][\mathrm{Org}])$, as shown in Fig. 3a. It should be noticed that the correlation coefficient become weaker ($R = 0.68$) if we consider the term squared organic vapor in the nucleation mechanism. This difference in correlation coefficient is rather small, when taking into account the condsiderable uncertainties in estimating the organic vapor concentration. These uncertainties, being much larger than those in the sulfuric acid concentration, accumulated in the term including squared organic vapor concentrations, thus automatically weakening the corresponding correlations. Meanwhile, it is also the reason that causes the larger $V_{90/10}$ in Eqs. (9) and (12) than that in Eqs. (10) and (11). Smallest variation, $V_{90/10} = 9.4$ is found in the model involving the sum of the vapor concentration with one nucleation coefficient A_{s} (see Fig. 3b). On the contrary, the largest variation, $V_{90/10} = 26.9$, results from the organics homogengenous homomolecular nucleation ($J = K_{\mathrm{Org}}[\mathrm{Org}]^2$).

3.2.3 Optimized separate nucleation coefficients

The estimated organic vapor concentration is approximately one order of magnitude higher than the observed sulfuric acid concentration, implying that nucleation may rely more on organic compounds. Hence, in this study, the optimized separate nucleation coefficients are evaluated by minimizing the sum of the squares of the differences between the observed and modelled nucleation rates. The values are listed in Table 3. A lower correlation coefficient corresponding to the organic vapor compared to that of sulfuric acid is shown as expected. High correlation coefficient ($R = 0.73$) is achieved with the homogenous nucleation model for sulfuric acid both homomolecularly and hetermolecularly with separate coefficients $K_{s1} = 5.3 \times 10^{-14}\,\mathrm{cm^3\,s^{-1}}$ and $K_{s2} = 5.8 \times 10^{-15}\,\mathrm{cm^3\,s^{-1}}$.

The observed formation rates are plotted versus the modeled formation rates applying the optimized nucleation coefficients in Fig. 4. Even though the correlation coefficient could reach to 0.72 in the mechanism involving the sum of the vapor concentration with separate sulfuric acid and organic activation coefficients ($A_{s1} = 2.0 \times 10^{-7}\,\mathrm{s}^{-1}$ and $A_{s2} = 2.8 \times 10^{-8}\,\mathrm{s}^{-1}$), the slope between the observed and modelled formation rates is 1.7, which means that the overall modelled values underestimate the real formation rates by almost 50 % (see Fig. 4a). On the other hand, the slope of Eq. (14) is 1.1, which is reasonable to explain the observed data.

The formation rate of each term could be calculated using the median values of observed sulfuric acid concentration ($4.9 \times 10^6\,\mathrm{cm}^{-3}$) and estimated organic vapor concentration ($5.7 \times 10^7\,\mathrm{cm}^{-3}$) of the whole investigated data set to multiply the corresponding nucleation coefficients. The contributions of the term only including the sulfuric acid ($[H_2SO_4]^2$) and the term involving organics ($[H_2SO_4][\mathrm{Org}]$) are 43 % and 57 %, respectively. Although these values could not quantitative the real contribution of organics exactly, it may reflect its important role in the atmospheric new particle formation process.

3.3 Sensitivity analysis of the related parameters

Several assumptions are made, estimating the low-volatility organic vapor concentrations. Firstly, the remaining growth rate is assumed to be attributed to the organic vapor, which might overestimate its contribution. Secondly, the properties of organic vapors participating in the nucleation process are still unclear. Meanwhile the determination of the growth rate might also cause a double deviation (Kulmala et al., 2012). Hence, the sensitivities of the correlation coefficients to the growth rate, mass and density of the condensation organic vapor are shown in Table 4. The obvious changes of the correlation coefficients are not shown and the error is smaller than 0.1, indicating the chang of assumptions could not have a great influence on the final results.

3.4 Case studies

Two cases of the NPF events have been classified based on the correlations between particle formation rate and sulfuric acid concentration in Beijing (Wang et al., 2011): Case I: the exponent in the correlation of the formation rate and sulfuric acid between 1 and 2, which implies that activation or kinetic nucleation is the possible nucleation mechanism; Case II: the exponent is larger than 2.5, which indicates that thermodynamic nucleation is the dominant mechanism. And more than half of the NPF events (10 in 17 investigated days) belong to the second case which is rarely observed in clean environments.

The mean CS (during 08:00–11:00 LT) on the Case II ($0.024 \pm 0.012\,\mathrm{s}^{-1}$) days is 1.7 times higher than that on Case I days ($0.014 \pm 0.006\,\mathrm{s}^{-1}$), which indicates more polluted situation on those days. Hence the potential higher newly formed particles (presented as the ratio of sulfuric acid and CS) in Case II is lower than that in Case I as expected (see Fig. 5). However, the mean particle formation rate J_3 in Case II ($7.5 \pm 11.2\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$) is typically significant higher than that in Case I ($3.6 \pm 2.1\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$). A formation rate could be simply expressed as the variation rate of the newly nucleated particles within the certain time period. The opposite trend between the newly formed particle conentration and particle formation rate indicates that on Case II days, more precursor such as organic vapors should be involved in the new particle formation process to “sharp” the variation of newly formed particles.

Here we explore the roles of organic vapor in two kinds of NPF events. Figure 6 presents the mean of daily correlation coefficients in different nucleation mechanisms. It is clear that the mean correlation coefficients in Case II are higher than that in Case I in all nucleation mechanisms involving the organic vapor. This phenomenon implies that the more important role of organic vapor in the new particle formation process on polluted days.

4 Conclusions

Although sulfuric acid has been identified as the key component in new particle formation in the polluted environment of Beijing, the growth rate of newly formed particles related to sulfuric acid could not explain the observed growth rates. Hence, the low-volatility organic vapor is needed to explain the observed growth. The involvement of organic vapors in the nucleation process was estimated in this study. Several nucleation mechanisms involving these organics vapors were tested and the relationships between observed particle formation rates J_3 and vapor concentrations were investigated using the data set of CAREBeijing 2008 campaign.

High correlation coefficient of $R = 0.67$ between the particle formation rate and organic vapor concentration was determined for the Beijing site. This is even higher than that between the formation rate and sulfuric acid concentration ($R = 0.66$). The formation rate correlates well with both the sulfuric acid and organic vapor concentrations, implying that both of them participate in the new particle formation process in Beijing. This is contrary to the clean environment sites, which are only dominated by a single precursor.

In the nucleation mechanisms with single nucleation coefficient (Eqs. 7–12), the highest correlation coefficient ($R = 0.73$) was achieved with the model describing the sum of sulfuric acid homogenous heteromolecular nucleation and homogenous homomolecular nucleation ($J = K_{SA}([H_2SO_4]^2 + [H_2SO_4][Org])$). The 10th and 90th percentiles of the nucleation coefficient K_{SA} are $3.3 \times 10^{-15}\,cm^3\,s^{-1}$ and $3.6 \times 10^{-14}\,cm^3\,s^{-1}$, respectively, with the value of $V_{90/10}$ is close to one order of magnitude. Meanwhile, the largest variations of $V_{90/10}$ and smallest correlation coefficient R are obtained in the nucleation mechanism involving the organics homogengenous homomolecular nucleation ($J = K_{Org}[Org]^2$), which may due to the uncentainty of the estimated organic vapor concentration.

High correlation coefficient ($R = 0.73$) was achieved with the model homogenous nucleation of sulfuric acid both homomolecularly and hetermolecularly with separate coefficients ($J = K_{s1}[H_2SO_4]^2 + K_{s2}[H_2SO_4][Org]$), where $K_{s1} = 5.3 \times 10^{-14}\,cm^3\,s^{-1}$ and $K_{s2} = 5.8 \times 10^{-15}\,cm^3\,s^{-1}$. The contributions of the sulfuric acid and the organics involving terms have been 43 % and 57 %, respectively.

Although large uncercentainties exist in determining the growth rate and estimating the organic vapor concentration, the sensitivity analysis showed that the assumptions won't have the obvious influence to the correlation coefficients, which indicates the results were reasonable in this study.

The roles of organic vapor in two kinds of NPF events which are distinguished by the exponent between particle formation rate and sulfuric acid concentration have been investigated. Higher correlation coefficients between particle formation rate and organic vapor concentrations in Case II ($n > 2.5$) than that in Case I ($n < 2.5$) suggest the important role of organic vapor in the new particle formation process during pollution days.

Even though Beijing results suggest that the organic vapor play important roles in the atmospheric new particle formation, the specific species of organics is still unknown. Further investigations on the roles of precursor in nucleation process are needed, including the measurements of the chemical compositions of nano-size particles.

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Table 1. Comparisons of the correlation coefficient R in different nucleation mechanisms with other studies.

	Beijing	Hyytiälä	HPB	Melpitz	SPC
Air mass type	Urban	Forest	Mountain	Rural	Rural
# Event	17	10	15	8	3
Sulfuric acid	0.66	0.58	0.17	0.68	0.58
Organic vapor	0.67	0.29	0.61	−0.23	0.07
Ref.	This study	Paasonen et al. (2010)			

Sulfuric acid means the nucleation mechanisms $J = A[H_2SO_4]$ and $J = K[H_2SO_4]^2$.
Organic vapor means the nucleation mechanisms $J = A_{Org}[Org]$ and $J = K_{Org}[Org]^2$.

Table 2. Percentile (10th, 25th, 75th and 90th), median and mean values of the nucleation coefficients of the whole dataset. $V_{90/10}$ is the ratio of 90th to 10th percentile values of the ratio between the observed and modeled particle formation rate. Correlation coefficients between observed and modeled particle formation rates are also presented.

Nucleation coefficient		Percentiles				Median	Mean	$V_{90/10}$	R
		10th	25th	75th	90th				
A_{Org} (10^{-8} s^{-1})	Eq. (7)	1.6	2.6	9.0	15.3	4.4	6.7	9.8	0.67
A_{s} (10^{-8} s^{-1})	Eq. (8)	1.5	2.3	8.1	13.6	4.1	6.0	9.4	0.69
K_{Org} (10^{-16} cm^3 s^{-1})	Eq. (9)	2.0	3.7	19.6	54.6	6.6	23.8	26.9	0.67
K_{het} (10^{-15} cm^3 s^{-1})	Eq. (10)	3.6	5.5	19.5	41.5	9.6	17.0	11.4	0.73
K_{SA} (10^{-15} cm^3 s^{-1})	Eq. (11)	3.3	5.1	17.6	35.9	9.0	15.0	10.8	0.73
K_{s} (10^{-16} cm^3 s^{-1})	Eq. (12)	1.9	3.4	17.6	43.9	6.0	18.8	23.4	0.68

Table 3. Values of optimized separate nucleation coefficients and the corresponding $V_{90/10}$ and R.

Nucleation mechanism	A_{s1}	A_{s2}	K_{s1}	K_{s2}	$V_{90/10}$	R
	A (10^8 s^{-1})		K (10^{-15} cm^3 s^{-1})			
$J = A_{s1}[H_2SO_4] + A_{s2}[Org]$	19.7	2.8	–	–	9.3	0.72
$J = K_{s1}[H_2SO_4]^2 + K_{s2}[H_2SO_4][Org]$	–	–	53.0	5.8	9.9	0.73

Table 4. Correlation coefficients in different assumptions.

Nucleation mechanism	correlation coefficient R				
	GR	GR/2[a]	2GR[b]	amu = 84 $\rho = 500\,\mathrm{kg\,m^{-3}}$	amu = 336 $\rho = 1900\,\mathrm{kg\,m^{-3}}$
$J = A_{\mathrm{Org}}[\mathrm{Org}]$	0.67	0.67	0.67	0.66	0.66
$J = K_{\mathrm{Org}}[\mathrm{Org}]^2$	0.67	0.67	0.67	0.66	0.66
$J = A_{\mathrm{s}}([\mathrm{H_2SO_4}]+[\mathrm{Org}])$	0.69	0.70	0.68	0.68	0.68
$J = K_{\mathrm{het}}[\mathrm{H_2SO_4}][\mathrm{Org}]$	0.73	0.73	0.73	0.72	0.72
$J = K_{\mathrm{SA}}([\mathrm{H_2SO_4}]^2+[\mathrm{H_2SO_4}][\mathrm{Org}])$	0.73	0.74	0.73	0.73	0.72
$J = K_{\mathrm{s}}([\mathrm{H_2SO_4}]^2+[\mathrm{H_2SO_4}][\mathrm{Org}]+[\mathrm{Org}]^2)$	0.73	0.73	0.73	0.72	0.72
$J = A_{\mathrm{s1}}[\mathrm{H_2SO_4}] + A_{\mathrm{s2}}[\mathrm{Org}]$	0.72	0.73	0.72	0.72	0.72
$J = K_{\mathrm{s1}}[\mathrm{H_2SO_4}]^2 + K_{\mathrm{s2}}[\mathrm{H_2SO_4}][\mathrm{Org}]$	0.73	0.74	0.73	0.73	0.72

[a] GR/2 means the organic vapor only contribute 50 % of the remaining growth rate.

[b] 2GR means the possible error made in determination the growth rate, the real growth rate is two times higher than the observed growth rate.

ACPD
13, 3419–3450, 2013

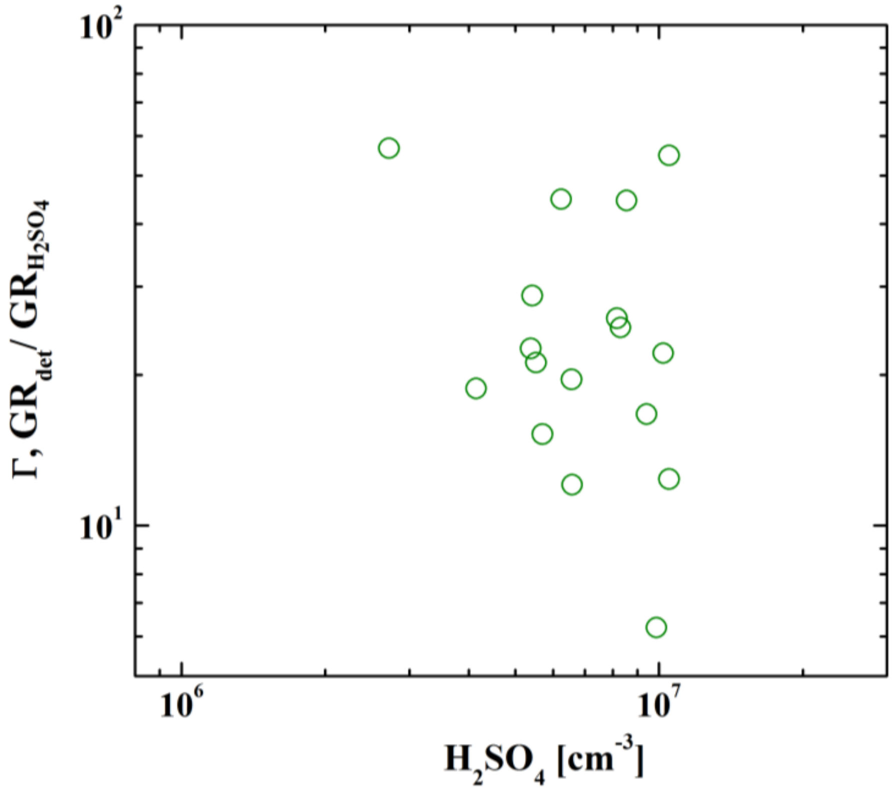

Fig. 1. Ratios between the observed growth rate from the particle number size distribution and the calculated growth rate contributed by sulfuric acid, as a function of the ambient sulfuric acid concentrations.

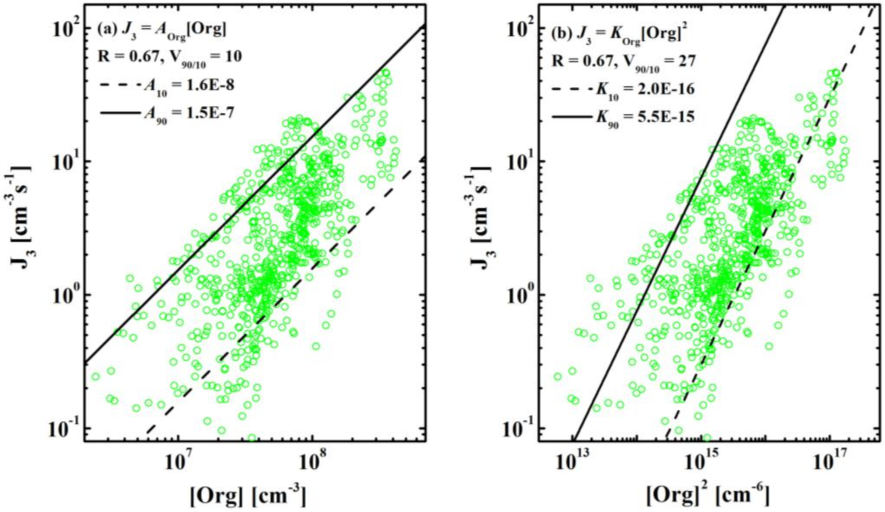

Fig. 2. The particle formation rate J_3 versus **(a)** organic vapor concentrations and **(b)** squared organic vapor concentrations. The solid and dash lines present the 90th and 10th percentile values of the nucleation coefficients, respectively.

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀◀
▶▶
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

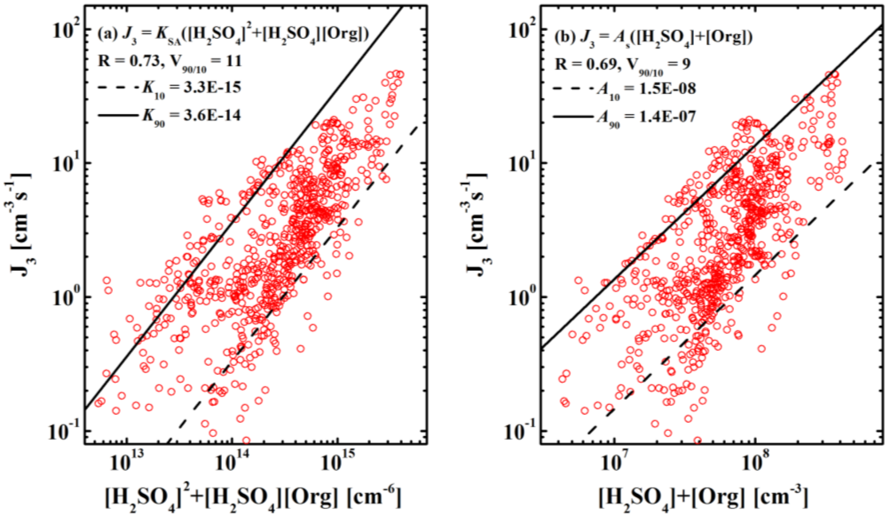

Fig. 3. The particle formation rate J_3 versus **(a)** the sum of the squared sulfuric acid concentrations and the product of sulfuric acid and organic vapor concentrations and **(b)** the sum of the sulfuric acid and organic vapor concentrations, **(b)** the product of sulfuric acid and organic vapor concentrations. The solid and dash lines present the 90th and 10th percentile values of the nucleation coefficients, respectively.

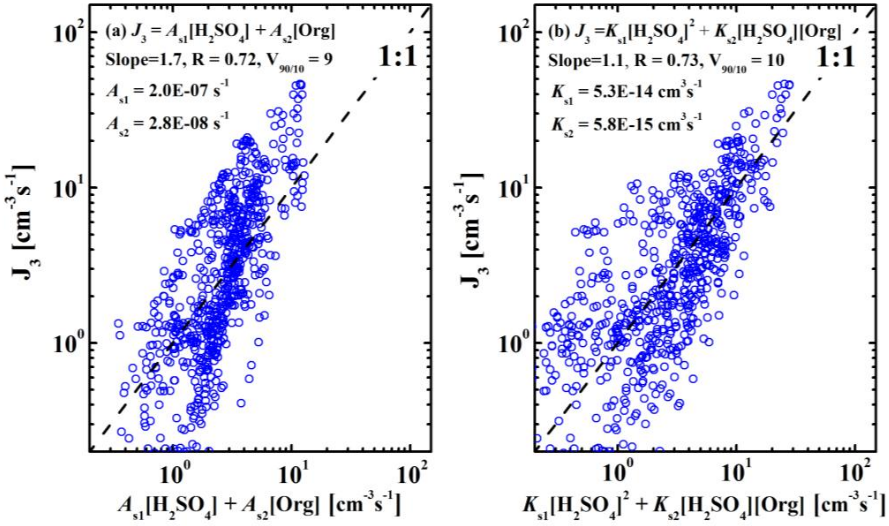

Fig. 4. The observed particle formation rate J_3 versus **(a)** the sum of the sulfuric acid and organic vapor concentrations multiplied with separate nucleation coefficients and **(b)** the sum of the squared sulfuric acid and the product of sulfuric acid and organic vapor concentrations multiplied with separate nucleation coefficients. The dash line presents the 1 : 1 line.

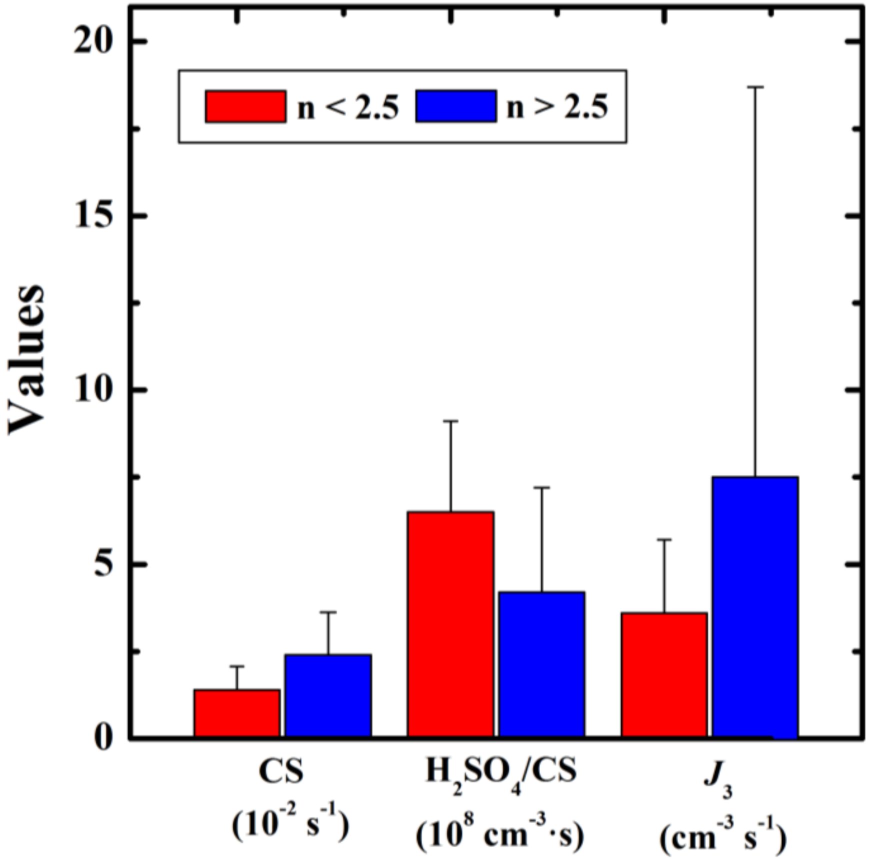

Fig. 5. Comparisons of different parameters between two kinds of NPF events days. Red ones indicate the days with the exponent smaller than 2.5, blue ones indicate the days with the exponent larger than 2.5.

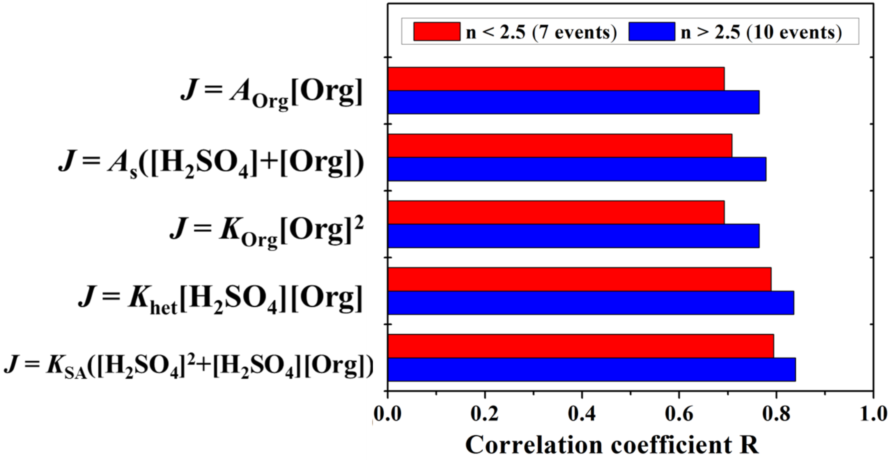

Fig. 6. Comparisons of correlation coefficients in different nucleation mechanisms between two kind of NPF events days. Red ones indicate days with the exponent smaller than 2.5, blue ones indicate the days with the exponent larger than 2.5.

ACPD
13, 3419–3450, 2013

Atmospheric new particle formation and organics at an urban site of Beijing

Z. B. Wang et al.