

Analysis on Concentration and Source Rate of Precursor Vapors Participating in Particle Formation and Growth at Xinken in the Pearl River Delta of China

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ABSTRACT

Concentration and source rate of precursor vapors participating in particle formation and subsequent growth were investigated during the Pearl River Delta intensive campaign (PRD2004, October 2004) in southeastern China. Four new particle formation event days and a typical non-event day were selected for our analysis. Atmospheric sulphuric acid, the important precursor vapor in nucleation and growth, were simulated with a pseudo steady-state model based on the measurements of SO₂, NO_x, O₃, CO, non-methane hydrocarbon (NMHC) and ambient particle number concentrations as well as modeled photolysis frequencies obtained from measurements. The maximum midday sulphuric acid concentrations vary from 4.53×10^7 to 2.17×10^8 molecules cm⁻³, the corresponding source rate via reaction of OH and SO₂ range between 2.37×10^6 and 1.16×10^7 molecules cm⁻³ s⁻¹. Nucleation mode growth rate was derived from size spectral evolution during the events to be 6.8–13.8 nm h⁻¹. Based on the growth rate, concentration of the vapors participating in subsequent growth were estimated to vary from 1.32×10^8 to 2.80×10^8 molecules cm⁻³ with corresponding source rate between 7.26×10^6 and 1.64×10^7 molecules cm⁻³ s⁻¹. Our results show the degree of pollution is larger in PRD. Sulphuric acid concentrations are fairly high and have a close correlation with new particle formation events. Budget analysis shows that sulphuric acid alone is not enough for required growth; other nonvolatile vapors are needed. However, sulphuric acid plays an important role in growth; the contribution of sulphuric acid to growth in PRD is 12.4%–65.2%.

Key words: particle formation and growth, sulphuric acid, pseudo steady state model, condensation sink, precursor vapors, source rate

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1. Introduction

Aerosol particles are ubiquitous in the Earth's atmosphere and affect our quality of life in many different ways (Seinfeld and Pandis, 1998), such as its health effects (Wichmann and Peters, 2000; Stieb et al., 2002) and its influence on regional pollution and climate change patterns (Ramanathan et al., 2001; Menon et al., 2002). Understanding these effects requires detailed information on the fate of aerosol particles. Key processes in this respect are “nucleation” (also known as new particle formation) and the subsequent growth of particles to larger sizes (Kulmala, 2003). Recently,

evidence of new particle formation inferred from the measured aerosol spectral evolution have emerged in field measurements performed on ships, aircraft, and fixed sampling sites (Kulmala et al., 2004, and references therein). Nucleation events typically lead to increases in number concentrations by factors of two to ten, and freshly nucleated particles typically grow to sizes between 10 and 100 nm during the course of a day (Stolzenburg et al., 2005).

Sulphuric acid has attracted the most attention in the study of nucleation. It is proposed to be one of the most important candidates having the ability of individual molecules to produce new particles in the

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atmosphere regarding its low vapor pressure (Kulmala et al., 2004). It has been included in almost all the nucleation theories, such as binary $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ nucleation (Kulmala and Laaksonen, 1990), ternary $\text{H}_2\text{SO}_4\text{-NH}_3\text{-H}_2\text{O}$ nucleation (Coffman and Hegg, 1995), ion-induced nucleation (Yu and Turco, 2000) and organic species enhanced nucleation (Zhang et al., 2004a). Sulphuric acid also participates in subsequent growth of particles, Boy et al. (2005) and Stanier et al. (2004) have shown that sulphuric acid was responsible for about 10% and almost 100% of the particle growth in remote forested and polluted environments, respectively.

Knowledge about sulphuric acid is important for analyzing formation and growth of aerosol particles. The concentration of sulphuric acid can be determined experimentally and numerically. The chemical ionization mass spectrometric (CIMS) technique measures gas phase sulphuric acid with the lowest detective limits of 10^4 molecules cm^{-3} (Eisele and Tanner, 1993), which has been used in several field measurements (e.g., Weber et al., 1995, 1997; Eisele and Tanner, 1993; Boy et al., 2005). Sulphuric acid is also calculated with pseudo steady-state model and the modeling results are in good agreement with the measurements (Weber et al., 1997; Boy et al., 2005).

The fact that newly formed particles are scavenged significantly or even totally before reaching detectable sizes has important consequences when interpreting atmospheric measurements, since newly formed nuclei will be scavenged away unless they grow sufficiently fast (Kerminen et al., 2001). The growth of fresh nuclei to detectable sizes and above requires in most cases the presence of nonvolatile condensable vapors other than H_2SO_4 (gas). These vapors are probably secondary organics, their total required concentration levels depend on the preexisting particle population (Kerminen et al., 2001; Kulmala et al., 2000). Thus, information on the concentration and source rate of the vapors participating in growth is important for the analysis of subsequent growth. The concentration of condensable vapor and its source rate during the nucleation and growth events can be analysed from measured aerosol spectral evolution and during new particle formation events the growth usually required a condensable vapor concentration of $< 10^7 - 3 \times 10^8$ cm^{-3} and a source rate of approximately $10^3 - 1.5 \times 10^7$ $\text{cm}^{-3} \text{ s}^{-1}$ to be sustained (Kulmala et al., 2001, 2005).

Recently, new particle formation events were observed in Beijing, China (Wu et al., 2007; Wehner et al., 2004). The Pearl River Delta of China is another region with serious aerosol pollution as a result of developing, high-speed economy (Zhang et al., 2004b). During the Pearl River Delta October intensive cam-

paign in 2004 (PRD2004) (Cheng et al., 2006; Ansmann et al., 2005), phenomena of new particle formation were observed on typical days at the Xinken site. However, there is no information on the concentration and source rate of precursor vapors participating in formation and subsequent growth of particles yet in this area. In this paper, four new particle formation event days (4–5, 7 and 21 October) and a typical non-event day (28 October) were selected, precursor vapors participating in formation and subsequent growth were analysed. We calculated sulphuric acid concentrations with a pseudo steady-state box model. The concentration and source rate of vapors participating in growth were estimated based on particle growth rate derived from size spectral evolution. The contribution of sulphuric to growth was also analyzed.

2. Experiment description

As part of PRD2004, continuous measurements of aerosol optical, chemical and physical properties, as well as related gas phase species were conducted at the Xinken site (22.6°N , 113.6°E). Xinken is a rural (or non-urban) site located at the artificial mound area near the mouth of the Pearl River of China.

The aerosol size distributions were measured from 3 October to 5 November. Under dry conditions (relative humidity, $\text{RH} < 10\%$) the particle number size distributions with electrical mobility diameter from 3–900 nm were measured with a Twin Differential Mobility Particle Sizer (TDMPMS). The particle number size distributions with aerodynamic diameters from 500 nm to 10 μm were measured with an Aerodynamic Particle Sizer (APS, MODEL TSI 3320) ($\text{RH} < 20\%$). A uniform aerodynamic diameters in the full range between 3nm and 10 μm are obtained from two instruments (Cheng et al., 2006). The number size distributions were complemented by concurrent measurements of airborne particles at four controlled RHs (30%, 55%, 75% and 90%) with a Humidified Differential Mobility Particle Sizer (HDMPS) to determine the size-resolved descriptive hygroscopic growth factors (i.e., how much a dry particle with certain size would grow as a result of increasing ambient RH) and the particle number size distributions at ambient RH (Birmili et al., 2004). For a more detailed description, the reader is referred to Cheng et al. (2006) and Ansmann et al. (2005).

The SO_2 concentrations were measured with a TECO SO_2 analyzer from 3 October to 5 November and averaged over 15 minute intervals. They varied considerably from 1.3×10^{11} to 5.35×10^{12} molecules cm^{-3} (1 ppb = 2.46×10^{10} molecules cm^{-3} at 298.25 K and 1013.25 hPa), with 7.19×10^{11} molecules cm^{-3} as

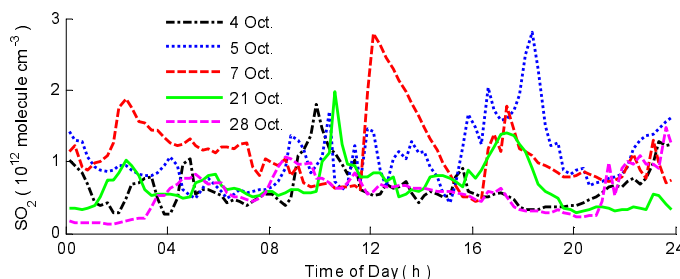


Fig. 1. SO₂ concentrations during study days at the Xinken site in PRD.

average. The minimum appeared on 15 October and the maximum was observed on 25 October. The SO₂ on the study days are shown in Fig. 1. The temperature during 3 and 31 October obtained from automatic meteorological stations varied in range from 293.15 K to 307.15 K with an average of 298.25 K. The relative humidity (RH, TH-16A, Wuhan Tianhong Corporation) from 6 October to 4 November was 25.3%–97.8%, with 64.5% as average.

3. Methodology

3.1 Simulation of sulphuric acid: pseudo steady-state model

In this study, a zero-dimensional Pseudo Steady-state Model similar to Boy et al. (2005) and Weber et al. (1997) was adopted. The budget equation of H₂SO₄ was shown as follows (Kulmala et al., 2001)

$$\frac{dC_{SA}}{dt} \approx 0 = Q - S \cdot C_{SA} - J_{SA} \cdot C_{SA}, \quad (1)$$

where C_{SA} is the sulphuric acid concentration (molecules cm⁻³), S is the condensational sink (s⁻¹) of sulphuric acid on aerosols, the nucleation term J_{SA} (molecules cm⁻³ s⁻¹) was usually neglected compared with condensation (Harrington and Kreidenweis, 1998; Weber et al., 1997; Boy et al., 2005). Q_{SA} is sulphuric acid production rate via reaction of SO₂ and OH and is expressed as

$$Q_{SA} = [\text{OH}] \times [\text{SO}_2] \times k. \quad (2)$$

The rate coefficient k is calculated using the temperature dependent rate equations from DeMore et al. (1997). For temperature 298.25 K the coefficient is 8.88×10^{-13} cm³ molecule⁻¹ s⁻¹.

The aerosol condensational sink (S) determines how rapidly condensable vapor molecules will condense onto pre-existing aerosols and can be calculated from

(Kulmala et al., 2001)

$$\begin{aligned} S &= 2\pi D \int_0^\infty d_p \beta_m(d_p) n(d_p) dd_p \\ &= 2\pi D \sum_i \beta_{m_i} d_{p_i} N_i. \end{aligned} \quad (3)$$

Here D is the diffusion coefficient of sulphuric acid (0.117 cm² s⁻¹) and the transitional correction factor β_m is typically calculated using the expression by Fuchs and Sutugin (1971). N is the number concentration and d_p is the diameter of particles in the i th size class (or size bin). Pre-existing particles between 3 nm and 10 μm were used to calculate the condensational sink, and the hygroscopic growth (Hämeri et al., 2001) correction was included to account for the real relative humidity.

Under the pseudo steady-state assumption, sulphuric acid concentration can be calculated as following

$$C_{SA} = Q_{SA}/S. \quad (4)$$

3.2 Nonvolatile vapors participating in growth: concentration and source rate

The concentration and source rate of condensable vapor participating in growth are analyzed using two equations describing the rate of change of vapor concentration and particle growth (Kulmala et al., 2001).

Considering condensable vapor molecules of some species (here we assume the vapors with the molecular properties of sulphuric acid), the time dependence of the vapor concentration (C_v) can be expressed as (Kulmala et al., 2005)

$$\frac{dC_v}{dt} = Q_v - S \cdot C_v, \quad (5)$$

Q_v is the source rate of the vapor and S is condensational sink to the pre-existing aerosols. The condensation itself is driven by the vapor pressure difference far away and on the surface of the pre-existing particle surface. In this work the vapor pressure at the surface is assumed to be zero, yielding a maximum mass flux

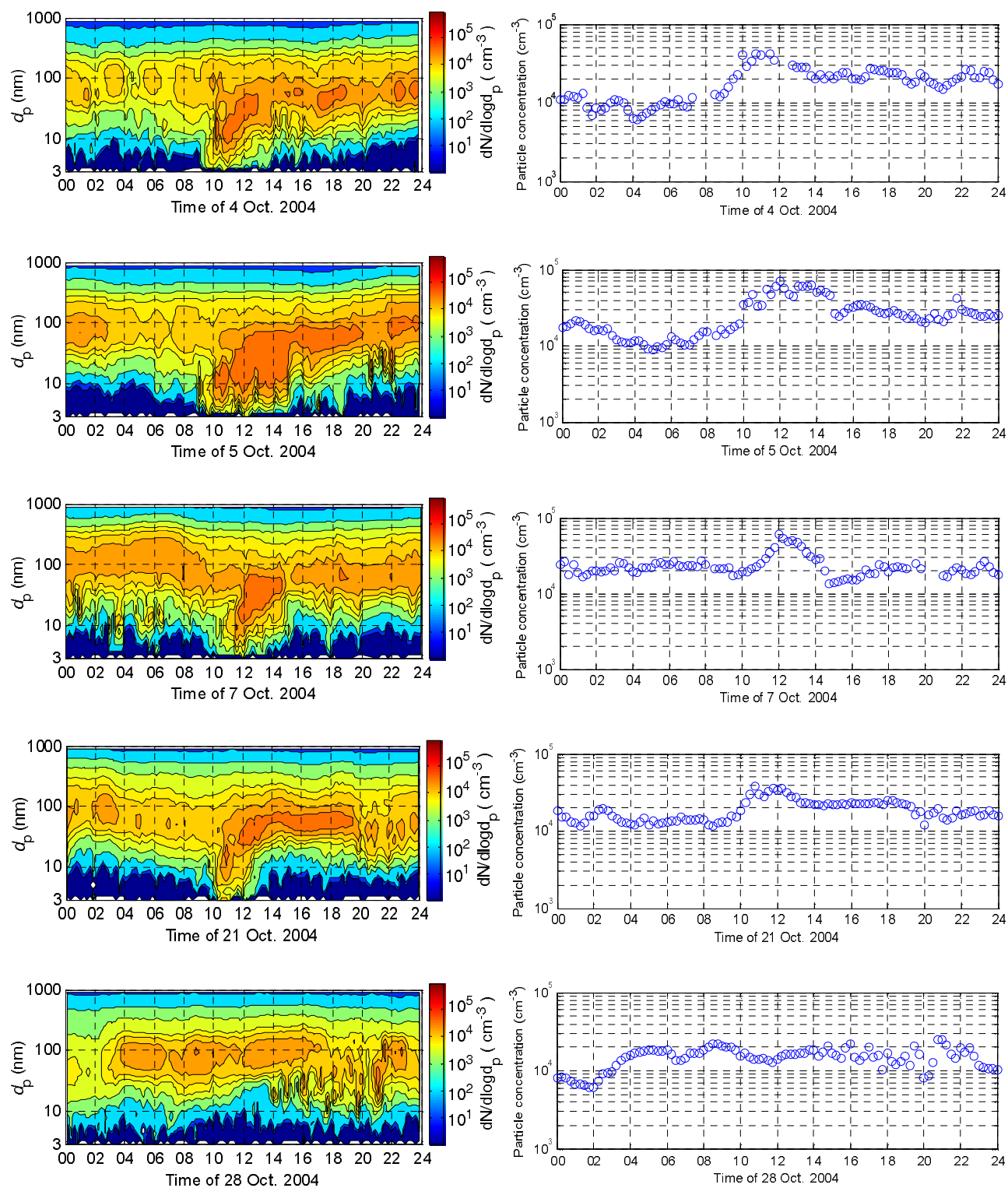


Fig. 2. Diurnal variation of particle size distribution and total number concentration.

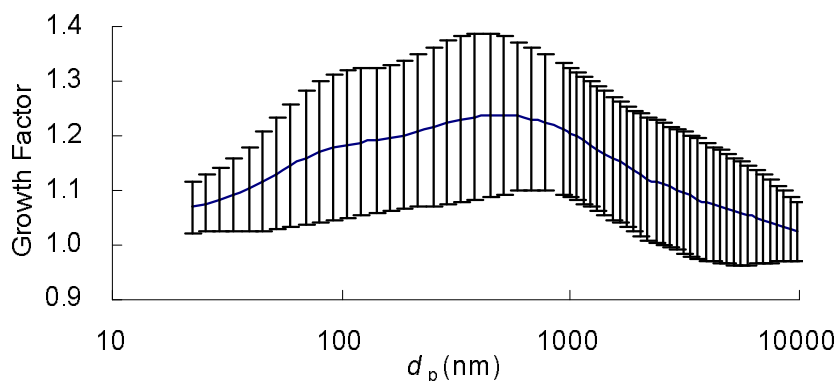


Fig. 3. Average growth factors and standard deviation from 23 to 30 October.

of condensable vapor to the aerosol phase. With this assumption, an unknown activity coefficient plays no role in the condensation flux.

The growth-rate (R) can be expressed as (Kulmala et al., 2005)

$$\frac{dd_p}{dt} = \frac{4m_v\beta_m D(C_v - C_s)}{d_p\rho}. \quad (6)$$

Here d_p is particle diameter, m_v is molecular mass of condensable vapors, and particle density ρ is assumed to be 1.7 g cm^{-3} (Cheng et al., 2006), the equilibrium vapor pressure of the condensing species is assumed to be negligible. Equation above can be integrated from $d_{p,0}$ to d_p to obtain (Kulmala et al., 2001)

$$C_v = \frac{\rho}{\Delta t D m_v} \left[\frac{d_p^2 - d_{p,0}^2}{8} + \left(\frac{4}{3\alpha} - 0.623 \right) \cdot \lambda \cdot \frac{d_p - d_{p,0}}{2} + 0.623\lambda^2 \ln \frac{2\lambda + d_p}{2\lambda + d_{p,0}} \right] \quad (7)$$

Where α is the mass accommodation coefficient (i.e., sticking probability, here assumed to be unity) and λ is the mean free path.

After calculating the vapor concentration (C_v) and condensation sink (S), the vapor source rate can be obtained by making a pseudo-steady state assumption as (Kulmala et al., 2005)

$$Q_v = S \cdot C_v \quad (8)$$

4. Results and discussions

4.1 Size distribution analysis and new particle formation events

The submicron size distributions measured at the Xinken site during PRD2004 exhibited a structure of two or three modes distributed log-normally, including

the nucleation mode, the accumulation mode and the Aitken mode.

A new nucleation mode is usually considered to be caused by the formation of new particles from precursor vapors (Kulmala et al., 1998, 2001), this character of new particle formation (NPF) is frequently observed in the Xinken time series. To reliably determine the processes and atmospheric conditions leading to NPF events, information about the times when events were recorded and when no particles are formed are needed. Using this information, it is later possible to analyze relevant atmospheric variables and correlate them with the NPF events. Some mathematical criterion or definition for an NPF event are proposed (e.g., McMurry et al., 2005; Mäkelä et al., 2000), while in this paper the criterion of Dal Maso et al. (2005) was used to classify NPF events for convenient and objective to operate.

During the 34 days from 3 October to 5 November when the size distributions were measured, four days (4, 5, 7, and 21 October) identified definitely as new particle formation events are selected for our analysis, a typical non-event day (28 October) is also included as a comparison (Fig. 2).

4.2 Aerosol condensation sink

The aerosol condensational sink is obtained directly from the size distribution measurements. The response of the ambient aerosol to humidity-induced growth was reflected in the calculated condensation sink (Kulmala et al., 2001; Hämeri et al., 2001). For the eight days from 23 to 30 October when hygroscopic parameters were measured, hygroscopic growth raised the dry S (S calculated from dry size spectrum) by an overall average factor of 1.36. Since hygroscopic parameters were not measured in four event days, the average growth factors of the eight days was used to get the corrected ambient S , the error is within 20% (Fig. 3).

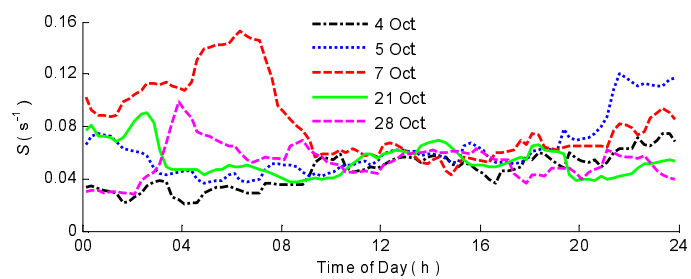


Fig. 4. Corrected S of study days.

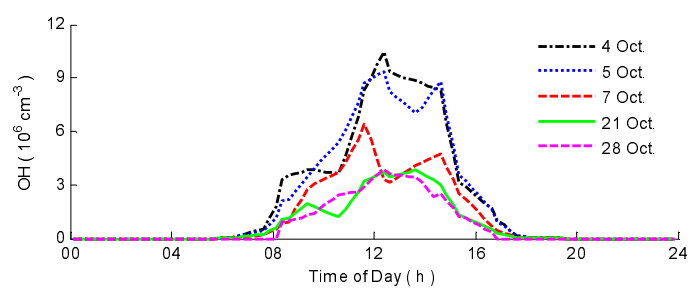


Fig. 5. OH concentrations during study days at the Xinken site in PRD.

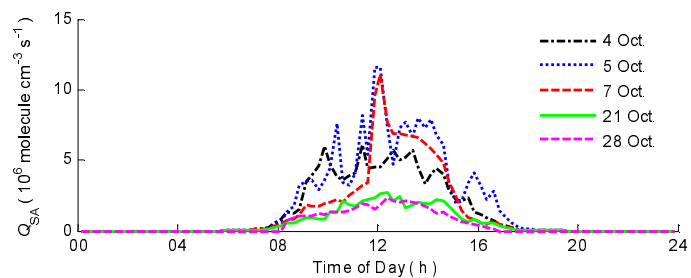


Fig. 6. Source rate of sulphuric acid at the Xinken site in PRD.

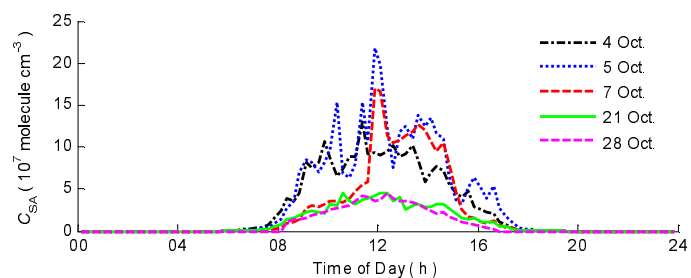


Fig. 7. Sulphuric acid concentrations at the Xinken site in PRD during study days.

The daily average S calculated in four event days range between 4.57×10^{-2} (4 October)– 8.33×10^{-2} (7 October) s^{-1} , the daily average S in the non-event day is $5.35 \times 10^{-2} \text{ s}^{-1}$ (Fig. 4).

4.3 OH concentrations

OH is an important species in the calculation of sulphuric acid concentrations. In the work of Boy et al. (2005), 14 reactions (reactions of OH with NMHC were simplified and combined into one reaction) were used to simulate OH. In our study, the parameterization of Ehhalt and Rohrer (2000) was used to get the hourly average OH concentrations during study days. The relation between OH calculated with Carbon Bond IV mechanisms (Gery et al., 1989) and the parameterization (Ehhalt and Rohrer, 2000) during 23 and 30 October was used to correct the OH calculated with the parameterization. The daily maximum OH of the four event days varied from 3.85×10^6 (21 October) to 1.04×10^7 (4 October) cm^{-3} and in the non-event day the maximum was $3.89 \times 10^6 \text{ cm}^{-3}$ (Fig. 5). Our results have been tested to be reasonable. In 2006, the OH was measured directly with a Laser-Induced Fluorescence in PRD, while the simulated OH results by the method here is within an error of 15% compared with the measurements.

4.4 H₂SO₄ concentrations

Source rates of sulphuric acid were first calculated from OH and SO₂ via photochemical reaction. The daily maximum source rate of the four event days range from 2.77×10^6 (21 October) to 1.16×10^7 (5 October) molecules $\text{cm}^{-3} \text{ s}^{-1}$, the maximum in non-event day is $2.37 \times 10^6 \text{ molecules cm}^{-3} \text{ s}^{-1}$ (Fig. 6).

Using the hygroscopic corrected aerosol condensation sink and simulated source rate of sulphuric acid as input, the daytime H₂SO₄ concentrations were calculated by the pseudo steady-state model described above. The maximum midday sulphuric acid concentrations varied between 4.60×10^7 (21 October) and 2.17×10^8 (5 October) molecules cm^{-3} in four event days and was $4.53 \times 10^7 \text{ molecules cm}^{-3}$ in non-event day (Fig. 7). Although atmospheric sulphuric acid concentration on the order of $10^8 \text{ molecules cm}^{-3}$ has been reported (e.g., Stolzenburg et al., 2005), compared with reports of 10^5 – $10^7 \text{ molecules cm}^{-3}$ in most areas of the world (e.g., Weber et al., 1995, 1997; Eisele and Tanner, 1993; Boy et al., 2005), sulphuric acid in PRD is fairly high, which might owe to the high SO₂ emission and OH concentration (although aerosol load is high, as shown from large S).

For an error estimation of our calculation, uncertainties related to sources and sinks of sulphuric acid was considered. H₂SO₄ is produced mainly by reaction

of SO₂ and OH radicals. The measured SO₂ concentration has an uncertainty of 5%. The error related to OH concentration is within 15%. For sink term, the error related to growth factor correction is within 20%, an accommodation coefficient of unity and other sources of error will cause uncertainty of 20% (Boy et al., 2005). Altogether, the maximum error in the calculated sulphuric acid concentration is within 60%.

4.5 Condensable vapors participating growth

The nucleation mode growth rate (R) can be derived directly from the size distribution measurements. The mode parameters (geometric mean diameter, geometric standard deviation and number concentration) were obtained by the automated fitting method of Hussein et al. (2005) at first. Then we fitted a first order polynomial to the geometric mean diameters of the nucleation mode growth during the formation burst by the method proposed by Dal Maso et al. (2005) to get the growth rate (Fig. 8). If the new particle mode was not well-behaved over the whole time period that it was visible, we chose a time period where the growth was close to constant and the data behaving particularly badly were omitted.

With fitted growth rate, the concentration and source rate of vapors participating in growth during the growth period were obtained by the method described above. The average aerosol condensation sink, sulphuric acid concentration and source rate during the events are also obtained. Since new particle formation events were usually observed to occur between 1000 LST and 1400 LST, the aerosol condensation sink, sulphuric acid concentration and source rate of the non-event day were averaged during the mean event period for a comparison. All of the results are shown in Table 1. Sulphuric acid plays an important role in growth; the contribution of sulphuric acid to particle growth during events are also investigated by analyzing the growth rate fraction and are shown in the table.

During the nucleation events, there is close interdependence between Q_v, C_v and S . This can be explained logically since sources that emit both gaseous (precursors for condensable vapors) and particulate pollutants result in simultaneous increases in both Q_v and S , sources emitting only gaseous pollutants increase Q_v , which then leads to larger S via an enhanced gas-to-particle transfer. The observed growth rate, condensation sink, concentration and source rate of vapors participating growth were similar with reports in polluted environments like New Delhi (Kulmala et al., 2005). The air mass of study days is more polluted compared with most of the “polluted” events observed in Beijing (Wu et al., 2007). The growth rate of nucleation mode

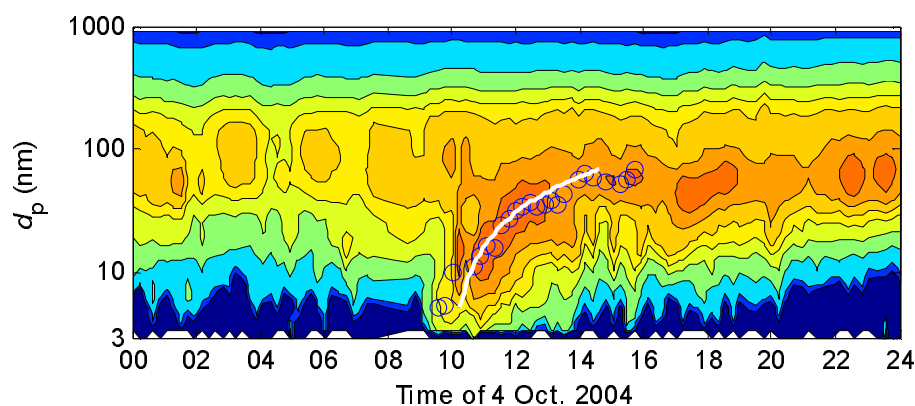


Fig. 8. Example of particle growth rate derived from fitting a first order polynomial to the geometric mean diameters of the nucleation mode growth during the formation burst. We present a surface plot of a new particle formation burst. Blue circles mark the growth mode geometric mean diameters obtained by the fitting procedure, the white line represents the first order polynomial fit result, from which we get the particle growth rate.

Table 1. Average characteristics of event and non-event days. S is the condensation sink during the event for event day and during average event period for a non-event day, R is the growth rate, C_V and Q_V are concentration and source rate of condensable vapors during events, C_{SA} and Q_{SA} are concentration and source rate of sulphuric acid during event for event day and during average event period for non-event day, R_{SA} are sulphuric acid contribution to growth.

Day	S (s^{-1})	R ($nm\ h^{-1}$)	C_V (cm^{-3})	Q_V ($cm^{-3}\ s^{-1}$)	C_{SA} (cm^{-3})	Q_{SA} ($cm^{-3}\ s^{-1}$)	R_{SA} (%)
4 Oct.	5.29×10^{-2}	10.3	2.50×10^8	1.32×10^7	8.12×10^7	4.29×10^6	32.5
5 Oct.	5.50×10^{-2}	6.8	1.32×10^8	7.26×10^6	8.60×10^7	4.76×10^6	65.2
7 Oct.	5.69×10^{-2}	11.1	2.59×10^8	1.47×10^7	7.37×10^7	4.23×10^6	28.5
21 Oct.	5.86×10^{-2}	13.8	2.80×10^8	1.64×10^7	3.48×10^7	2.03×10^6	12.4
28 Oct.	5.48×10^{-2}	—	—	—	2.80×10^7	1.50×10^6	—

particles is always high compared with the clean environments (Kulmala et al., 2005; Wu et al., 2007). The probable reason for this is the higher concentrations of precursor gases which leads to a rapid condensation onto preexisting particles.

The average condensation sink of the study days is comparable. There is a close correlation between sulphuric acid concentrations and new particle formation events, but other factors such as meteorological conditions and other precursor gases may have influence.

Our results also show that sulphuric acid alone is not always enough for subsequent growth; rather, other non-volatile vapors are needed and they are most probably organic vapors of low volatility. During new particle formation events, the contribution of sulphuric acid to nucleation mode growth is 12.4%–65.2%. Compared with the forest areas in southern Finland (Boy et al., 2005), sulphuric acid may play a more important role in particle growth.

5. Conclusions

In this paper, the concentration and source rate of

precursor vapors participating in the formation and subsequent growth of particles in PRD of China are analyzed. Four days with new particle formation events and a typical non-event day during the PRD2004 at Xinken site were selected. The contribution of sulphuric acid to particle growth was also investigated based on the analyzed results.

Sulphuric acid is an important species in nucleation and subsequent growth of new particles. The atmospheric sulphuric acid was modeled with a pseudo steady state model. The maximum midday sulphuric acid concentrations varied from 4.53×10^7 to 2.17×10^8 molecules cm^{-3} . The source rate of sulphuric acid via reaction of OH and SO_2 range between 2.37×10^6 and 1.16×10^7 molecules $cm^{-3}\ s^{-1}$. Sulphuric acid concentrations in PRD are fairly high compared with reports in most other areas of the world, which might owe to the high SO_2 emission and OH concentration.

The total concentration and source rate of condensable vapors participating in nucleation mode growth are derived from measured size spectral evolution. During the event days, the particle growth rate range

was between 6.8–13.8 nm h⁻¹. The total concentration of condensable vapors varies from 1.32×10^8 to 2.80×10^8 molecules cm⁻³, and the corresponding source are between 7.26×10^6 and 1.64×10^7 molecules cm⁻³ s⁻¹. The observed growth rate, condensation sink, concentration, and source rate of vapors participating in growth were similar with reports in other polluted environments.

Sulphuric acid concentrations have close correlation with new particle formation events, but other factors such as meteorological conditions and other precursor gases may have influence. During new particle formation events, sulphuric acid alone is not enough for subsequent growth of nucleated particles. The growth of fresh nuclei to detectable sizes and above requires the presence of non-volatile condensable vapors other than H₂SO₄ (gas). However, sulphuric acid plays an important role in subsequent growth, the contribution of sulphuric acid to growth is 12.4%–65.2%.

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