

## **Author comment on “A closure study of cloud condensation nuclei in the North China Plain using droplet kinetic condensational growth model” by F. Yang et al.**

We thank the reviewers for their useful comments. Below are our point-by-point responses.

### **Anonymous Referee #2**

#### **General Comment**

**This work performs a CCN closure study using observations with a CCN counter over the North China Plain, a kinetic growth model that simulates the CCN counter, and an equilibrium model. Effects from kinetics, solubility, mixing state, accommodation coefficients, and counter residence time etc are examined. The paper contains useful and interesting results, but can be further improved. I recommend its publication after addressing the following points.**

**1. A major deficiency is that the equations provided are not sufficient for a complete understanding of the treatment of mixing state. Key equations are needed that are associated with internal mixing (ammonium sulfate shell plus insoluble core) and the external mixing model. Also, what is so special about the mass fraction = 0.6? Table 1 indicates that further decrease of the solubility may lead to the conclusion of internal mixing better than external mixing.**

Our reply: The aerosols are assumed to be a mixture of ammonium sulfate and insoluble material. For internal mixing state, each droplet has an insoluble core and a shell of ammonium sulfate solution after aerosols absorb water from the environment. The equilibrium vapor pressure over the droplet is then the equilibrium vapor pressure over ammonium sulfate solution with the curvature effect. This can be derived from Equations (3) and (2). We use Equation (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. For external mixing state, some particles are pure ammonium sulfate and the others are pure insoluble materials. The equilibrium vapor pressure over the ammonium sulfate solution can be derived from Equations (3) and (2); and the kinetic growth of the droplet can be calculated based on Equation (1). The insoluble aerosols are hydrophobic and do not act as CCN. We only calculate the growth of the soluble aerosols in this case.

We varied the mass fraction of ammonium sulfate from 1 to 0.1 for both internal and external mixing states. For internal mixture, a soluble mass fraction of 0.2 – 0.5 can lead to the best closure. For external mixture, a soluble mass fraction of 0.4 – 0.7 fits best. It is seen that the best-fit composition changes with supersaturation and mixing state. 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 that may be used in a

large scale model for the area. Our previous conclusion that “60-70% mass fraction of ammonium sulfate externally mixed with insoluble material can lead to the calculated CCN concentrations fitting the observations best 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” was based on calculations using a soluble mass fraction of 0.6-1.0. This conclusion has changed after we extended the range of soluble mass fraction. This discussion has been added to the manuscript and detailed results can be seen in the new Table 1 in the manuscript.

**2. There are much less data points in Fig 4 compared to the Figs 1-3. Why? If some averaging is made, it needs to be described.**

Our reply: Figure 4 indeed shows the averaged CCN number concentration. Both the observed and calculated CCN are averaged over the experimental time period for each supersaturation. This is to show the difference between the equilibrium model and the kinetic growth model. The description of this averaging was added in the manuscript.

**3. Based on the discussion, scatter or differences can arise from several factors such as kinetic effect, solubility, mixing state, and mass accommodation coefficient. How about their relative importance? A comparative study should be useful, and effects of size truncation, the counter detectable radius and residence time should be included in the relative importance study.**

Our reply: Each of these factors 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.

CCN Closure is sensitive to mixing state only when the soluble mass fraction is small. 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 slightly less predicted CCN than internal mixing state for a fixed soluble mass fraction.

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 ( $<0.5 \mu\text{m}$ ), 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 ( $>0.5 \mu\text{m}$ ), and the resident time is shorter ( $<10\sim 30 \text{ s}$ ), 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 ( $>0.5 \mu\text{m}$ ), and the resident time is longer ( $>30 \text{ s}$ ), kinetic limitation does not influence CCN closure. Both the kinetic growth model and equilibrium model can be used to predict CCN concentration. 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.

More discussion about the kinetic effect, solubility, mixing state, and mass accommodation coefficient were added in the manuscript.

**4. The aerosol measurements used have an upper truncation radius of 375nm; however, larger particles likely exist in nature. Neglect of larger particles in calculation will lead to underestimation of CCN, other things being equal. Examination of potential effect of this size truncation, together with the other factors, is in order.**

Our reply: We should notice that the aerosol measurement equipment has an upper truncation radius of 375 nm. The aerosol number concentration in Wuqing was about 10000 ~ 40000 per cubic centimeter (Deng et al. 2011) during the experimental period and the number concentration peaks at radii of 50-100 nm. Particles with radii larger than 375 nm only occupy a very small number fraction (less than 1%) of the total aerosols. Neglecting these larger aerosols in the calculation will only slightly underpredict CCN concentrations. This discussion has been added in the manuscript.

#### **A. Laaksonen (Referee)**

**This paper presents a closure study of CCN concentrations in a polluted environment in North China. CCN concentrations were measured at different supersaturations using a continuous flow CCN counter. Measured particle size distributions were used as a basis for the closure study, in which the particles were assumed to be either internal or external mixtures of ammonium sulfate (AS) and insoluble matter. CCN concentrations were calculated using a (non-equilibrium) condensational growth model, and alternatively using the Köhler theory. It was concluded that the best agreement with theoretical and measured CCN concentrations is achieved using an external mixture with a 60-70% mass fraction of AS. Discrepancies between the predictions from the condensational growth model and Köhler theory were discussed in light of kinetic effects taking place inside the CCN flow tube.**

**I think that this paper could ultimately be published in ACP. I especially like the discussion of the kinetic effects inside the CCN counter. However, I find the closure study oversimplified, and to some extent contradictory to the authors' previous work, and therefore suggest major revisions.**

**In the previous paper (Deng et al., 2011) dealing with the same data as the current paper, it was stated, based on measurements of size-resolved activation ratios, that "...the aerosols in the North China Plain consist of highly soluble material. Soluble fractions of more than 83% calculated based on the Köhler theory with assumed aerosol composition of ammonium sulfate and insoluble core, are needed to activate these particles". This seems contradictory to the**

**information given in Fig. 2, which suggests that even an AS mass fraction of 60% yields too high modelled CCN concentrations. The reason for this apparent discrepancy should be clarified. Furthermore, it would be interesting to know how low AS mass fraction (in internal mixture) is needed for achieving reasonable agreement with the measurement.**

Our reply: In the kinetic growth model in this manuscript, we calculate the growth of the particles at a certain supersaturation using droplet condensational growth equation (Equation 1 in the manuscript). By varying the composition of the aerosols, we predict CCN number concentration and try to compare with the observation. Based on the reviewer's comment (and also reviewer #2's comment), we varied the mass fraction of ammonium sulfate from 1 to 0.1 for both internal and external mixing states in this revised manuscript. For internal mixture, a soluble mass fraction of 0.2 – 0.5 can lead to the best closure. For external mixture, a soluble mass fraction of 0.4 – 0.7 fits the observation best. It is seen that the best-fit composition changes with supersaturation and mixing state. As the reviewer pointed out, an AS mass fraction of 60% yields too high modeled CCN concentrations. Our previous conclusion that “60-70% mass fraction of ammonium sulfate externally mixed with insoluble material can lead to the calculated CCN concentrations fitting the observations best in the North China Plain during the time period of the field observations,.....” was based on calculations using an AS mass fraction from 1 to 0.6. This conclusion has changed after we extended the range of soluble mass fraction in the calculations. Detailed results can be seen in the new Table 1 in the manuscript and more discussion has been added to the paper.

Deng et al. (2011) observed the size-resolved activation ratio curves at different supersaturations. The dry diameter with 50% activation ratio is assumed to be the critical dry diameter at a given supersaturation. For example, the activation ratio of aerosols with 200 nm dry diameter at supersaturation of 0.058% was 50% in their experiment. Therefore, 200 nm was assumed to be the critical dry diameter at supersaturation of 0.058%. By assuming that aerosol composition was AS with an insoluble core (i. e., internal mixture), and varying the volume fraction of AS, Deng et al. (2011) found that aerosols with 200 nm dry diameter must have 83% volume fraction of AS to have a calculated critical supersaturation of 0.058% based on Köhler theory. The aerosol soluble fraction inferred from their study looks different from our study because of the following reasons: (1) Deng et al. (2011) used volume fraction of AS while we use mass fraction of AS. (2) Deng et al. (2011) determined the critical dry diameter based on the size-dependent activation ratio (50% in their study). This method has been used in some other experimental studies (Gunthe et al., 2009; Rose et al., 2010). However, the critical dry diameter determined this way depends on the value of activation ratio. For example, in Fig. 7 of Deng et al., the critical dry diameter is 300 nm if it is assumed to be the dry diameter with 80% activation ratio at supersaturation of 0.058%. Aerosols with 300 nm dry diameter then must have volume fraction of AS smaller than 83% to have a calculated critical supersaturation of 0.058% based on Köhler theory. In the equilibrium model in our study, we vary the mass fraction of AS and calculate the critical supersaturation for all droplets based on classical Köhler theory. Droplets with critical supersaturation smaller than the supersaturation in CCN counter are considered as CCN. (3) We also use the kinetic condensational growth model in our study. The calculated CCN concentration based on this method is the sum of particles with the radius larger than the detectable radius at resident time. This would also lead to some difference of the soluble fraction

in our study and Deng et al. (2011).

**Secondly, the external mixture of AS and insoluble matter with a size-independent AS mass fraction appears oversimplified and also contradictory to the data in Deng et al. (2011). With such an external mixture, the insoluble particles should not be able to activate at all, so that the activated fraction will simply decrease linearly with decreasing AS mass fraction, and a reasonable agreement with the measured CCN will be achieved just by decreasing the AS mass fraction enough. However, the size resolved activation fractions in Deng et al. (2011) indicate that above a dry diameter of 100 nm (150 nm), more than 90% of the aerosol activates at a supersaturation of 0.72% (0.36%), and therefore the 60-70% external mixture employed in the present paper appears contradictory to the measurements.**

Our reply: Our conclusion of 60-70% external mixture of AS and insoluble material in the last version of the manuscript was based on calculations using an AS mass fraction from 1 to 0.6. This conclusion has been changed after the revision of the manuscript. Based on the reviewer's comment, we varied the mass fraction of ammonium sulfate from 1 to 0.1 for both internal and external mixing states in this revised manuscript. We now conclude that a soluble mass fraction of 0.2 – 0.5 can lead to the best closure for internal mixture and that a soluble mass fraction of 0.4 – 0.7 fits the observation best for external mixture. As the reviewer pointed out, the external mixture with an AS mass fraction of 0.4 – 0.7 is contradictory to the measurements in Deng et al. (2011). It should be noted that our model only considers some ideal and simple scenarios (in this paper, internal mixture and external mixture). For internal mixing state, particles in one bin can either be all activated as CCN or completely stay unactivated. For external mixing state, all insoluble particles cannot be activated as CCN. Therefore an activation ratio of 90% would correspond to a soluble number fraction of 90% in the case of external mixture, as the reviewer has already implied. However, aerosol composition and mixing state are very complex in reality. It may not be a complete internal mixture, or a complete external mixture. For example, each particle in the same size bin may have various mass fraction of AS: from 0 (pure insoluble) to 1 (pure ammonium sulfate). Therefore, a 90% activation ratio may correspond to 10% insoluble particles and 90% internally-mixed particles. Our conclusion is that an internal mixture of 0.2 – 0.5 soluble material and an external mixture of 0.4 – 0.7 soluble material can both be used to predict CCN in the experimental area. Our purpose is to provide a simple parameterization of CCN prediction in a large scale model for the area.

**In general, I think that when polluted regions are being considered, the use of ammonium sulfate and insoluble matter with a constant mass fraction throughout the whole aerosol size range is too simple regardless of the mixing state assumed. In any case, there are so many unknowns (including the accommodation coefficient) that there are multiple ways of achieving an apparently reasonable closure, and the question then is, what is the value of such closures? Unfortunately, no chemical composition data or growth factors appear to be available to the authors. Nevertheless, I believe that a better use can be made of the size distributions, together with the size resolved activation ratios.**

Our reply: We agree with the reviewer that using a constant mass fraction of AS throughout

the whole aerosol size range is very simple. Many factors may affect the calculated CCN concentration such as chemical composition of aerosols, mixing state, surface tension, and water accommodation coefficient. Therefore, best agreements between calculated and observed CCN concentrations can be achieved in many ways, as the reviewer pointed out. Our purpose is to provide a simple parameterization method that may be used in a large scale model for the area. More important, we try to find if CCN closure is sensitive to the growth model (equilibrium model vs. kinetic model), and how important the kinetic effect could be in CCN closure.

**I suggest that the authors select a few cases, based on Fig. 1, for a closer scrutiny. For example, take a couple of cases in which the data points are close to the 1:1 - line, a couple cases in which the calculated CCN is much above the 1:1 -line, and a case from the few data points in which the calculated CCN is below the 1:1 -line, and examine the measured size distributions. How do the size distributions differ? Can they be described as superpositions of two or more lognormal modes? If so, could some well reasoned compositions be assigned to the different modes, so that the aerosol is both internally and externally mixed? In this way, perhaps a closure with measured CCN can be obtained in such a way that the modeled data is also in accord with the measured activation fractions. This would make the study much more convincing.**

Our reply: There are usually two modes of aerosols (diameter smaller than 750 nm) at the experimental time in Wuqing. The modal diameters are 20 - 30 nm and 100 - 200 nm for the two modes. But aerosols in the smaller mode cannot be activated at any supersaturation in the experiment, even they are assumed to be pure ammonium sulfate. Therefore there was only one mode in the activated bins. Therefore it is reasonable to assume aerosol composition is constant over the size range for the purpose of this study.

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