**Atmospheric
Chemistry
and Physics**

A closure study of cloud condensation nuclei in the North China Plain using droplet kinetic condensational growth model

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Abstract. Aerosol size distribution and cloud condensation nucleus (CCN) number concentration were measured in the North China Plain from 31 December 2009 to 20 January 2010. The CCN closure study was performed using these data and droplet kinetic condensational growth model. The calculated CCN concentration with the assumption of pure ammonium sulfate aerosol is 40–140 % higher than that observed for the supersaturations in this study. A sensitivity test on aerosol solubility and mixing state indicates that 0.2–0.5 mass fraction of ammonium sulfate for internal mixture can lead to a ratio of 0.82–1.30 for the calculated to observed CCN concentrations, and that 0.4–0.7 mass fraction of ammonium sulfate for external mixture results in a ratio of 0.74–1.25 in the North China Plain during the time period of the field observations, suggesting that a relatively simple scheme may be used for CCN prediction in climate models for this region. Finally, we compare the calculated CCN concentrations from the kinetic condensational growth model and the equilibrium model. The kinetic condensational growth model can simulate droplet growth in a time period under a certain supersaturation, while the equilibrium model only predicts whether a certain aerosol can be activated as CCN under that supersaturation. The CCN concentration calculated with the kinetic model is higher than that with the equilibrium model at supersaturations of 0.056 % and 0.083 %, because some particles that are not activated from the equilibrium point-of-view can grow large enough to be considered as CCN in the kinetic model. While at a supersaturation of 0.17 %, CCN concentration calculated with the kinetic model is lower than that with the equilibrium model, due to the limitation of droplet kinetic growth. The calculated CCN concentrations using the kinetic model and the equilibrium model are the same at supersaturations of 0.35 % and 0.70 %.

1 Introduction

Aerosols play an important role in cloud physics, climate and hydrological cycle. Previous studies have shown that the increase of aerosol number concentration, due to either natural or anthropogenic sources, can increase CCN concentration and enhance cloud albedo (Twomey, 1977). In addition, more aerosols that lead to higher CCN concentration and smaller cloud droplets for fixed liquid water, can suppress precipitation and, thus, extend the cloud lifetime and increase fractional cloudiness (Albrecht, 1989). However, the aerosol-cloud interaction is very complex and uncertain (IPCC, 2007; Lohmann and Feichter, 2005) because aerosol size distributions, chemical compositions, mixing states and meteorological parameters can all affect the properties of the clouds (Ackerman et al., 2000; Nenes et al., 2002; Peng and Lohmann, 2003; Rotstayn and Liu, 2003).

Many investigations have been carried out to study the aerosol effects on clouds and climate (e.g., Ackerman et al., 2004; Anderson et al., 2003; Boucher and Lohmann, 1995; Feingold et al., 2003; Lohmann and Feichter, 1997; Penner et al., 2004; Xue and Feingold, 2006). Studies showed that cloud droplets were smaller in polluted clouds than those in clean clouds over the Atlantic Ocean (Brenguier et al., 2000; Schwartz et al., 2002). Ship tracks are famous evidences of the Twomey effect (Ferek et al., 1998). Some observations of ship tracks (Ferek et al., 2000) and boundary layer clouds (Heymsfield and MacFarquhar, 2001; Hudson and Yum, 2001) confirm that precipitation can be suppressed by aerosols. In addition, satellite data revealed plumes of reduced cloud particle size and suppressed precipitation originating from some major urban areas and industrial facilities such as power plants (Rosenfeld, 2000).

A major challenge of understanding the aerosol effects on clouds and climate is to know the ability of aerosol particles acting as CCN at a specific ambient supersaturation. Satellites, networks of ground-based instruments and dedicated field experiments are used to continuously observe the aerosol distribution and composition at different regions (Bates et al., 1998; Delene and Ogren, 2002; Kaufman et al., 2002; Ramanathan et al., 2001). Studies show that different compositions of aerosol particles have different chemical properties, resulting in different CCN activation (Bilde and Svenningsson, 2004; McFiggans et al., 2005). Laboratory studies show that the activation of pure black carbon particles requires higher supersaturations than that predicted by calculations where the particles are represented as insoluble and wettable spheres, and that the addition of a small amount of NaCl to the black carbon particles greatly enhanced their CCN efficiency (Dusek et al., 2006). In addition to the chemical composition of aerosol, the size distribution, the mixing state and a detailed knowledge of how different compounds interact with water, are required to accurately predict how a realistic aerosol population will undergo cloud nucleation (Andreae and Rosenfeld, 2008; McFiggans et al, 2006; Ward et al., 2010). Two different types of mixture, internal mixture and external mixture, are often observed in field measurements (Väkevä et al., 2002; Schwarz et al., 2006) and used in model studies (Textor et al., 2006; Wang et al., 2010). For example, field measurements by Väkevä et al. (2002) showed that externally mixed aerosol was sometimes observed at urban and forest sites in Finland and a coastal site in western Ireland. Schwarz et al. (2006) presented results that the number fraction of internally mixed black carbon particles range from 0.2 to 0.8.

Closure studies of CCN have been carried out for more than 20 yr based on both aircraft and ground-based measurements. The earlier attempts to achieve CCN closure include studies by Bigg (1986) and Quinn et al. (1993). Bigg (1986) predicted CCN concentrations 3–5 times higher than the observed CCN concentrations under polluted aerosol conditions, while the CCN concentration predicted by Quinn et al. (1993) based on an ammonium sulfate assumption was a factor of 2 higher than the measured CCN concentrations at 0.3 % supersaturation. VanReken et al. (2003) predicted CCN concentration using classical Köhler theory (Köhler, 1936) assuming an idealised composition of pure ammonium sulfate for the aerosols. Their analysis indicates that there was generally good agreement between the predicted and observed CCN concentrations: at a supersaturation of 0.2 %, the predicted CCN is 5 % higher than that observed; while at a supersaturation of 0.85 %, the predicted CCN is 20 % higher. As the compositions of the aerosols in the environment are very complex (Kanakidou et al., 2005; Murphy et al., 2006; Zhang et al., 2007), Köhler theory has been extended to include organic species or insoluble matters (Facchini et al., 1999; Kulmala et al., 1997; Laaksonen et al., 1998; Seinfeld and Pandis, 1998; Shulman et al., 1996), and has been

proved successful by laboratory studies (Bilde and Svenningsson, 2004; Henning et al., 2005; Raymond and Pandis, 2002, 2003; Svenningsson et al., 2006). Another method derived from Köhler theory is called "κ-Köhler theory", which employs a single parameter κ to describe the solubility effect on CCN activation (Petters and Kreidenweis, 2007). Conant et al. (2004) indicated that the lack of aerosol-CCN closure brings into question either (1) our fundamental understanding of the role of aerosol composition on the CCN spectrum or (2) the techniques used to determine CCN spectrum or composition and mixing state. Therefore, in order to improve the aerosol-CCN closure, chemical properties of aerosols have been widely studied. Although the two questions above have not been completely solved, the roles of chemical properties including solubility, surface tension and oxidation state in CCN activation are now better understood (Bougiatioti et al., 2009; Broekhuizen et al., 2004, 2006; Cantrell et al., 2001; Ervens, 2007; Jurányi et al., 2010; Wang et al., 2010).

Classical Köhler theory predicts the critical supersaturation of a particle and, thus, does not incorporate any potential kinetic limitations to cloud droplet formation (Ruehl et al., 2008). Chuang et al. (1997) showed that neglecting kinetic limitations on the water uptake of cloud droplets can lead to overestimations in cloud radiative forcing calculations. Nenes et al. (2001) identified three mechanisms that lead to kinetic limitations for cloud droplet activation. The first mechanism that limits the formation of activated droplets is the "inertial mechanism" described by Chuang et al. (1997), where the timescale of cloud formation is not sufficient for these particles with a large dry diameter and a very low critical supersaturation to reach their critical diameter. The second mechanism is that the particle initially grows, but subsequently evapourates to stay as an interstitial aerosol particle before it can activate, which is called "evapouration mechanism". Thirdly, some particles can initially activate, but become interstitial aerosols through the so-called "deactivation mechanism". The water vapour mass accommodation coefficient also has a strong effect on the condensation rate of water and remains an outstanding uncertainty in quantifying the indirect effect of aerosols on climate forcing. Literature values of water accommodation coefficient span two orders of magnitude, from 0.01 to 1.0 (e.g., Davidovits et al., 2004; Laaksonen et al., 2005; Marek and Straub, 2001; Mozurkewich, 1986; Shaw and Lamb, 1999). Shantz et al. (2010) showed that water accommodation coefficient is about 0.04, while Voigtländer et al. (2007) indicates that it is larger than 0.30 using a flow chamber experiment. Ruehl et al. (2008) suggest that for some air masses, accurate quantification of CCN concentrations may need to account for kinetic limitations.

In this paper, we present a CCN closure study using data from the North China Plain and droplet kinetic condensational growth model. Section 2 will describe the observed data, while the theory of droplet condensational growth will

be discussed in Sect. 3. Section 4 will present the results and discussion. The conclusion will be presented in Sect. 5.

2 Data description

This study uses data from experiments carried out at Wuqing in the North China Plain, which is sometimes heavily polluted by anthropogenic aerosols, from 31 December 2009 to 20 January 2010. Wuqing is located between the high aerosol optical depth centres of Beijing and Tianjin, and represents a suburban background state in the North China Plain region (Xu et al., 2011). Many observations and studies have been operated in the North China Plain. For example, Wu et al. (2008) studied the particle number size distribution in the urban atmosphere of Beijing, while Liu et al. (2011) studied the hygroscopic properties of aerosols in the Wuqing region in summer. Our study focuses on the aerosol activation properties in this region in winter. No precipitation or fog occurred at Wuqing during the experiment, and the dominant wind direction was southerly which means that a high level of pollution could be transported to the site from the major source regions of eastern Tianjin. The aerosol size distribution and the CCN number concentration were measured during the experiment. Details of the aerosol and CCN instrumentations and data in our study can be found in Deng et al. (2011).

Aerosol number size distributions (radius from 7 to 375 nm), which were obtained by a Scanning Mobility Particle Sizer (SMPS, Model 3936, TSI, USA) with a time resolution of five minutes, are divided into 110 bins with the same logarithmic interval. The SMPS consist mainly of Differential Mobility Analyzer (DMA, Model 3081) and Condensation Particle Counter (CPC, Model 3772). The aerosol measurement equipment in this study has an upper truncation radius of 375 nm and does not include larger particles. However, it should be noted that aerosol number concentration in Wuqing was about $10\,000$–$40\,000\,\text{cm}^{-3}$ (Deng et al., 2011) during the experimental period and larger particles only occupy a small number fraction (less than 1 %) of the total aerosols because the particles are mainly from pollution in this area. This neglect of larger particles will only slightly underpredict CCN concentrations.

The CCN concentrations at a given supersaturation (nominally 0.07, 0.10, 0.20, 0.40 and 0.80 %) were obtained from a continuous-flow dual CCN counter (CCN-200, DMT) (Roberts and Nenes, 2005; Lance et al., 2006). The CCN counter was calibrated with ammonium sulfate particles (Rose et al., 2008), and the calibration shows that the effective supersaturations were 0.056, 0.083, 0.17, 0.35 and 0.70 % for corresponding measurements (Deng et al., 2011). These calibrated supersaturations are used in the calculations of CCN concentration in this study. The measured particle diameter range is from 0.75 to 10 µm using the CCN counter. However, the practical upper size for the CCN counter is probably much smaller than 10 µm for instrumental and size distribution reasons.

3 Model and method

The diffusive growth rate of a droplet has the form (Pruppacher and Klett, 1997, p. 511)

$$r\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{D(e - e_r(T))}{\frac{\rho_w RT}{M_w} + \frac{e_s(T)D\rho_w L}{Tk}\left(\frac{LM_w}{RT} - 1\right)} \tag{1}$$

where e is the water vapour pressure in the ambient air, e_r the water vapour pressure over the droplet surface, e_s the equilibrium vapour pressure over a flat water surface, r the radius of the droplet, T the ambient air temperature, R the universal gas constant, and L the latent heat of water condensation; M_w and ρ_w are, respectively, the molecular weight and density of water; D and k are, respectively, the effective diffusion coefficient of water vapour in the air and effective thermal conductivity of air, including the gas kinetic effects. e_r can be expressed as

$$e_r = e_s a_w \exp\left(\frac{2\sigma M_w}{\rho_w RTr}\right) \tag{2}$$

where a_w is the water activity and σ is the surface tension over the droplet surface. The parameterization of water activity for a solution of ammonium sulfate is represented by the polynomial expression, as below, in this paper (Tang and Munkelwitz, 1994)

$$a_w = 1.0 - 2.715 \times 10^{-3}x + 3.113 \times 10^{-5}x^2$$
$$- 2.336 \times 10^{-6}x^3 + 1.412 \times 10^{-8}x^4 \tag{3}$$

where x is the mass fraction of ammonium sulfate in the solution.

The composition of aerosol particles was first assumed to be pure ammonium sulfate. The reasons are that: (1) ammonium sulfate is the main chemical material in the aerosols in urban area (Wang et al., 2006); (2) the chemical properties of ammonium sulfate are well understood, especially the water activity (Tang and Munkelwitz, 1994); (3) a previous study in Wuqing found that the growth properties of the more hygroscopic particles are close to pure ammonium sulfate, indicating that these particles contain large fractions of inorganic compounds (Liu et al., 2011). The same assumption can be found in previous studies (Dusek et al., 2003).

In the CCN closure in this study, we also assume that the aerosols consist of ammonium sulfate and insoluble materials. We change the mass fraction of ammonium sulfate in the aerosols to test the effect of aerosol solubility on CCN closure. Both internally and externally mixed aerosols are investigated. The internal mixture state is represented as an insoluble kernel with an ammonium sulfate shell, and the external mixture state is pure ammonium sulfate aerosol externally mixed with the insoluble material.

Both the kinetic condensational growth model (Eq. 1) and the equilibrium model (Eq. 2) are used to predict CCN number concentrations at a given supersaturation. The observed 110 bins of aerosols are used as inputs to both models. The equilibrium model can predict the critical supersaturation of the particle with a given dry radius. Particles with the critical supersaturation smaller than the ambient supersaturation can be considered as CCN. However, the equilibrium method has a defect: particles may not have enough time to grow to their critical sizes. It has been shown that particles sometimes are not in equilibrium with the environment and the kinetic effect leads to limitations of droplet activation in clouds (Nenes et al., 2001). This kinetic limitation effect may also exist in CCN counters. In this study, a kinetic condensational growth model is used to simulate particle growth in the CCN counter. We first calculate the initial equilibrium radius of each bin at the measured temperature, pressure and at a relative humidity of 85 % using Eq. (2). Then we calculate the growth of the droplets with time at the measured supersaturations using the condensational growth model (Eq. 1). The water accommodation coefficient for this study is taken to be 0.04 on the basis of the laboratory studies of Shaw and Lamb (1999). We also did a sensitivity test on the effect of water accommodation coefficient on droplet growth rate using values of 0.3 and 1.0.

Based on the setup of the CCN counter (Deng et al., 2011), we consider that the time for particles to stay in the counter (resident time) is roughly 10 s. Because the CCN instrument can measure droplet size from 0.75 to 10 μm in diameter, we consider particles that grow larger than 1.0 μm after the resident time as CCN in the kinetic model calculation, although some of them may not be "activated" in the classical equilibrium method. The calculated CCN number concentration using the kinetic condensational growth model is then compared with that from the equilibrium model. Details of the comparison can be found in Sect. 4.3.

4   Results and discussion

4.1   CCN Closure using droplet kinetic condensational growth model

Figure 1 shows the comparison of calculated and observed CCN number concentrations during the experiment time at different supersaturations. The calculated CCN number concentration is obtained from the kinetic condensational growth model, as discussed in Sect. 3. Aerosols are first assumed as pure ammonium sulfate and the water accommodation coefficient is 0.04. The averages and standard deviations of the calculated and measured CCN concentrations for each supersaturation are also shown in Fig. 1. It can be noted that the calculated CCN concentration is 140, 100, 40, 40 and 50 % higher than the observed CCN concentration on average at supersaturations of 0.056, 0.083, 0.17, 0.35 and 0.70 %, respectively.
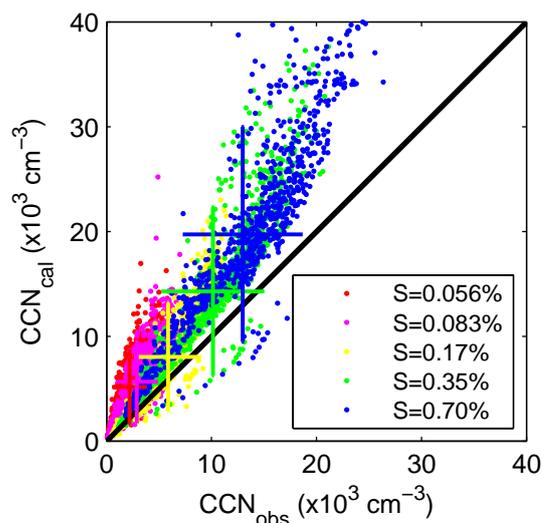

Fig. 1. Comparison between the calculated and observed CCN number concentration during 31 December 2009 and 20 January 2010 at Wuqing. The composition of aerosol is assumed to be pure ammonium sulfate and the water accommodation coefficient is 0.04. Different colours represent different supersaturations (red: $S = 0.056$ %; pink: $S = 0.083$ %; yellow: $S = 0.17$ %; green: $S = 0.35$ %; blue: $S = 0.70$ %). The centre of the cross represents the mean calculated CCN concentration and the mean observed CCN concentration at each supersaturation. Horizontal and vertical bars indicate the standard deviations of the observed CCN and calculated CCN concentrations, respectively.

The possible reasons for the overestimation of CCN concentration using the kinetic model include: (1) aerosols are assumed to be pure ammonium sulfate in the model, while the ambient aerosols may contain some insoluble material; (2) the high concentration of aerosol particles lead to consumption of water vapour and a lower supersaturation than expected in the CCN counter. In fact, there is some evidence that the actual supersaturation in the CCN counter is lower than the expected value, especially at higher CCN concentration (Lathem and Nenes, 2011).

4.2   Sensitivity to aerosol solubility and mixing state

Previous studies showed that the amount of the soluble matters (Petters and Kreidenweis, 2008; Koch et al., 2011; Khvorostyanov and Curry, 2007), slightly soluble organics (Bilde and Svenningsson, 2004), and the surface active compounds (Facchini et al., 1999; Henning et al., 2005) can all influence the aerosol activation behaviour. It has been demonstrated that the calculated CCN concentration was highly sensitive to the assumed aerosol mixing state and that the lack of mixing state measurements precludes a quantitative evaluation of its effect on CCN closure (Stroud et al., 2007). Ervens et al. (2010) studied the impact of the assumed aerosol mixing state and composition on calculated CCN concentration and found that for an aerosol with small
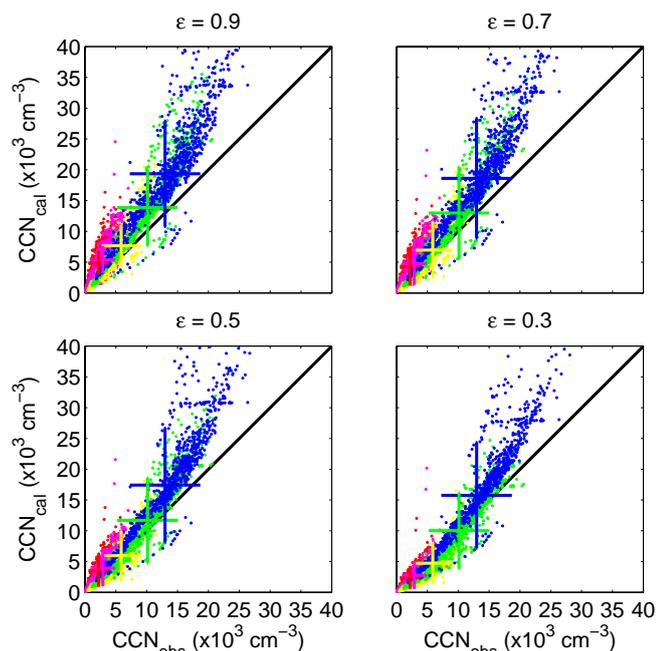
Fig. 2. Comparison between the calculated and observed CCN number concentration for four different mass fractions of ammonium sulfate (ε) at different supersaturations. For each aerosol, ammonium sulfate is assumed to be internally mixed with an insoluble core. Colour coding of supersaturations and the representation of mean and standard deviation is as in Fig. 1.

Fig. 3. Comparison between the calculated and observed CCN number concentration for 4 different mass fractions of ammonium sulfate (ε) at different supersaturations. The insoluble material is assumed to be externally mixed with ammonium sulfate. Colour coding of supersaturations and representation of mean and standard deviation is as in Fig. 1.

organic mass fraction, the assumption of organic composition/mixing state is not crucial, while for high organic mass fraction, predicted CCN number concentrations are quite sensitive to the assumptions on mixing state/composition.

To investigate the sensitivity of closure results to aerosol solubility and mixing state, we first assume that aerosol is composed of internally-mixed ammonium sulfate and insoluble material. We vary the mass fraction of ammonium sulfate (ε) in the model from 0.9 to 0.3. When aerosols absorb water from the environment during the hygroscopic growth, each droplet is assumed to have an insoluble core and a shell of ammonium sulfate solution. The equilibrium vapour pressure over the droplet is then the equilibrium vapour pressure over ammonium sulfate solution with the curvature effect. This can be derived from Eqs. (2) and (3). We then use Eq. (1) to calculate the kinetic growth of the droplets. Droplet size is determined from the size of the insoluble core and the amount of the ammonium sulfate solution.

Figure 2 shows the comparison of the calculated and observed CCN number concentrations at different supersaturations for mass fraction of ammonium sulfate from 0.9 to 0.3. It can be seen that the calculated CCN concentration is decreasing with the decrease of ammonium sulfate mass fraction. The ratio of the calculated to the measured CCN concentration for different mass fraction of ammonium sulfate (from 1.0 to 0.1) and five supersaturations is shown in
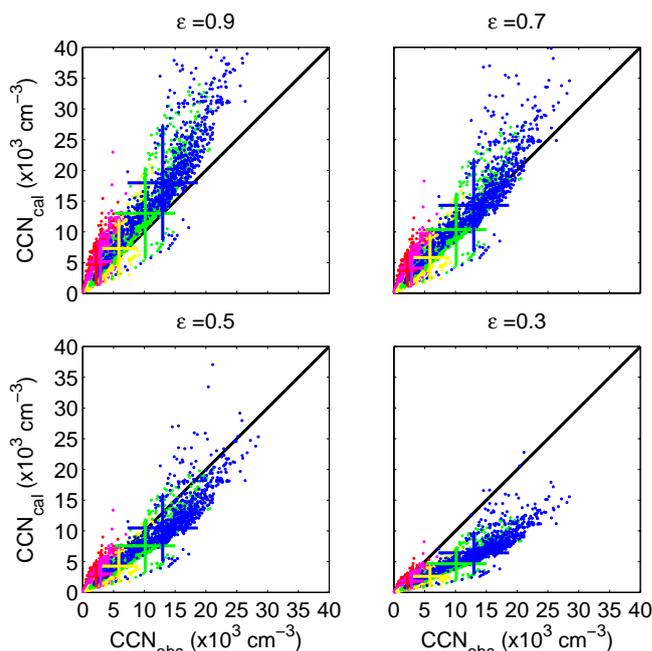
Table 1a. The best-fit mass fraction of ammonium sulfate is 0.3, 0.3, 0.5, 0.3 and 0.2 at supersaturations of 0.056 %, 0.083 %, 0.17 %, 0.35 % and 0.70 %, respectively.

Secondly, we assume that ammonium sulfate is externally mixed with insoluble material. Externally mixed aerosols were observed at many places (e.g., Väkevä et al., 2002) and have been assumed in many regional scale models (Koch et al., 1999; Chin et al., 2000; Boucher and Anderson, 1995; Barth et al., 2000). The insoluble aerosols are hydrophobic and do not act as CCN. We only calculate the growth of the soluble aerosols in this case. The equilibrium vapour pressure over the ammonium sulfate solution can be derived from Eqs. (2) and (3); and the kinetic growth of the droplet can be calculated based on Eq. (1). Figure 3 shows the calculated and measured CCN concentrations for various mass fraction of ammonium sulfate assuming the aerosols are external mixture. The ratio of the calculated to the measured CCN concentration is also shown in Table 1b. It is seen that the best-fit mass fraction of ammonium sulfate is 0.4, 0.5, 0.7, 0.7 and 0.6 at supersaturations of 0.056 %, 0.083 %, 0.17 %, 0.35 % and 0.70 %, respectively, for external mixing state.

It should be noted that external mixing state can generally lead to a better CCN closure than the internal mixing state for a certain mass fraction of soluble material in this study. The results indicate that the assumption of an internal mixture of 20–50 % ammonium sulfate and some insoluble

Table 1. Ratio of calculated to observed CCN number concentration on average at five supersaturations (S) for different ammonium sulfate mass fraction (ε) and mixing state. For each setup of the composition, we also calculated the averaged CCN_{cal}/CCN_{obs} over all the supersaturations. The kinetic model is used and the mass accommodation coefficient of water is 0.04.

(a)

	Internal mixture									
S (%)/ϵ	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
0.056	2.36	2.22	2.09	1.96	1.84	1.60	1.38	1.09	0.83	0.44
0.083	1.96	1.86	1.75	1.65	1.46	1.36	1.19	0.95	0.75	0.37
0.17	1.37	1.30	1.24	1.18	1.13	1.01	0.91	0.81	0.62	0.39
0.35	1.41	1.37	1.32	1.28	1.24	1.15	1.07	0.99	0.83	0.62
0.70	1.52	1.49	1.46	1.43	1.40	1.34	1.28	1.21	1.08	0.88
Ave	1.72	1.65	1.57	1.50	1.42	1.30	1.16	1.01	0.82	0.54

(b)

	External mixture									
S (%)/ϵ	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
0.056	2.36	2.15	1.93	1.71	1.48	1.25	1.01	0.77	0.52	0.26
0.083	1.96	1.79	1.61	1.42	1.23	1.04	0.84	0.64	0.43	0.22
0.17	1.37	1.25	1.12	0.99	0.86	0.72	0.59	0.45	0.30	0.15
0.35	1.41	1.28	1.16	1.02	0.89	0.75	0.60	0.46	0.31	0.16
0.70	1.52	1.39	1.25	1.10	0.96	0.81	0.65	0.50	0.34	0.17
Ave	1.72	1.57	1.41	1.25	1.08	0.91	0.74	0.56	0.38	0.19

material for aerosols or the assumption of an external mixture of 40–70 % ammonium sulfate and some insoluble material for aerosols can generally lead to a good agreement between the calculated and observed CCN concentration in the experimental area. Actually the aerosol composition and mixing state are very complex. Ma et al. (2011) suggested that both internal and external mixing states exist at Wuqing, the experimental site in North China Plain. In general, aerosol composition and mixing state are both time-dependent and size-dependent. Our purpose is to provide a simple parameterization method for CCN prediction that may be used in a large scale model for the area.

In summary, solubility and mixing state each plays an important role under certain conditions at Wuqing in the experimental period. For example, CCN closure is more sensitive to solubility for external mixture, and for internal mixture with soluble mass fraction smaller than 0.4; but less sensitive to solubility for internal mixture when soluble mass fraction is larger than 0.4 (Figs. 2–3 and Table 1). CCN closure is sensitive to mixing state only when the soluble mass fraction is small (Figs. 2–3 and Table 1). This means that if aerosols contain large amount of soluble materials, mixing state is not important for predicting CCN number concentration, although external mixing state would lead to a slightly less predicted CCN than internal mixing state for a fixed soluble mass fraction.

It should be noted that this study assumes uniform composition for the entire aerosol size distribution and the experimental period. However, the aerosol soluble mass fraction may be different at different sizes and at different times in reality. We, therefore, investigated the aerosol number size distributions for cases that are above, nearly on, and below the 1:1 line in Fig. 1 to see if the three categories have different size modes (and hence possibly different composition). Results show that cases above the 1:1 line usually have smaller aerosol sizes and higher number concentrations, while cases on the 1:1 line and below the 1:1 line usually have larger aerosol sizes and lower number concentrations. The differences in the shape of the size distribution as well as the integral number concentration imply that aerosols in different categories can possibly have different sources or processes. An extensive analysis of the size distribution data and investigation of this result is beyond the scope of the present manuscript and will be the focus of a future study.

4.3 Kinetic effect

Previous studies often used the equilibrium model to calculate CCN number concentration (Broekhuizen et al., 2006; Jurányi et al., 2010; Wang et al., 2010). However, kinetic limitation is an important factor affecting droplet nucleation process and the equilibrium model can sometimes lead to a discrepancy in the calculated and observed droplet numbers (Nenes et al., 2001). Here, we compare the calculated
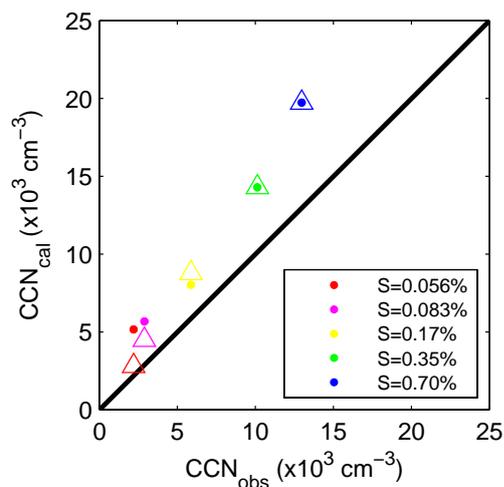
Fig. 4. Comparison between the average calculated CCN number concentration using the kinetic model (dot) and that using the equilibrium model (triangle). Different colours represent different supersaturations as before.

Fig. 5. Growth curves of four selected bins at each supersaturation (S): the smallest bin of aerosols (bin 1), the largest bin of aerosols (bin 110), the smallest bin of aerosols that can be considered as CCN based on the kinetic model (dashed black lines; bin 66 at $S = 0.056\%$, bin 64 at $S = 0.083\%$, bin 57 at $S = 0.17\%$, bin 42 at $S = 0.35\%$, bin 29 at $S = 0.70\%$) and the smallest bin of aerosols that can be considered as CCN based on the equilibrium model (solid gray lines: bin 75 for $S = 0.056\%$, bin 68 for $S = 0.083\%$, bin 55 for 0.17%, bin 42 for $S = 0.35\%$, bin 29 for $S = 0.70\%$). A particle is considered as CCN if its radius is larger than $0.5\,\mu m$ (red dashed line) at $10\,s$ using the kinetic model. The initial radii of selected bins and the time for these bins to grow to a detectable size can be seen in Table 2. The composition of aerosols is pure ammonium sulfate and the water accommodation coefficient is 0.04.

CCN number concentrations from the kinetic condensational growth model and the equilibrium model. As discussed in Sect. 3, the kinetic model considers a particle as CCN if its radius is larger than $0.5\,\mu m$ after the resident time ($10\,s$), while in the equilibrium model a particle is considered as CCN if its critical supersaturation is smaller than the ambient supersaturation. The composition of dry aerosols is considered as pure ammonium sulfate in both models. The water accommodation coefficient is first set to be 0.04 on the basis of the laboratory study of Shaw and Lamb (1999). A sensitivity study on the water accommodation coefficient is also performed.

Figure 4 shows the averaged CCN number concentrations calculated from the kinetic and equilibrium models for various supersaturations. Both the observed and calculated CCN are averaged over the experimental time period for each supersaturation. Results for the kinetic model in Fig. 4 are the same as in Fig. 1. It is seen that CCN number concentration calculated with the kinetic model is 84 % and 26 % higher than that by the equilibrium model at supersaturations of 0.056 % and 0.083 %, respectively, while it is 9 % lower than that by the equilibrium model at a supersaturation of 0.17 %. Both models calculate the same CCN number concentration at supersaturations of 0.35 % and 0.70 %. The reasons for this behaviour will be discussed below.

Figure 5 shows the growth curves of various bins at different supersaturations. Four bins are selected for each supersaturation: the smallest bin (bin 1), the largest bin (bin 110), and two intermediate bins including the smallest bin that can be considered as CCN in the kinetic model, and the smallest bin that can be considered as CCN in the equilibrium model. It can be seen that there are three types of growth characteristic for the intermediate bins. (1) Particles cannot
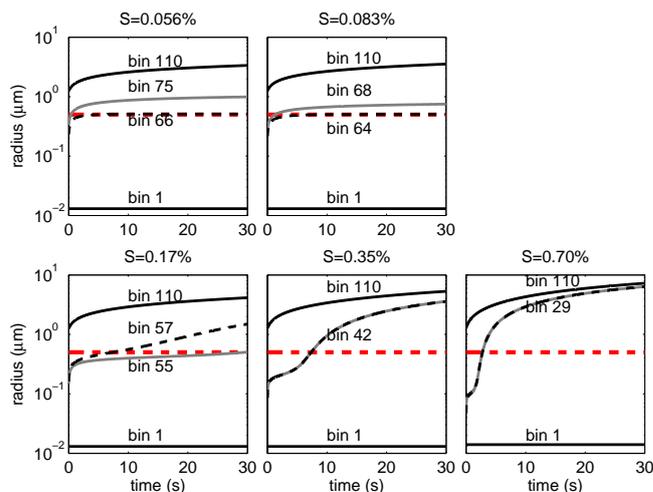
be activated in the equilibrium model, but can still be considered as CCN based on the kinetic model, because their radii are larger than $0.5\,\mu m$ at $t = 10\,s$ (e.g., bin 66 at a supersaturation of 0.056 %, bin 64 at a supersaturation of 0.083 %). Therefore, the kinetic model calculates higher CCN number concentration than the equilibrium model at supersaturations of 0.056 % and 0.083 % for this study. (2) Particles can be activated in the equilibrium model, but cannot be considered as CCN in the kinetic model, because their radii are smaller than $0.5\,\mu m$ at $t = 10\,s$ (e.g., bin 55 at a supersaturation of 0.17 %). In this case, the kinetic model calculates lower CCN number concentration than the equilibrium model. (3) The smallest bin that can be considered as CCN based on the equilibrium model is consistent with that predicted by the kinetic model (e.g., bins 42 and 29 for the supersaturations of 0.35 % and 0.70 %, respectively, in this study), leading to the same calculated CCN number concentration.

Analysis above indicates that the detectable radius of CCN counter and the resident time of aerosols in the column are very important parameters in the kinetic model. We define r_k as the smallest aerosol radius that can grow larger than the detectable radius after the resident time in the counter based on the kinetic model, and r_e as the smallest activated aerosol
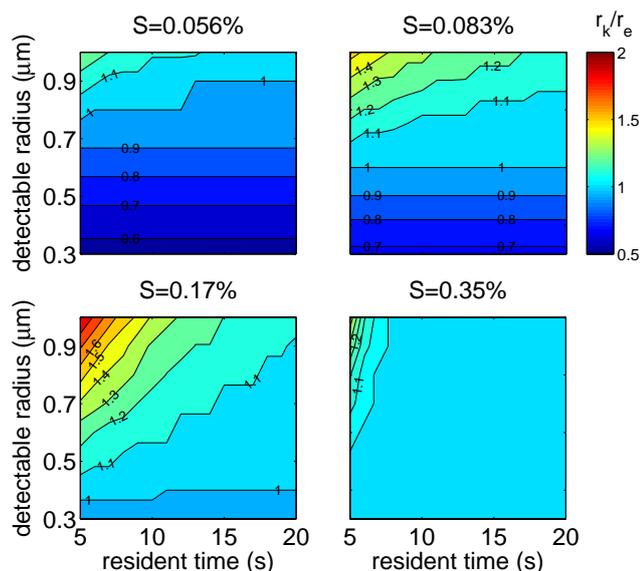
Fig. 6. Variation of r_k/r_e at different resident times and detectable radii for different supersaturations. r_k represents the smallest aerosol radius that can grow larger than the detectable radius after the resident time in the counter based on the kinetic model, while r_e represents the smallest activated radius calculated with the equilibrium model. The isopleths are stepped because the detectable radius varies from 0.3 to 1.0 µm with an interval of 0.1 µm, and the resident time varies from 5 to 20 s with interval of 1 s. In addition, the aerosol size distribution is represented with discrete bins.

radius based on the equilibrium model. Figure 6 shows the ratio of r_k to r_e at different resident times (5–20 s) and different detectable radii (0.3–1.0 µm) for various supersaturations. The composition of aerosols is assumed as pure ammonium sulfate and the water accommodation coefficient is 0.04. It should be noted that r_k is smaller than r_e only at lower supersaturations ($S = 0.056$ and 0.083 %), indicating that the kinetic model will predict higher CCN number concentration than the equilibrium model because some "unactivated" particles are large enough to be considered as CCN. This suggests that if a CCN counter has small detectable radius, very low supersaturations should be avoided for CCN measurements. It is also seen in Fig. 6 that if the resident time is small (e.g., 7 s and smaller) and the detectable radius is large (e.g., 0.8 µm and larger), r_k is larger than r_e in this study, indicating that the CCN number concentration calculated with the kinetic model will be lower than that from the equilibrium model due to the kinetic limitation. In general, if particles stay in the column long enough, the kinetic limitation will have a small effect on CCN prediction. At supersaturations of 0.35 % and higher (0.70 %), both resident time and detectable radius have a small impact on CCN prediction using the kinetic model.

The mass accommodation coefficient of water has been widely studied. A value of 1.0 has been used by Mozurkewich et al. (1986). However, results showed that the

Table 2. The time for various bins to grow larger than 0.5 µm to be detected at different supersaturations. Water accommodation coefficient $\alpha = 0.04$, 0.3 and 1.0.

Supersaturation (%)	Initial Radius (nm)	$\alpha = 0.04$	$\alpha = 0.3$	$\alpha = 1.0$
0.056	103	0.40 s	0.20 s	0.17 s
0.083	80	1.3 s	0.62 s	0.54 s
0.17	50	30 s	14 s	12 s
0.35	31	7.3 s	3.0 s	2.5 s
0.70	20	2.7 s	1.0 s	0.83 s

water accommodation coefficient is only 0.04 on the basis of the laboratory studies of Shaw and Lamb (1999). Recent studies have shown that the mass accommodation coefficient is larger than 0.3 in a flow chamber (Voigtländer et al., 2007). To investigate the sensitivity to the water accommodation coefficient (α), the simulations presented above ($\alpha = 0.04$) were repeated with $\alpha = 0.3$ and $\alpha = 1.0$. We focus on the smallest activated bin at each supersaturation based on the equilibrium model. The time for these particles to grow larger than 0.5 µm radius for different α (0.04, 0.3 and 1.0) is shown in Table 2. It can be seen that less time is needed if the water accommodation coefficient is higher. However, analysis indicates that if α is larger than 0.3, the value of α has little influence on droplet growth and, hence, CCN number concentration prediction, while α as small as 0.04 has significant influence on droplet growth and the calculated CCN concentration due to the kinetic limitation.

It should be noted that although particles detected by the CCN counter at a given supersaturation are considered as CCN, they may not be actually activated in the classical way. Figure 7 shows the time when a particle (pure ammonium sulfate) with certain initial dry radius can grow to its critical radius at a given supersaturation in the CCN counter. It can be seen that the time decreases as the supersaturation increases: it is longer than 100 s at a supersaturation of 0.056 %, while only on the order of seconds at a supersaturation of 0.70 %. It is also relatively larger at both the small-size end and the large-size end. A particle with a large dry radius and at a low critical supersaturation especially needs a long time to reach its critical radius because the linear growth rate is inversely proportional to droplet size. This kinetic mechanism that limits the formation of activated droplets is described by Chuang et al. (1997). At the small-size end, a particle also needs a longer time to reach its critical radius because the driving force (vapour difference between the ambient and the particle surface) for droplet growth becomes smaller as the particle grows closer to its critical radius. The result suggests that many droplets would not have sufficient time to grow to their critical radii in the CCN counter. However, the CCN counter cannot distinguish whether the droplets are really activated as CCN, but can
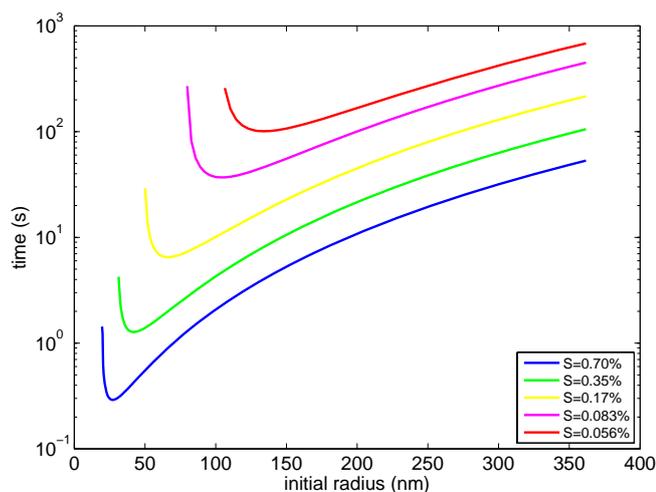
Fig. 7. The time required for particles to grow to their critical radii at different supersaturations. The x-coordinate is the initial dry radii of aerosols, the composition of aerosols is ammonium sulfate and different colours represent different supersaturations. Water accommodation coefficient is 0.04.

only detect droplets with radii larger than its detectable radius and count them as CCN.

It is generally seen that the sensitivity of CCN closure to kinetic effect is very complex and depends on supersaturation, resident time, detectable radius and mass accommodation coefficient. At higher supersaturation (0.35 % and 0.7 % in this study), kinetic effect has little influence on CCN closure; at lower supersaturation (0.056 %, 0.083 % and 0.17 % in this study), kinetic effect can influence CCN closure in several ways: (a) if the detectable radius is small (<0.5 μm), some "unactivated" particles may be large enough to be counted as CCN. A kinetic growth model can then predict more realistic and higher concentration of CCN than the equilibrium model in this case. (b) if the detectable radius is large (>0.5 μm), and the resident time is shorter (<10–30 s), some particles may not have time to grow large enough to be counted as CCN due to kinetic limitation. Therefore, the kinetic growth model should be used to predict CCN concentration under this condition. (c) if the detectable radius is large (>0.5 μm), and the resident time is longer (>30 s), kinetic limitation does not influence CCN closure. Both the kinetic growth model and equilibrium model can be used to predict CCN concentration. In addition, CCN closure is sensitive to mass accommodation coefficient if it is very small (<0.1). On the opposite, if the mass accommodation coefficient is larger than 0.1, it has little influence on CCN closure.

5   Conclusions

This study focuses on the CCN closure at Wuqing, a site in the North China Plain where high aerosols number concentrations existed, from 31 December 2009 to 20 Jan-

uary 2010. The input initial dry aerosols to the kinetic condensational growth model and equilibrium model were observed by SMPS. The CCN concentrations were observed by a CCN counter. The kinetic model overpredicts the CCN concentrations by 40–140 % in comparison with the observations for the supersaturation range in this study if assuming the aerosols are pure ammonium sulfate. Sensitivity of CCN closure to the aerosol mass fraction of soluble material and mixing state were investigated. Two extreme mixing states of aerosols were considered, including internally-mixed ammonium sulfate and insoluble material, and externally-mixed ammonium sulfate and insoluble material. Increasing the insoluble matters in the aerosols can decrease the calculated CCN number concentration and, thus, make the calculated CCN number concentration closer to the observed. It is found that external mixing state can lead to even less calculated CCN number concentration than the internal mixing state for a certain mass fraction of soluble material. Reasonable agreement of calculated CCN number concentrations with observed ones is obtained when we assume 0.2–0.5 mass fraction of ammonium sulfate internally mixed with insoluble material or 0.4–0.7 mass fraction of ammonium sulfate externally mixed with insoluble material in aerosols. It also should be noted that the results are valid for the winter season in the Wuqing area, while results in other seasons may be different because of different aerosol sources, meteorology and atmospheric chemistry processing.

CCN number concentrations calculated with the kinetic model and the equilibrium model were compared in this study. A particle is considered as CCN if its radius is larger than 0.5 μm after resident time (10 s) in the kinetic model, while a particle is considered as CCN if its critical supersaturation is smaller than the ambient supersaturation in the equilibrium model. The CCN number concentration calculated with the kinetic model is higher than that by equilibrium model at the supersaturations of 0.056 % and 0.083 %, because particles that are not activated at these supersaturations can grow larger than 0.5 μm at 10 s. However, the CCN number concentration calculated with the kinetic model is lower than that with the equilibrium model at a supersaturation of 0.17 %, because particles that can be activated based on the classical equilibrium theory cannot grow larger than 0.5 μm at 10 s due to kinetic limitation, hence, are not counted as CCN in the kinetic model. Analysis indicates that the detectable radius of CCN counter and the resident time of particles in the column can affect the calculated CCN number concentration at lower supersaturations based on the kinetic model. If a CCN counter has small detectable radius, very low supersaturations should be avoided for CCN measurements. If the resident time of particles in the CCN counter is short, kinetic limitation on droplet growth must be considered. Generally if particles stay in the column long enough, the kinetic limitation will have small effect on CCN prediction. At higher supersaturations, both resident time and detectable radius have small impact on CCN prediction using

the kinetic simulation. The influence of the water accommodation coefficient on droplet growth was also investigated. Larger water accommodation coefficient ($\alpha > 0.3$) does not significantly limit droplet growth but smaller α (0.04) has great influence on droplet growth.

Edited by: D. Covert

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