Atmos. Chem. Phys. Discuss., 10, 2711–2729, 2010
www.atmos-chem-phys-discuss.net/10/2711/2010/

Atmospheric Chemistry and Physics Discussions

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

The roles of sulfuric acid in new particle formation and growth in the mega-city of Beijing

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Received: 15 December 2009 – Accepted: 18 January 2010 – Published: 3 February 2010

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Simultaneous measurements of gaseous sulfuric acid and particle number size distributions were performed to investigate aerosol nucleation and growth during CAREBeijing-2008. The analysis of the measured aerosols and sulfuric acid with an aerosol dynamic model shows the dominant role of sulfuric acid in new particle formation (NPF) process but also in the subsequent growth in Beijing. Based on the data of twelve NPF events, the average formation rates (2–13 $cm^{-3}\,s^{-1}$) show a linear correlation with the sulfuric acid concentrations (R^2=0.85). Coagulation seems to play a significant role in reducing the number concentration of nucleation mode particles with the ratio of the coagulation loss to formation rate being 0.41±0.16. The apparent growth rates vary from 3 to 11 $nm\,h^{-1}$. Condensation of sulfuric acid and its subsequent neutralization by ammonia and coagulation contribute to the apparent particle growth on average 45±18% and 34±17%, respectively. The 30% higher concentration of sulfate than organic compounds in particles during the seven sulfur-rich NPF events but 20% lower concentration of sulfate during the five sulfur-poor type suggest that organic compounds are an important contributor to the growth of the freshly nucleated particles, especially during the sulfur-poor cases.

1 Introduction

Atmospheric aerosols influence climate through affecting the radiative budget of the atmosphere and acting as cloud condensation nuclei, negatively impact human health, and degrade visibility (e.g., Sokolik and Toon, 1996; Jung and Kim, 2006). New particle formation (NPF), one of the important sources of ambient aerosols, is frequently observed worldwide (Kulmala et al., 2004; Kulmala and Kerminen 2008). NPF is characterized by a sharp increase in number concentrations of nucleation mode particles and subsequent growth of freshly nucleated particles. Atmospheric measurements show that new particle formation rates, defined for 3 nm particles, typically vary from 1

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to 70 cm^{-3} s^{-1}; the growth rate of freshly nucleated particles has been measured in the range of 1–20 nm h^{-1}, with the higher values observed during summertime (Kulmala et al., 2004; Wu et al., 2007). However, the species that participate in the nucleation process and subsequent growth are presently not known for certain. Atmospheric observations and laboratory experiments suggest that sulfuric acid often plays a dominant role (Birmili et al., 2003; Boy et al., 2005), but other species, such as organic compounds, have also been speculated to be important in new particle formation and growth (O'Dowd et al., 2002; Zhang et al., 2004; Barsanti et al., 2009). Coagulation is also important for NPF events, reducing nucleation mode particle number concentrations but leading to particle growth (Kerminen and Kumala, 2002). A few investigations about NPF events have been done in China, but all of them only reported some parameters such as the occurrence frequency, formation rate, and growth rate of NPF events (Wu et al., 2007; Liu et al., 2008; Lin et al., 2007; Wiedensohler et al., 2009). The precursors, such as sulfuric acid, and the role of coagulation for NPF and growth have not been studied in detail.

In this paper, we report simultaneous measurements of particle number size distributions from 3 to 900 nm and concentrations of gaseous sulfuric acid to investigate aerosol nucleation and growth during the Campaign of Atmospheric Research in Beijing and Surrounding Areas in the summer of 2008 (CAREBeijing-2008). An analysis of the measured aerosols and sulfuric acid with an aerosol dynamic model is performed to identify the species responsible for NPF and growth. The formation rates and apparent growth rates of freshly nucleated particles are estimated, and the roles of intramodal coagulation among nucleation mode particles (i.e. self-coagulation) and extramodal coagulation between the nucleation mode particles and preexisting particles (i.e. intermodal coagulation) are assessed.

2 Methodology

2.1 Experimental method

Regional NPF events were observed by a twin differential mobility particle sizer (TDMPS) on the roof of a building (about 15 m above the ground level) on the campus of Peking University (PKU), which is located in the northwestern urban area of Beijing, outside the fourth-ring road, from 12 July to 25 September during CAREBeijing-2008. There were twelve regional NPF events during the measurement period. Simultaneous measurements of gaseous sulfuric acid were performed by an atmospheric pressure-ion drift-chemical ionization mass spectrometer (AP-ID-CIMS).

The TDMPS measured the particle number size distributions from 3 to 900 nm (Stokes diameter) with a time resolution of 10 min. It consisted of two Hauke-type differential mobility analyzers and two condensation particle counters (model 3010 and model 3025, TSI Inc., St. Paul, MN, USA), as previously described by Wu et al. (2007). The relative humidity within the whole system was kept below 30%. Size-dependent losses due to diffusion within the inlet were corrected with empirical particle loss corrections as given by Willeke and Baron (1993).

The AP-ID-CIMS was developed at the Texas A&M University. Unlike a traditional AP-CIMS (Eisele and Tanner, 1993), AP-ID-CIMS utilized a special ion-drift tube (Fortner et al., 2004) capable of operating at one atmospheric pressure to confine and regulate the ion-molecular reaction between nitrate anions (NO_3^-) and gaseous H_2SO_4 (Arnold and Fabian, 1980) thus to achieve better detection precision. Typically, ambient air was sampled at 1.2 m^3 min^{-1} through a 30 cm long, 10 cm diameter inlet to minimize wall loss. AP-ID-CIMS was continuously and sequentially monitoring both reagent and product ions. Each measurement cycle was about 12 s. The corresponding detection limit was about 1.4×10^5 cm^{-3} based on three times of the standard deviation (3σ) of the baseline noise. Variation of the in-situ instrument response to primary H_2SO_4 standards was within 36% of the average value. The H_2SO_4 data used in this work was 10 min averaged to keep consistent with the TDMPS. More detailed information of

H_2SO_4 observation during CAREBeijing-2008 was discussed in a companion paper of this special issue (Zheng et al., 2010).

2.2 Aerosol dynamic modeling

For each particle number size distribution, the nucleation mode was fit with a lognormal distribution, characterized by the total mode number concentration, N, geometric mean diameter, D_g, and geometric standard deviation, σ_g. Least squares fit was performed with manually set limits and adjusted to capture the region around the peak of the distribution (Heintzenberg, 1994). The parameters N, D_g, σ_g are time dependent, as nucleation mode particles grow and evolve.

The average formation rate (FR) is calculated from:

$$\mathrm{FR} = \frac{dN}{dt} + F_{\mathrm{coag}} + F_{\mathrm{growth}} \tag{1}$$

where F_{coag} is the coagulation loss of nucleation mode particles (Eq. 2), and F_{growth} is the flux of particles growing out of 25 nm.

$$F_{\mathrm{coag}} = \left(\sum_i K_i N_i \right) \times N \tag{2}$$

where N_i is the particles number concentration of the ith bin and K_i is the Brownian coagulation coefficient between the nucleation mode and the ith bin particles.

The apparent particle growth rate (GR) is expressed as (Heintzenberg, 1994):

$$\mathrm{GR} = \frac{\Delta D_g}{\Delta t} \tag{3}$$

This apparent growth process is mainly caused by three mechanisms: intramodal coagulation, extramodal coagulation with larger preexisting particles, and vapor condensation.

When the concentration of photochemically produced gaseous sulfuric acid in the atmosphere is much greater than its saturation value (Marti et al., 1997), sulfuric acid is widely believed to participate in the nucleation process and its condensation will contribute to particle growth. As ammonia is abundant in the Beijing area (2–30 ppb), neutralization of sulfuric acid by ammonia is expected to occur readily to form ammonium sulfate. It is also supported by the ratio of sulfate to ammonium ($[SO_4^{2-}]/2[NH_4^+]$=1.1±0.4) in particles from 40 to 400 nm (corresponding to 60 to 600 nm in vacuum dynamic diameter with the assumed particle density of 1.5 g cm^{-3}) determined by an AeroDyne aerosol mass spectrometer (AMS, detailed description about AMS in He et al., 2009). The rate of sulfuric acid condensation and neutralization process is limited by the condensation of sulfuric acid which can be modeled as coagulation between nucleation mode particles and H_2SO_4 molecules. Coagulation can scavenge the newly formed particles and also affect the apparent growth rate due to the high concentrations of particles produced by nucleation and the preexisting particles (Stolzenburg et al., 2005).

The time rates of change of the modal parameters due to these three mechanisms are approximated by assuming that the mode is in the free molecule regime and applying a first-order transition regime correction (Stolzenburg et al., 2005). The time derivatives of the three modal parameters are obtained from the time derivatives of the zeroth, first and second moments (M_k, k=0,1,2) in particle volume ($v=\pi D_p^3/6$) of the mode where

$$M_k(t) \equiv \int_{\text{mode}} v^k n(v,t) d\ln v = N(t) \cdot D_g^{3k}(t) \cdot \exp\left[\frac{9}{2} k^2 \ln^2 \sigma_g(t)\right] \tag{4}$$

$$n(v,t) \equiv \frac{dN}{d\ln v} = \frac{1}{3}\frac{dN}{d\ln D_p}$$

For intramodal coagulation, the time derivatives of the moments can be written as

$$\frac{dM_k}{dt} = \frac{1}{2}\int_{v_2}\int_{v_1}\left[(v_1+v_2)^k - v_1^k - v_2^k\right]\beta(v_1,v_2)n(v_2,t)n(v_1,t)d\ln v_1 d\ln v_2 \quad (5)$$

where $\beta(v_1,v_2)$ is the Fuchs (1964) transition regime collision frequency function for particles of volumes v_1 and v_2 and both integrals are over the nucleation mode.

Extramodal coagulation depletes small particles in the nucleation mode more rapidly than larger ones, thereby shifting the modal size to larger particles and contributing to apparent growth. For extramodal coagulation the time derivatives of the moments can be written as

$$\frac{dM_k}{dt} = -\int_{v_1}\int_{v_2} v^k\beta(v_1,v_2)n(v_1,t)n(v_2,t)d\ln v_2 d\ln v_1 \quad (6)$$

where the outer integral (v_1) is over the nucleation mode and the inner integral (v_2) is over the extramodal region above the nucleation mode.

The rate of sulfuric acid condensation and neutralization process is limited by the condensation of sulfuric acid which can be modeled as coagulation between nucleation mode particles and H_2SO_4 molecules. So the time derivatives can be written as

$$\frac{dM_k}{dt} = N_s(t)\int_{v}\left[(v+v_n)^k - v^k\right]\beta(v,v_s)n(v,t)d\ln v \quad (7)$$

where v_n and v_s are the respective volumes of $(NH_4)_2SO_4$ and H_2SO_4 molecules, N_s is the number concentration of H_2SO_4 molecules, where $\beta(v,v_s)$ is the Fuchs (1964) transition regime collision frequency function for nucleation mode particles of volumes v and H_2SO_4 molecules of volumes v_s, and the integral is over the nucleation mode.

Intramodal and extramodal coagulation loss rates of the nucleation mode particles are also separately obtained from the Moment Method above.

Hygroscopic growth factors of the nucleation mode particles are obtained from Biskos et al. (2009), and those of larger particles are calculated from our earlier measurements.

3 Results and discussion

The NPF events have been observed at PKU with a frequency of 10–70% based on the long-term measurement since March 2004. The NPF events usually occur in conjunction with high wind speed from the north, low relatively humidity (below 45%), and intense solar radiation. A higher NPF frequency and larger formation rates were observed in spring, but a lower NPF frequency and higher growth rates were observed in summer (Wu et al., 2007).

For the twelve NPF events during CAREBeijing-2008, we determined the average formation rates and apparent growth rates in the ranges of 2–13 $cm^{-3}\,s^{-1}$ and 3–11 $nm\,h^{-1}$, respectively, which are within the corresponding ranges in the summer from 2004 to 2008 (i.e., 2–21 $cm^{-3}\,s^{-1}$ and 0.3–12 $nm\,h^{-1}$, respectively). Our present formation rates are lower than those of 20–70 $cm^{-3}\,s^{-1}$ in Atlanta; the present growth rates are comparable to typical particle growth rates of 1–20 $nm\,h^{-1}$ (Kulmala et al., 2004).

3.1 New particle formation

NPF events occurred when the sulfuric acid concentration was relatively high, larger than about 5×10^6 cm^{-3}, while the average sulfuric acid concentration for non-NPF days was about 2×10^6 cm^{-3}. The sulfuric acid concentration necessary for NPF occurrence in Beijing is similar to that previously reported (McMurry et al., 2005). Figure 1 shows that the nucleation mode particle number concentration increases quite fast following the sharp increase of sulfuric acid concentration during NPF events. A linear correlation between the average sulfuric acid concentrations and average formation rates for each NPF event is showed in Fig. 2 (R^2=0.85), indicating that sulfuric acid plays

a dominant role in NPF in Beijing. It has been previously reported that the mass size distributions of sulfate, ammonium, and oxalate shifted to smaller sizes on NPF event days compared with non-NPF event days in 2006 (Yue et al., 2009) and NPF events may involve sulfuric acid, ammonia, and oxalic acid. During the CAREBeijing-2008 campaign, similar phenomena were also found for sulfate and ammonia in particles from 40 to 400 nm.

The ratio of coagulation loss to formation rate is 0.41±0.16, suggesting that coagulation between particles decreases the formation rate by about 40%. Hence, coagulation is important for NPF events, since this process decreases the nucleation mode particle number concentration but leads to apparent growth of newly nucleated particles. The sum of intramodal and extramodal coagulation losses estimated with the Moment Method agrees well with the coagulation loss calculated with Eq. (2) and their ratio is 0.98±0.26, indicating that the two methods are consistent and comparable. The contributions of intramodal coagulation and extramodal coagulation to the coagulation loss are similar, with a ratio of 0.97±0.48. Both preexisting particles and high number concentrations of the nucleation mode particles explain the loss of nucleation mode particles, suppressing the existence of the freshly nucleated particles.

3.2 Growth of the freshly formed particles

If the growth of nucleation mode particles is only caused by condensation of sulfuric acid and subsequent neutralization by ammonia to form $(NH_4)_2SO_4$, the calculated growth rates of the nucleation mode particles can not explain the higher apparent growth rates. Similar phenomena were also reported by Stolzenburg et al. (2005): sulfate and ammonium were found to be the only constituents of the 6–10 nm particles (Smith et al., 2005) but could not explain the particle growth in Atlanta. Another study by Korhonen et al. (2005) also concluded that coagulation growth is non-negligible when considering particle growth. During some of the cases, the particle growth process lasted through the whole afternoon and the particles grew up to about 100 nm, which would impose an important effect on the properties of the CCN activity.

The apparent growth rates and calculated growth rates caused by the condensation and neutralization of sulfuric acid, intramodal coagulation, and extramodal coagulation on different NPF days during CAREBeijing-2008 are depicted in Fig. 3, showing that these three mechanisms account for 79±31% of the apparent growth rates, with the contributions of condensation and neutralization of sulfuric acid to be 45±18% and coagulation to be 34±17%. The contributions of intramodal and extramodal coagulation are comparable, accounting for 19±12% and 15±7%, respectively. Sulfate and ammonium account for (52±14)% and organic matters take up (36±13)% in 40–400 nm particles during these NPF events with their total contribution being (89±8)%. It suggests that organic matters may also contribute to the particle growth significantly.

On the basis of the calculated and the apparent growth rate, we classify NPF events into two categories: If the condensation of sulfuric acid contributes more than 50% to the apparent growth rate subtracting the coagulation growth, the particle chemical compositions are mainly sulfate (the sulfur-rich type). In contrast, if the condensation of sulfuric acid contributes less than 50%, other species other than sulfur dominate the growth process (the sulfur-poor type). During the CAREBeijing-2008 campaign, seven events of the sulfur-rich type and five events of the sulfur-poor type are identified (Fig. 3a). The condensation and subsequent neutralization of sulfuric acid accounts for 54±15% of the apparent growth rates during the sulfuric-rich NPF events and 27±6% during the sulfuric-poor NPF events. While the magnitude of the coagulation growth rate for sulfur-rich and -poor cases are nearly identical; coagulation growth is responsible for 30–50% and 10–30% in the measured growth rates for these two cases, respectively. The concentration of sulfate in 40–400 nm particles is about 30% higher than organic compounds during the sulfuric-rich NPF events, but is about 20% lower for the sulfuric-poor NPF events (Fig. 3c). Hence, we conclude that the unaccountable apparent growth rate (the apparent growth rate subtracting the contribution of the condensation and neutralization of sulfuric acid and coagulation) is mainly contributed by organic compounds. It is also reported that organic compounds rather than sulfate dominate the composition of 10–33 nm particles during NPF events in Tecamac,

Mexico (Smith et al., 2008).

The sulfur-rich NPF events occurred with slightly higher sulfuric acid concentrations ($(8\pm1)\times10^6$ cm^{-3}) than sulfur-poor type ($(7\pm2)\times10^6$ cm^{-3}). The sulfur-rich NPF events corresponded to a higher formation rate but lower apparent growth rate than the sulfur-poor type by 17% and 45%, respectively (Fig. 3b). The average ratio of intramodal coagulation growth to the extramodal coagulation growth during the sulfur-rich NPF events was 1.6±0.7, significantly higher than that during the sulfur-poor type (0.7±0.3). There are several plausible explanations for such a difference. First, higher formation rates of the sulfur-rich NPF events rapidly increase the number concentrations of nucleation mode particles and lower apparent growth rates suppress the transfer of aerosols from the nucleation to the Aitken mode, both leading to higher number concentrations of nucleation mode particles and promoting the intramodal coagulation process and higher intramodal coagulation growth rates. Alternatively, the condensational sinks of preexisting particles of these two type NPF events were similar, indicating nearly identical surface area concentrations during these two types of NPF events. The surface area concentration reflects one of the key elements of the extramodal coagulation.

3.3 Case study of sulfur-rich and sulfur-poor NPF events

The NPF event on 31 August is a typical sulfur-rich NPF event. The corresponding average formation rate is 6 cm^{-3} s^{-1} and apparent growth rate is 4 nm h^{-1}. An obvious growth of the particle volume size was also observed. When the newly formed particles grow into the size that can be detected by AMS, the growth of sulfate was observed subsequently (Fig. 4), while it is not true for other compositions. Moreover, the average mass size distributions show that the mass concentration of sulfate is significantly higher than that of organic compounds during the event (between 14:00 and 18:00 LT, Fig. 4g). This confirms that sulfate is the most important contributor to the particle growth during this sulfur-rich NPF event: the condensation of sulfuric acid and its subsequent neutralization accounts for about 60% of the apparent growth rate (cf. Fig. 3a).

The NPF event on 18 September with an average formation rate of 2 cm^{-3} s^{-1} and an apparent growth rate of 6 nm h^{-1} belongs to the sulfur-poor type (Fig. 4a). In contrast to the case on 31 August, the mass concentration of organic compounds is significantly higher than that of sulfate during the event, as shown in Fig. 4h. It means that the contribution of organic compounds to particle growth is larger than that of sulfate.

4 Conclusions

Twelve regional NPF events were discerned and analyzed based on the measured aerosols and sulfuric acid with an aerosol dynamic model during the CAREBeijing-2008 campaign. Sulfuric acid plays a dominant role both in the new particle formation and subsequent growth processes. It has a linear correlation with the average formation rates (R^2=0.85) during the NPF events; its condensation and subsequent neutralization by ammonia contributes 45±18% to the apparent growth rate on average. Coagulation plays a significant role in reducing the number concentration of nucleation mode particles and contributing to the apparent growth of the freshly formed particles. On average, the ratio of coagulation loss to the formation rate is 0.41±0.16 and coagulation contributes 34±17% to the apparent growth rate. The condensation and neutralization of sulfuric acid together with coagulation accounts for 80–100% of the apparent particle growth rate among seven sulfur-rich NPF events, during which sulfate is the major composition of the ultrafine particles. While for the five sulfur-poor NPF events, the concentrations of sulfate in ultrafine particles is significantly lower than those of organic compounds, that is to say organic compounds are the major composition. Organic compounds are responsible for the particle growth, besides condensation and neutralization of sulfuric acid and coagulation, especially during the sulfur-poor NPF events.

During some cases the growth processes last through the whole afternoon, causing the particles grow up to 100 nm, which will impose significant effect on CCN. In addition, the different shares of sulfate and organic compounds in these particles will lead to

different hygroscopic growth property and CCN activity.

Acknowledgements. This work as part of the Campaign of Atmospheric Research in Beijing and surrounding areas in 2008 is supported by Beijing Council of Science and Technology. It is also supported by the National Natural Science Foundation of China (20637020, 20977001) and European Integrated project on Aerosol Cloud Climate and Air Quality interactions (EU-CAARI, No. 036833-2).

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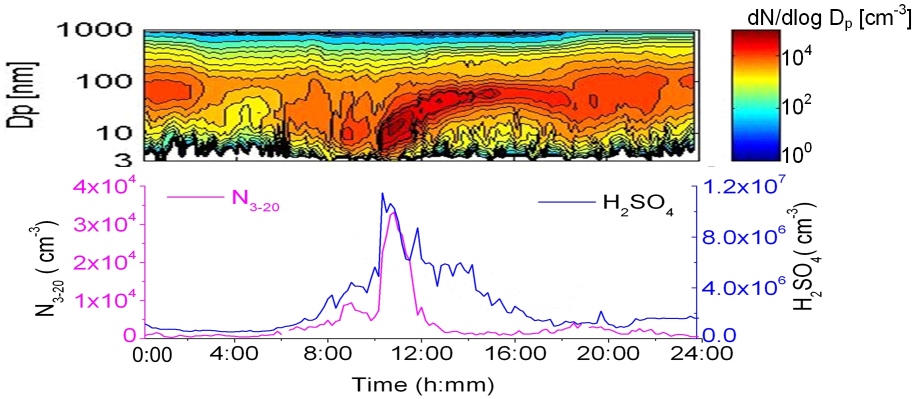

Fig. 1. Particle number size distributions, particle number concentrations (3–20 nm) and sulfuric acid concentrations on a NPF day, 12 August 2008 (Local Time).

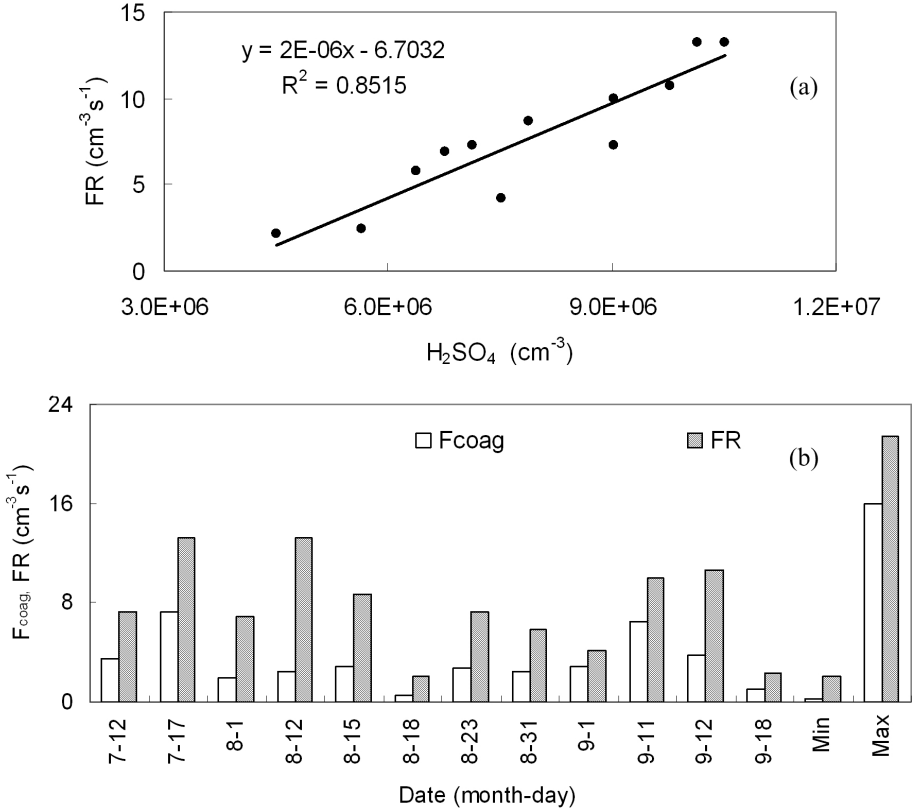

Fig. 2. Relationship of average formation rate (FR) and sulfuric acid concentration **(a)** and relationship of average coagulation loss (F_{coag}) and formation rate **(b)** during NPF events. Min and Max are the minimum and maximum values from June through August from 2004 to 2008, respectively.

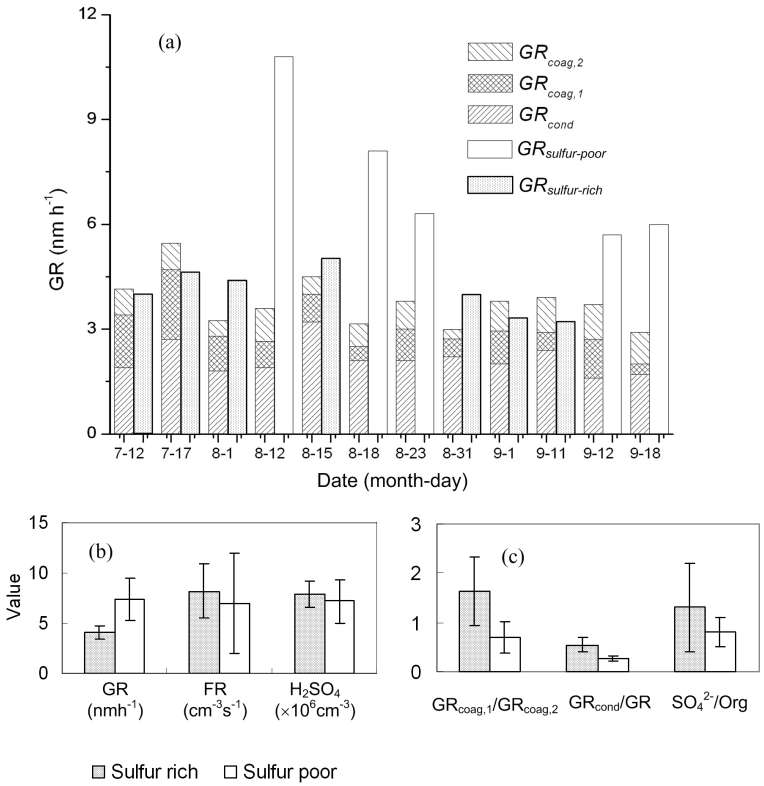

Fig. 3. Apparent growth rates of NPF events and the growth rates caused by the three different mechanisms **(a)** and comparison of important parameters (**b** and **c**) during the two types of NPF events. GR means growth rate; GR_{cond} is the growth rate caused by the condensation and neutralization of sulfuric acid; $GR_{coag,1}$ and $GR_{coag,2}$ are the intramoal coagulation growth rate and extramodal coagulation growth rate, respectively. SO_4^{2-} and Org are mass concentrations of sulfate and organic compounds in 40–400 nm particles, respectively.

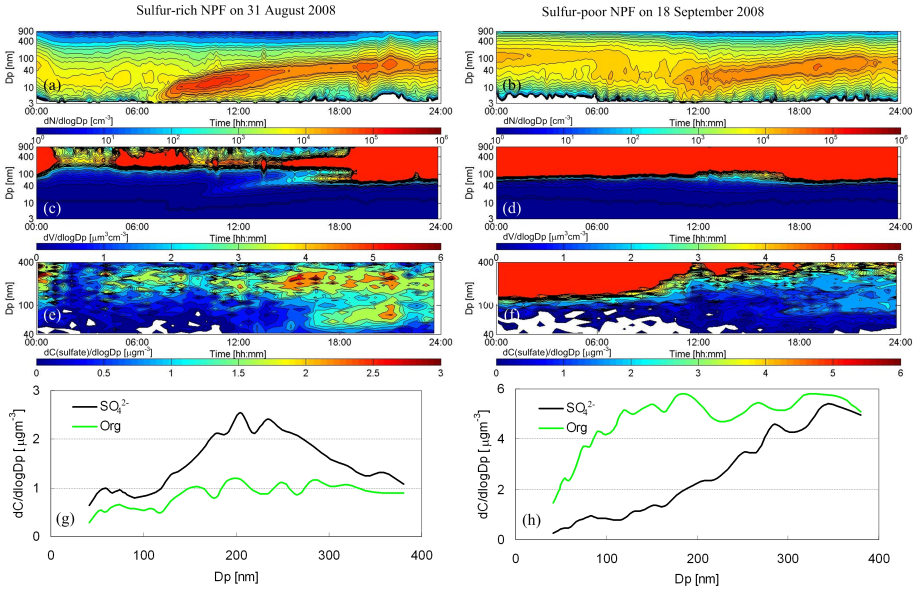

Fig. 4. Particle number size distributions (**a** and **b**), particle volume size distributions (**c** and **d**), sulfate mass size distributions (**e** and **f**), and comparison of average mass size distributions between sulfate and organic compounds from 14:00 to 18:00 LT (**g** and **h**) on sulfur-rich and sulfur-poor NPF event days, respectively.

ACPD
10, 2711–2729, 2010