A point-by-point reply to the comments

Reviewer 1#

I suggest the authors check the data again. Because all the discussions are based on the good quality data.

The explanation of the data inconsistency between figure 1 and previously published paper are still confusing.

The explanation indicated that the fitted data (background or polluted cases) have higher AR than the observed data (all averaged together). Does that suggest you need to check your fitting criteria/methods?

In addition, if there is calibration and correction method applied to the raw data. It will affect both observed data and fitted data. Why only observed data will have a slight lower MAF?

Re: Thanks for the suggestion. We do check the data carefully again. We are confident in the data quality. The reviewer is right, and if the correction is applied to the raw data, both the observed and fitted data will be affected. Thus, we also got a slight lower MAF for the fitted data (not shown in Figure 1). In the previously published paper, we didn't ignore and process some data points when the MAF value >1, which resulted in larger mean MAF. But in this paper, the data points with MAF > 1.0 were forced to 1 when D_p>300 nm, which we thought could be activated completely at even lower supersaturations but the MAF would never be >1.0. This has been stated in the revised paper (please see Page 11, lines 199-204).

Reviewer 2#

P16147 L10 These "relative deviations" are because of particle loss in the nafion dryer? Also, it is not clear what the "kinetic limitations" are.

Re: the relative deviations are due to the influence of dehydration-related particle mobility changes inside DMA. According to Mikhailov et al., 2009, void fractions as well as residual water in dried aerosol particles that are not water-free (due to kinetic limitations of drying or stable hydrate formation) should be taken into account in Kohler model calculations of hygroscopic growth and CCN activation.

First, if the dehydration processes (efflorescence, restructuring, or desorption) inside DMA are completed within 0.1 s, then the resulting changes in particle mobility diameter should be fully captured with deviations <1%. And also, kinetically limited dehydration processes that lead to progressive changes of particle mobility on a time scale of 0.1–10 s should significantly influence the particle sizing (deviations >1%) and lead to a broadening of the measured size distributions. Dehydration processes progressing on time scales >10 s should have no effect on particle sizing (no change of mobility diameter and no broadening of size distribution).

Thanks for your explanation. I agree that void fractions and residual water should be taken into account; however, how can you do this with the measurements you have made?

Here is how I would proceed: You are making the assumption that drying imposed by the nafion, and by the dry sheath air inside the DMA, are sufficient to remove water associated with the ambient particles. Why not state this assumption, and move on without reference to "kinetic

limitations" or Mikhailov et al. (2009)?

Re: Yes, you are correct, and your statement is exactly our assumption. Thank you! It has been revised (see Page 7, lines 107-108).

P16147L25

It is the inner diameter, not the outer diameter, that is relevant.

Re: it is just the outer diameter.

It's the inner diameter that is important. Please report that value.

Re: The inner diameter is 0.38 inch. (Revised)

P16148L19

"..temperature stability was zero." I don't understand what you are referring to here.

Re: here it means the data is invalid if the "temperature stability" was flagged as "0". And for the valid data, the "temperature stability" was flagged as "1". The sentence has been revised.

Thanks for your explanation. Why can't you explain what is meant by "stability"? Isn't this the average difference between what is preset and what is measured?

Re: sorry for not explaining it clearly. But you've got the point. The "temperature stability" refers to the T_1, T_2 and T_3 in cloud chamber of the CCNc, which is set to obtain the target supersaturations. If the average differences between preset T_1, T_2 and T_3 and the measured values are larger than 0.4 °C, the "temperature stability" is flagged as "0". Thus, the data is invalid and will be removed. This has been revised in the paper(see Page 9, lines 150-153)

P16148L21

Here you define the "aerosol number (CN) size distribution spectrum." How is this different from the PSD mentioned on P16147L1 and on P16148L24?

Re: that's exactly the same thing. We have corrected all of them to particle number size distribution in the revised paper.

PSDs are shown in Figure 2 (revision). It is not clear how the quantity on the Y axis, once integrated over all sizes, becomes the CN concentration referred to in the text. For example, on L241 we are told that the CN concentration is ~1.7x104 cm-3. Typically in aerosol science the PSD is dN/dlogD and the latter has dimension cm-3. How are we to interpret the "N" on the Y axis of Figures 2a-c? For an example see here in their Figure 12a (Atmos. Chem. Phys., 13, 7263–7278, 2013).

Re: Thanks for pointing this. It should be dN/dlogD (cm-3) in Figure 2. The figures have been revised. (see Figure 2)

P16152L6

It is the "CCN activity", not the "aerosol activity", that is the focus here.

Re: corrected.

Please see L227 in the revision. This was not "corrected." If you do not feel the correction is needed, just say so in your response.

Re: sorry for my carelessness, I agree your suggestion. It has been corrected in the revision. (see Page 13, line 241)

P16153L26

Here is a relevant reference.

Snider, J.R., and, S.Guibert, J.-L. Brenguierand J.-P.Putaud, Aerosol activation in marine stratocumulus clouds: Part – II Köhler and parcel theory closure studies, J. Geophy. Res., 108, doi:10.1029/2002JD002692, 2003

Re: the reference has been added.

I see this paper in the References, but I do not see it cited in the text.

Re: Added it this time. (Page 4, line 27)

P15154L7

What are "bulk ARs"?

Re: bulk ARs means the ratio of NCCN to NCN, which is calculated from the total CN and CCN number concentrations. Thus, we called it bulk ARs. For the size-resolved CCN measurements, we can get size-resolved ARs from size-resolved CCN and CN number concentrations.

Thanks for your explanation; however, what you wrote (revision) needs to be removed from the middle of the paragraph that discusses the size-resolved AR. I recommend that the removed text beput somewhere else (e.g., at the end of the paragraph). For example, on L52, you could state: "The bulk activation ratio (bulk AR) is defined as the CCN-measured concentration divided by the CN concentration. These values were measured in ambient air, every ?? minutes, and without particle size selection in the DMA."

Re: Thanks a lot for your comments. In this revision, this has been revised as follows (also see Page 10, lines 161-166),

"The size-resolved CCN activation ratio (size-resolved AR) is defined as the $dN_{CCN}/dlogD_p$ divided by the $dN_{CN}/dlogD_p$. These values were measured by SMPS-DMT-CCNc with particle size selection in the DMA. The bulk activation ratio (bulk AR) is defined as the total CCN concentration divided by the total CN concentration. The total CCN and CN number concentrations are integrated by the measured CCN and CN size distribution respectively over the whole size range."

P16155L2What you are calling the "estimate" is the summed product of AR(D) and PSD(D)? Right? By "Observation" you are talking about the direct measurement of the ambient Nccn(S) made _without_ the DMA in front of the CCN instrument. I did not see mention of the ambient Nccn(S) measurement (without the DMA in front) in Section 2.1.

Re: We used a Scanning Mobility Particle Sizer (SMPS), combined with a Droplet Measurement Technologies-Cloud Condensation Nuclei Counter (DMT-CCNc) (Lance et al., 2006), for size-resolved CCN measurements as well as particle number size distribution (PSD) measurements. The SMPS is just the DMA.

To estimate NCCN, estimated CCN size distributions at the five supersaturations were calculated by multiplying the campaign-averaged CCN efficiency spectrum with the actually measured PSD. The estimated NCCN at the five supersaturations was then calculated by integrating the estimated CCN size distribution over the whole size range. The measured CCN size distributions are integrated to produce the observed NCCN.

Thanks for the explanation. In the revision, do you explain what you mean by the "observed NCCN"?

Re: Yes. This has also been explained in the text. (see Page 16, lines 321-328; Page 18, lines

376-379)

P16155L19

I would reword this because the Figure 7 shows how the difference (estimated minus observed) varies with chi-org. The latter is the independent variable. There are other places in the manuscript where "sensitivity" is used. I would change the word order in some of these instances too. E.g., P16145L26. There are other places too.

Re: revised. Because in the revised version, the sensitivity of oxidation level (using f44, the fraction of m/z 44 in total organics, as an indicator) of organics to estimatimation of NCCN is also examined. The section is thus rewritten (see Section 4.4, and Figure 5 and Figure 6).

In my opinion this argument is presented backwards, both in the original manuscript, and in the revision.

Here is an example from the abstract (revised):

"The sensitivity of volume fraction of organic aerosols (chi-org) as well as oxidation level (using f44, the fraction m/z 44 in total organics, as an indicator) of organics on estimating NCCN is examined."

I feel that the authors should reword these statements. Here is a suggested replacement sentence for the sentence above:

"The sensitivity of the estimated CCN number concentration (NCCN) to both volume fraction of organic material (chi-org) and aerosol oxidation level (using f44, the fraction m/z 44 in aerosol organic material) are examined."

Re: thank you very much for correcting the presentation regarding to this part. We totally agree to your comments and correction. That has been revised carefully (see Page 2, lines 2-5)

Another example is seen on L65 (revision). Going back to what I said in my first review, I feel that the authors should be focused on how NCCN is sensitive to aerosol chemical composition, not the other way around.

Re: revised as "…The aim of this paper is to examine the sensitivity of CCN activity to aerosol physicochemical properties (especially aerosols containing large amounts of organics, as well as the oxidation level)…" (see pages 6, lines 66-68)

Another example is L294 (revision).

Re: revised as "…we examine the sensitivity of N_{CCN} to both volume fraction of organics (x_{org}) and oxidation or aging of organics based on measurement at Xinzhou site…." (see Page 16, lines 307-309)

Another example is the caption of Figure 5 (revision).

Re: revised as "…The sensitivity of N_{CCN} to both organics volume fraction (x_{org}) and oxidation level (using f_{44}, the fraction of m/z 44 in aerosol organic material) of organics at supersaturation levels of" (see the caption of Figure 5)

Another example is L396 (revision)

Re: revised as "…we examine the sensitivity of N_{CCN} to both volume fraction of organics (x_{org}) and oxidation or aging of organics based on measurement at Xinzhou site." (see Page 20, lines 409-412)

Additional comments:

According to Petters et al. (ACP, 2007), the kappa for ammonium sulfate is 0.61 and the kappa for

ammonium nitrate is 0.67 (see their Table 1; CCN derived kappa). Hence, the sentence on L181 (revision) is backwards.

Re: revised. Thanks a lot for your careful check.

L117 (revision) – here you are referring to the "overall relative error"

Re: corrected. Thank you very much.

L275 (revision) – The sentence needs work (…."it should be caution")

Re: revised. (Page 15, lines 289-290)

L345 (revision) – misspelled word "usully")

Re: corrected.

L388 (revision) – This mentions "local primary biomass burning" but I do not see discussion of the topic in the analysis section of the manuscript.

Re: revised as "…CCN efficiency was largely reduced by local air masses..." (see Page 19, line 401)

General – if the subscript is "org" for chi, it should also be "org" for epsilon (i.e., not "Org").

Re: corrected.

Impacts of organic aerosols and its oxidation level on CCN activity from measurement at a suburban site in China

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Abstract

This study is concerned with the impacts of organic aerosols on CCN activity based on field measurements made at a suburban site in north China. The sensitivity of the estimated CCN number concentration (N_{CCN}) to both volume fraction of organic ~~aerosols~~material (x_{org}) ~~as well as~~and aerosol oxidation level (using f_{44}, the fraction of m/z 44 in ~~total organics, as an indicator) of organics on estimating N_{CCN} is~~aerosol organic material) are examined. A strong dependence of CCN number concentration (N_{CCN}) on the x_{org} and f_{44} was noted. The sensitivity of volume fraction of organics to N_{CCN} increased with increasing x_{org}. The impacts of the aerosol particles oxidization or aging level on estimating N_{CCN} were also very significant. When the particles were mostly composed of organics (x_{org}>60%), the N_{CCN} at the supersaturation of 0.075% and 0.13% was underestimated by 46% and 44% respectively if aerosol particles were freshly emitted with primary organics (f_{44}<11%); while the underestimation decreased to 32% and 23% at the corresponding supersaturations if the particles were with more hygroscopic secondary organics(f_{44}>15%). The N_{CCN} at the supersaturation of 0.76% was underestimated by 11% and 4% respectively at f_{44}<11% and f_{44}>15%. But for the particles composed of low organics (e.g. x_{org}<40%), the effect caused by the f_{44} was quite insignificant both at high and low supersaturations. This is due to that the overall hygroscopicity of the particles is dominated by inorganics such as sulfate and nitrate, which are more hygroscopic than organic compounds. Our results indicated that it would decrease the uncertainties in estimating N_{CCN} and lead to a more accurate estimation of N_{CCN} to

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increase the proportion of secondary organics, especially when the composition of the aerosols is dominated by organics.

The applicability of the CCN activation spectrum obtained at Xinzhou to the Xianghe site, about 400 km to the northeast of Xinzhou, was investigated, with the aim of further examining the sensitivity of ~~CCN~~N_{CCN} to aerosol type. Overall, the mean CCN efficiency spectrum derived from Xinzhou performs well at Xianghe when the supersaturation levels are > 0.2% (overestimation of 2-4%). However, N_{CCN} was overestimated by ~20% at supersaturation levels of < 0.1%. This suggests that the overestimation is mainly due to the smaller proportion of aged and oxidized organic aerosols present at Xianghe compared with Xinzhou.

1. Introduction

To reduce the uncertainty of aerosol indirect effects on the radiative balance of the atmosphere, it is important to gain a good knowledge of the ability of aerosol particles to form cloud condensation nuclei (CCN) at the typical supersaturations found in the atmosphere. The CCN activity of aerosol particles is governed by the Köhler theory (Köhler, 1936). This theory determines CCN from aerosol particle size and physicochemical properties, which include the molar volume, activity coefficient, and effect on surface tension (McFiggans et al., 2006). These properties, however, are difficult to measure.

Researchers have proposed single-parameter models to parameterize the CCN activation and hygroscopicity of multi-component aerosols (Hudson and Da, 1996; Rissler et al., 2006; Petters and Kreidenweis, 2007; Wex et al., 2007). Field experiments have been conducted with the aim of better characterizing particle physicochemical parameters influencing cloud CCN activation. Due to the large spatial variability of aerosol types and compositions, the CCN activation efficiency varies greatly over different regions. CCN number concentrations (N_{CCN}) can often be better predicted in the background atmosphere (Chuang et al., 2000; Dusek et al., 2003; VanReken et al., 2003; Snider et al., 2003; Rissler et al., 2004; Gasparini et al., 2006; Stroud et al., 2007; Bougiatioti et al., 2009).

The largest errors are associated with urban emissions (Sotiropoulou et al., 2007). This is likely due to the organics component of aerosol particles, which have the largest uncertainty and are not fully understood. Biomass burning aerosols and secondary organics formed from the oxidation of common biogenic emissions are often more difficult to activate (Mircea et al., 2005; VanReken et al., 2005; Lee et al., 2006; Varutbangkul et al., 2006; Clarke et al., 2007; Rose et al., 2010; Engelhart et al.,

2012; Paramonov et al., 2013; Lathem et al., 2013; Mei et al., 2013b; Zhang et al., 2014). Particles with aged/oxidized secondary organic components (e.g., organic acids) have been shown to be more hygroscopic (Raymond and Pandis, 2002; Hartz et al., 2006; Bougiatioti et al., 2011), but still much less hygroscopic than inorganic species. The sensitivity of estimated N_{CCN} to organics have been examined in a number of recent studies (Wang et al., 2008; Reutter et al., 2009; Ervens et al., 2010; Kammermann et al., 2010; Ward et al., 2010; Zhang et al., 2012; Mei et al., 2013a). It is widely known that the estimated N_{CCN} is sensitive to changes in organics due to the latter's complex components. The amounts and hygroscopicity parameter of organics (κ_{org}) vary substantially and lead to significant biases in estimating CCN concentrations and aerosol indirect forcing (Sotiropoulou et al., 2007; Hings et al., 2008; Liu and Wang, 2010). Therefore, field investigations regarding CCN activity and organics impacts, especially in heavily polluted regions, are pivotal to better parameterize CCN in climate models.

Northern China is a fast developing and densely populated region of China, where aerosol loading is high (Li et al., 2007, 2011), the particle composition is complex, and severe haze pollution episodes are common (Guo et al., 2014). In recent years, CCN measurements have been collected during field campaigns carried out in the region (Wiedensohler et al., 2009; Gunthe et al., 2011; Yue et al., 2011; Deng et al., 2011, 2013; Zhang et al., 2014). These studies have presented different perspectives on the influence of particle size and composition on CCN activity. For example, Deng et al. (2013) evaluated various schemes for CCN parameterization and recommended that the particle number size distribution (PSD) together with inferred mean size-resolved activation ratios can be used to estimate CCN number concentrations without considering the impact of particle composition. However,

Zhang et al. (2014) demonstrated that the 30–40% uncertainties in N_{CCN} are mainly associated with changes in particle composition. None of the above-mentioned studies have investigated the impact of organics on estimating N_{CCN} in Northern China. Zhang et al. (2012) noted a more significant influence of organics on CCN activity but without concerning the influences of particles oxidation or aging on CCN activity; in addition, the campaign average mass fraction of organics in their study was < 20%.

The aim of this paper is to examine the sensitivity of ~~changes in~~CCN activity to aerosol physicochemical properties (especially aerosols containing large amounts of organics, as well as the oxidation level~~) to CCN activity;~~), and also to see how much uncertainty is incurred by applying the CCN efficiency spectra measured at one site to another site in a heavily polluted region. The instrumentation and data used in the study are described in section 2. The method for calculating the hygroscopicity parameter (κ_{chem}) is introduced in section 3. The sensitivity of x_{org} as well as oxidation level of organics on estimating N_{CCN} in section 4, and the ability of the CCN efficiency spectrum observed at the Xinzhou site to represent CCN at the Xianghe site, are also presented and discussed at the last part of this section. Conclusions from the study are given in section 5.

2. Measurements and data

An intensive observation period field campaign similar to the Aerosol-CCN-Cloud Closure Experiment (Zhang et al., 2014), called the Atmosphere, Aerosol, Cloud, and CCN (A^2C^2) experiment, was conducted from 22 July to 26 August of 2014 at Xinzhou (38.24^{o}N, 112.43^{o}E; 1500 m above sea level), a city with a population of 0.51 million in Northern China. The site is located about 360 km southwest of the metropolitan Beijing area and about 10 km south of the local town center. The site is surrounded by agricultural land (e.g., corn) with little local pollution

plums from motor vehicles and industrial activities. Sitting between two mountains (Taihang Mountain to the east and Lüliang Mountain to the west), the site also experiences air masses from Xinzhou City to the north and from Taiyuan City to the south, the capital of Shanxi Province. Air masses from the northeast and southwest dominate over the site during summer. Depending on the wind direction, measurements at the Xinzhou site can detect air parcels of urban, rural, or mixed origins, including both fresh biogenic emissions around the site and aged aerosols from advection.

2.1 Instruments and measurements

During the field campaign, a Scanning Mobility Particle Sizer (SMPS), combined with a Droplet Measurement Technologies-Cloud Condensation Nuclei Counter (DMT-CCNc) (Lance et al., 2006), was used for size-resolved CCN measurements as well as particle number size distribution (PSD) measurements. The measured aerosol PSD is within the size range of 14-600 nm. Aerosol chemical composition was measured simultaneously by an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) (Sun et al., 2012).

The aerosol inlet for the size distribution measurements was equipped with a TSI Environmental Sampling System (Model 3031200), which consists of a sharp-cut PM_1 cyclone and a bundled nafion dryer. The size-resolved CCN efficiency spectra were measured by coupling the DMT-CCN_C used with the SMPS (Rose et al., 2008). In this step, the particles are rapidly dried with RH < 30% upon entering the Differential Mobility Analyzer (DMA). Thus, size selection is effectively performed under dry conditions. The nafion dryer and the sheath air inside the DMA are sufficient to remove residual water associated with the ambient particles. Relative

deviations in particle diameter should be < 1~~% except for potential kinetic limitations (Mikhailov et al., 2009).~~%. The sample flow exiting the DMA was split into two parts: 0.3 lpm for the CPC and 0.5 lpm for the CCN counter (CCN_C). The DMA, controlled by TSI-AIM software, scanned one size distribution every five minutes. The CCN_C was operated at a total flow rate of 0.5 lpm with a sheath-to-aerosol flow ratio of 10. The inlet RH for CCNc was < 30%. During the field campaign, the mean sample temperature and pressure measured by CCN_C sensors was (24.3±1.4) ℃ and (898.4±11.7) hPa. The supersaturations levels of CCN_C were calibrated with ammonium sulfate before and after the field campaign, following the procedures outlined in Rose et al. (2008). During each CCN measurement cycle, calibrated effective supersaturations were set at 0.075%, 0.13%, 0.17%, 0.39%, and 0.75%. The overall relative error (1σ) for the supersaturation levels was estimated to be < 3.5%. The completion of a full measurement cycle took 50 minutes (10 minutes for each supersaturation level).

The measurement of non-refractory submicron aerosol species including organics, sulfate, nitrate, ammonium, and chloride were made with an ACSM. During the field campaign, ambient aerosols were drawn inside through a ½ inch (outer diameter, the inner diameter is 0.38 inch) stainless steel tube at a flow rate of ~3 L min^{-1}, of which ~84 cc min^{-1} was sub-sampled into the ACSM. An URG cyclone (Model: URG-2000-30ED) was also positioned in front of the sampling inlet to remove coarse particles with a cut-off size of 2.5 μm. Before sampling into the ACSM, aerosol particles were dried using a silica gel desiccant. The residence time in the sampling tube was ~5 s. The ACSM was operated at a time resolution of ~15 min with a scan rate of mass spectrometer at 500 ms amu^{-1} from m/z 10 to 150. Regarding the calibration of the ACSM, mono-dispersed, size-selected 300-nm ammonium nitrate

particles within a range of concentrations were sampled into both the ACSM and a condensation particle counter (CPC). The ionization efficiency (IE) was then determined by comparing the response factors of the ACSM to the mass calculated with known particle size and number concentrations from the CPC. More detailed descriptions of the operation and calibration of the ACSM are given in Sun et al. (2012) and Ng et al. (2011). The campaign averaged mass concentration of PM_1 is 31.6 μg m^{-3}.

In addition to the ACSM, the black carbon (BC) in $PM_{2.5}$ was simultaneously measured at a time resolution of 5 min by a seven-wavelength aethalometer (Model AE31, Magee Scientific Corporation). The campaign averaged mass concentration of BC is ~2.5 μg m^{-3}. During the experiment, the campaign area was generally hot and dry, with an average temperature of 21.6℃ and an average ambient RH of 69.5%.

2.2 Data

The raw CCN data were first filtered according to instrument recorded parameters (e.g., temperature and flow). For example, if the relative difference between the actual and preset sample flows was larger than 4%, the data are flagged as invalid. The data is also excluded if the "temperature stability" was flagged as "0". ~~These flagged data are not used for further analysis.~~Here, the "temperature stability" refers to the T_1, T_2 and T_3 in cloud chamber of the CCNc, which is set to obtain the target supersaturations. If the average differences between preset T_1, T_2 and T_3 and the measured values are larger than 0.4 ˚C, the "temperature stability" is flagged as "0". Thus, the data is invalid and will be removed. A multiple charge correction and transfer function (Deng et al., 2011) is applied to each PSD as well as to the CCN efficiency spectrum. ~~The CCN activation ratio (AR) is the ratio of N_{CCN} to CN~~

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~~concentration (N_{CN}). Bulk AR is calculated from the total N_{CN} and N_{CCN}. For the size-resolved CCN measurements, we get size-resolved AR from size-resolved CCN and CN number concentrations.~~

——Size-resolved CCN and PSD data, measured with a DMT-CCNc and a SMPS (with a particle size range of 10-700 nm) on 7-21 July 2013 at Xianghe (Zhang et al., 2014), are used in this study for comparisons with CCN activity at the Xinzhou site. Aerosol mass concentrations were processed using the ACSM standard data analysis software (version 1.5.3.0). Detailed procedures for the data analysis have been described by Ng et al. (2011) and Sun et al. (2012). The size-resolved CCN activation ratio (size-resolved AR) is defined as the $dN_{CCN}/dlogD_p$ divided by the $dN_{CN}/dlogD_p$. These values were measured by SMPS-DMT-CCNc with particle size selection in the DMA. The bulk activation ratio (bulk AR) is defined as the total CCN concentration divided by the total CN concentration. The total CCN and CN number concentrations are integrated by the measured CCN and CN size distribution respectively over the whole size range.

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3. Derivation of κ_{chem}

In this study, we calculate κ_{chem} based on bulk chemical composition observations made during the field campaign. The method is very similar to that used by Zhang et al., (2014). As proposed by Petters and Kreidenweis (2007), κ_{chem} can be predicted using a simple mixing rule based on chemical volume fractions for a given internal mixture:

$$\kappa_{chem} = \sum_i \varepsilon_i \kappa_i \qquad (1)$$

where κ_i and ε_i are the hygroscopicity parameter and volume fraction, respectively, for the individual (dry) components in the mixture and i is the number of components in the mixture.

Measurements from the ACSM in Xinzhou show that the composition of submicron particles was dominated by organics, followed by sulfate, ammonium, and nitrate. The contribution of chloride was negligible (volume fraction of about < 2%). The analysis of the anion and cation balance suggests that anionic species (NO_3^-, SO_4^{2-}) were essentially neutralized by NH_4^+ over the relevant size range. For refractory species, BC represented a negligible fraction of the total submicron aerosol volume (< 3%). Sea salt and dust are usually coarse mode particles with particle sizes > 1 μm (Whitby, 1978). The contribution of such types of aerosols is thus expected to be negligible for sizes < 1 μm. Therefore, the submicron particles measured by the ACSM mainly consisted of organics, $(NH_4)_2SO_4$, and NH_4NO_3. The particle hygroscopicity is thus the volume average of the three participating species:

$$\kappa_{chem} = \kappa_{org}\varepsilon_{org} = \kappa_{org}\varepsilon_{org} + \kappa_{(NH_4)_2SO_4}\varepsilon_{(NH_4)_2SO_4} + \kappa_{NH_4NO_3}\varepsilon_{NH_4NO_3} \quad (2)$$

Here, the values of κ for $(NH_4)_2SO_4$ and NH_4NO_3 are 0.6761 and 0.6167, respectively. The following linear function derived by Mei et al. (2013) was used to estimate κ_{org} in this study: $\kappa_{org} = 2.10 \times f_{44} - 0.11$, where f_{44} is the fraction of m/z 44 in total organics. The mean value of κ_{org} during the field campaign is 0.115±0.019.

4. Results and discussion

4.1 CCN efficiency spectra

During the field campaign at the Xinzhou site, ~790 size-resolved CCN efficiency spectra at five supersaturation levels ranging from 0.075% to 0.76% were measured. Figure 1 shows campaign averaged spectra of the measured CCN efficiency at Xinzhou for supersaturation levels of 0.075%, 0.13%, 0.17%, 0.39%, and 0.76%. The observed averaged CCN efficiency spectra during Xianghe campaign in

summer 2013 are also shown. ~~The~~Note that the maximum activation fraction (MAF) for Xianghe site showed in Figure 1 is slight lower than that we plotted in Zhang et al.(2014). Because some data points when the MAF value >1 were not processed previously, as resulted in larger mean MAF. But in this paper, the data points with MAF > 1.0 were forced to 1 when D_p>300 nm, which could be completely activated at even lower supersaturations but the MAF would never be larger than 1.0. In Figure 1, the right panels show the mass concentration fraction of particle chemical compositions at Xinzhou (top panel) and Xianghe (bottom panel) during their respective observation periods. Significant differences in size-resolved CCN efficiency spectra at the two sites are seen. Aerosol particles at Xinzhou activate more efficiently (higher values of AR) at a given particle diameter (D_p) for the same supersaturation level. In the other words, a larger D_p was required to reach the same activation efficiency at Xianghe. This suggests that aerosol properties at each site differ.

The slope of AR with respect to diameters near D_p when AR=50% (defined here as the cut-off diameter, D_{cut}) provides information about the heterogeneity of the composition for size-resolved particles. For an ideal case when all CCN-active particles have the same composition and size, a steep change in AR from 0 to 1 would be observed as D_p reached D_{cut}. A gradual increase in size-resolved AR with D_p suggests that aerosol particles have different hygroscopicities. The steeper slopes of AR around D_{cut} observed at Xinzhou suggest that the particle composition was less heterogeneous with more hygroscopicity than particles at the Xianghe site. This can be partially explained by the magnitudes of the mean κ_{chem} at the two sites (0.42 at Xinzhou and 0.38 at Xianghe). Also, the f_{44} is greater at Xinzhou than at Xianghe. The *m/z* 44 signal is mostly due to acids (Takegawa et al., 2007; Duplissy et al., 2011) or

233 acid-derived species, such as esters. f_{44} is closely related to the organic oxidation level
234 (Aiken et al., 2008). Oxidized/aged acids are generally more hygroscopic and easily
235 activated. Moreover, the primary inorganic particles at the Xinzhou site are sulfates,
236 with a mass fraction that is two times greater than that measured at Xianghe.
237 Therefore, particles at the Xinzhou site consist of more hygroscopic sulfate-dominant
238 inorganics and aged/oxidized secondary organics and can thus be more efficiently
239 activated at a given D_p, as shown in Fig. 1.

240 **4.2 Air mass influences on CCN activity: a case study**

241 Because air mass back trajectories combined with ambient air measurements can
242 be used for analyzing large-scale air pollutant transport and source identification at a
243 receptor site (Stohl, 1996; Rousseau et al., 2004), in this study, we calculated five-day
244 (120 hr) back trajectories using the Hybrid Single-Particle Lagrangian Integrated
245 Trajectory (HYSPLIT) model (Draxler and Hess, 1998) with National Centers for
246 Environmental Prediction (NCEP) reanalysis data. TrajStat software (Wang et al.,
247 2009) has been used to calculate trajectories. The arrival height of the trajectories at
248 the Xinzhou site was at the surface.

249 Three cases were selected to study air mass influences on ~~aerosol~~CCN activity:
250 (1) Case 1, 19 August 2014, 19:00-21:00 local time (LT); (2) Case 2, 9 August 2014,
251 03:00-10:00 LT; and (3) Case 3, 29 July 2014, 00:00-12:00 LT. Each case is
252 associated with a different CCN efficiency spectrum, i.e., top, middle, and bottom
253 panels of Fig. 2 are for Cases 1, 2, and 3, respectively. Their respective back
254 trajectories are shown in Fig. 3.

255 In Case 1, air trajectories (red line in Fig. 3) originated from the southwest and
256 passed through northern Shaanxi Province and northwestern Shanxi Province, then

rounded back to the site from the north/northeast. So, aerosols in this case are closely associated with air parcels north/northeast of the site. The trajectories were very short, suggesting that the air flow was slow during the observational period. Under these circumstances, aerosol loading would be largely impacted by local sources around the site. A high mass fraction of organics (> 60%) with low f_{44} (~10%) and κ_{chem} (< 0.3) values was measured during the observational period. Furthermore, the PSD showed one peak mode with D_p = 56 nm and a high N_{CN} (~1.7×10^4 cm^{-3}), but low mass concentration of PM_1 (28.36 μg m^{-3}). This suggests that particles may be composed of freshly emitted primary aerosols (the biogenic emissions from the plants and trees around the site). This type of aerosol is usually less hygroscopic with a single peak mode primarily composed of fine particles (Whitby, 1978; Hussein et al., 2005). These aerosols cannot activate efficiently. The maximum activation fraction (MAF) shown in the top right panel of Fig. 2 is less than 0.6 at all supersaturation levels for particles with D_p > 300 nm, indicating that the particles should be largely externally mixed aerosols.

In Case 2 (blue line in Fig. 3), air parcels moved rapidly from the west to the site. The site should then be influenced by the large-scale transport of air masses. For this case, aerosols contain a small amount of organics (< 30%), but have high f_{44} (~14%) and κ_{chem} values (~0.5). The PSD showed a double peak mode with an N_{CN} of ~1.3×10^4 cm^{-3} and a relatively high mass concentration of PM_1 (81.45 μg m^{-3}). The double peak mode suggests that aerosols in this case are a mixture of aerosols from local sources and from other regions (Whitby, 1978; Dal Maso et al., 2007). Because aerosols are aged and oxidized during long-distance transport, these particles are usually composed of secondary organic and inorganic components with more hygroscopicity (Weber et al., 1999; Verver et al., 2000). These aerosols can activate

efficiently. The MAF is close to 1 and the slopes of AR around D_{cut} are steep at all supersaturation levels (middle right panel of Fig. 2). This CCN efficiency spectrum is similar to the ideal spectrum of pure ammonium sulfate.

In Case 3 (green line in Fig. 3), air parcels travelled from the northwest to the site. Air masses arriving at the site in this case had passed over densely populated regions with more heavy pollution. A gradual increase in size-resolved AR with D_p is seen (bottom right panel of Fig. 2). This is attributed to the diversity in aerosol hygroscopicity because of the complex nature of the chemical composition of aerosol particles.

4.3 Correlation of N_{CN} and N_{CCN}

Figure 4 shows N_{CN} as a function of N_{CCN} for different supersaturation levels at the Xinzhou and Xianghe sites. They showed high or moderate correlations at high supersaturation levels (e.g., R^2 = 0.57 at Xinzhou and R^2 = 0.85 at Xianghe at a supersaturation level of ~0.8%), but quite poor correlations at low supersaturation levels. Although Andreae (2009) proposed using the relationship of CCN and CN, or even aerosol optical depth (AOD), to parameterize CCN in models, it ~~should be caution if one uses the correlation~~would lead to large uncertainties especially ~~for those cases at low~~ when the supersaturations ~~because of the spatial variation in CCN activity for maritime and continental aerosols~~are low. It was noticed that there was an apparent higher degree of correlation at Xianghe site for each supersaturation than that derived at Xinzhou site. In view of the similar regimes from which the data are taken and the same instruments by which they have been collected, the discrepancy between Xianghe and Xinzhou should be caused largely by the spatial variations of aerosols types. These variations are primarily attributed to variations in aerosol particle size, i.e., the shape of the PSD as well as particle composition. As presented by Zhang et al. (2014),

the relationship between bulk activation ratios and N_{CN} was complex under polluted conditions and was heavily dependent on the physicochemical properties of atmospheric aerosols.

4.4 Impact of x_{org} on N_{CCN}

Precise quantification of N_{CCN} is crucial for understanding aerosol indirect effects and characterizing these effects in models. A CCN closure study is useful to examine the controlling physical and chemical factors and to help verify experimental results. N_{CCN} is usually derived from measured aerosol properties, such as PSD and composition or hygroscopicity based on the Köhler theory. Achieving such closure under heavily polluted conditions is more challenging, especially due to the complex effects of organics on CCN activity. In this section, we examine the sensitivity of N_{CCN} to both volume fraction of organics (x_{org}) ~~as well as~~and oxidation or aging of organics ~~to N_{CCN} estimation~~ based on measurement at Xinzhou site. During the observed period, aerosols at the Xinzhou site were dominated by organics, with 12%, 23%, 39%, and 25% of the data points corresponding to x_{org} >60 %, 50%<x_{org} <60 %, 40%<x_{org} <50 % and x_{org} <40 %, respectively. For the purpose of examining the sensitivity of estimated N_{CCN} to x_{org} and oxidation/aging level, we sorted the size-resolved CCN data when the x_{org} >60 %, 50%<x_{org} <60 %, 40%<x_{org} <50 % and x_{org} <40 %. Furthermore, for each level of x_{org}, we tested the impacts on N_{CCN} estimation both from the most oxidized (with f_{44} of higher than 15%) and least oxidized (those primary organic aerosols with f_{44} of lower than 11%) organic particles. For example, the size-resolved CCN data points during the period when x_{org} >60 % and also f_{44} >15% was averaged to generate the averaged CCN efficiency spectra at the five supersaturations respectively. Then we used the produced averaged CCN efficiency spectra to estimate N_{CCN}.

Estimated CCN size distributions at the five supersaturations were firstly calculated by multiplying the averaged CCN efficiency spectrum (by using the averaged CCN efficiency spectra, the aerosol particles were assumed with uniform chemical composition without considering the effects of the temporal variations of the activation curves on CCN activity) with the actually measured PSD. Then, we integrated the estimated CCN size distribution over the whole size range to generate estimated N_{CCN}. While the measured CCN size distributions are integrated to produce the observed N_{CCN}.

Observed and estimated N_{CCN} at four supersaturation levels (0.075%, 0.13, 0.17 and 0.76%) were showed in Fig 5. The data points presented more disperse and weaker correlations at lower supersaturations. The sensitivity of volume fraction of organics to N_{CCN} increased with increasing x_{org}. This is especially for the case of these primary organic particles with f_{44}<11%: the slopes obtained from a linear fit of estimated and measured N_{CCN} in Fig 6 decreased rapidly (almost with a decrease of ~50%) when the x_{org} varied from <40% to >60% at supersaturations of 0.075%, while it didn't exhibit a lot of reduction (merely ~10%) along with the increasing of x_{org} for the supersaturation of 0.76%. N_{CCN} was estimated most accurately at higher supersaturation levels. This is likely because a large fraction of particles was already CCN-active. Also, particle composition has relatively less influence on CCN activation at high supersaturations (Twohy and Anderson, 2008). For the oxidized or aged particles with f_{44}>15%, the slopes still follow the similar tendency with the variations of x_{org} at low and high supersaturations but changed more smoothly to the x_{org} attributing to the oxidized/aged organic particles being more hygroscopic.

However, the impacts of the aerosol particles oxidization level on estimating N_{CCN} were also very significant. For example, when the particles were composed by

large amounts of organics (x_{org}>60%), the N_{CCN} at the supersaturation of 0.075% and 0.13% was underestimated by 46% and 44% respectively at f_{44}<11%, while the underestimation decreased to 32% and 23% at the corresponding supersaturation level at f_{44}>15%. The N_{CCN} at ss=0.76 was underestimated by 11% and 4% respectively at f_{44}<11% and f_{44}>15%. One thus could conclude that the estimation of N_{CCN} would be largely improved if the aerosol particles were aged with high oxidation level, especially when the chemical composition of the particles is dominated by organics. But for the particles with relative low organics (x_{org}<40%), the effect caused by the f_{44} was quite insignificant both for high and low supersaturations. In Fig 6, the slopes were all around 1.0 at the two cases of f_{44}<11% and f_{44}>15%. This can be easily explained. When x_{org} is less than 40%, the overall hygroscopicity of the particles is dominated by inorganic species such as sulfate and nitrate, which are more hygroscopic (κ_{inorg} ~~usully~~usually larger than 0.6) than organic compounds (κ_{org} ~~usully~~usually smaller than 0.2). As a result, a larger fraction of particles can be activated. According to the simple mixing rule based on chemical volume fractions proposed by Petters and Kreidenweis (2007), the contribution from organics is quite small. If x_{org} is greater than 60%, organics will dominate the overall particle hygroscopicity. Particles with a large f_{44} are much more hygroscopic and thus strongly influence the estimated N_{CCN}. Our results indicated that increasing the proportion of secondary organics would decrease the uncertainties in estimating N_{CCN} and lead to a more accurate estimation of N_{CCN}.

4.5 Applicability of CCN efficiency spectra

As a means of testing the applicability of the CCN activation spectra, campaign mean CCN efficiency spectra at different supersaturations observed at the Xinzhou

site is used to estimate N_{CCN} at the Xinzhou and Xianghe sites respectively, which helps to further examine the sensitivity of N_{CCN} to aerosol type. Data from the two sites were measured during the warm season so that the effect of temporal variations in aerosols on CCN levels is reduced. Fitted campaign mean CCN efficiency spectrum at the five supersaturations at Xinzhou (corresponding to spectra in Fig. 1) is multiplied by dry PSDs actually measured at Xinzhou and at the Xianghe site respectively. This generates estimated CCN size distributions at the two sites. They are then integrated over the whole size range (14-600 nm and 10-700 nm at the Xinzhou and Xianghe sites, respectively) to obtain the estimated N_{CCN}. The measured CCN size distributions at each site are integrated to produce the observed N_{CCN}.

Figure 7 shows estimated N_{CCN} as a function of measured N_{CCN} for different supersaturation levels at the two sites. N_{CCN} at Xinzhou was underestimated by 4-5% at supersaturation levels of 0.39% and 0.76%, and was slightly overestimated (~2%) at Xianghe for the same supersaturation levels. Good agreement is seen at the 0.39% and 0.76% supersaturation levels for data from both sites ($R^2 > 0.92$). N_{CCN} at Xinzhou was underestimated by ~7% at supersaturation levels < 0.1% ($R^2 = 0.87$). At Xianghe, however, N_{CCN} was overestimated by 19-23% at supersaturation levels < 0.1% although the correlation between calculated and measured N_{CCN} was good. Because size-resolved CCN efficiency spectra were applied here, excluding the impact of particle size, the influence of chemical composition on CCN activation can be investigated. The poor estimates of CCN at low supersaturation levels could be attributed to the high sensitivity of N_{CCN} to chemical composition. Because the mass fractions of inorganics and organics measured at the two sites are similar (Fig. 1) and the hygroscopicity for inorganic components is fixed, this overestimation is attributed to the smaller proportion of aged and oxidized organic aerosols at Xianghe compared

with aerosols at Xinzhou (f_{44} = 17% and 11% at Xinzhou and Xianghe, respectively).

5. Summary and conclusions

In this study, we have investigated the impacts of particle physicochemical properties on CCN activity based on field measurements obtained from 22 July to 26 August of 2014 in the suburb of Xinzhou, China. Five-day back trajectories combined with measurements were analyzed to examine air mass influences on CCN activity. CCN efficiency was largely reduced by local ~~primary biomass burning events~~air masses, and the MAF was low to <60%, suggesting externally-mixed and the heterogeneity of particle composition for local emitted aerosols. The CCN activation efficiency was enhanced significantly when the site was under the influence of air transported from far away, during which aerosols could be mixed well with more hygroscopic secondary organic and inorganic components. The relationship between N_{CN} and N_{CCN} was generally poor. Large errors would arise if using the former to estimate the latter, especially under low supersaturation conditions.

The sensitivity of N_{CCN} estimation to both x_{org} ~~as well as~~and f_{44} ~~on estimating N_{CCN}~~ has also been examined. A strong dependence of N_{CCN} on the both two parameters was noted. The sensitivity of N_{CCN} to volume fraction and particles oxidization or aging level of organics ~~to N_{CCN}~~ increased with ~~increasing~~increase of x_{org}. And also this dependence weakens as the supersaturation level increases. When the particles were mostly composed of organics (x_{org}>60%), the N_{CCN} at the supersaturation of 0.075% and 0.13% was underestimated by 46% and 44% respectively if aerosol particles were freshly emitted with primary organics (f_{44}<11%); while the underestimation decreased to 32% and 23% at the corresponding supersaturations if the particles were with more hygroscopic secondary organics(f_{44}>15%). The N_{CCN} at the supersaturation of 0.76% was underestimated by

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11% and 4% respectively at f_{44}<11% and f_{44}>15%. But for the particles composed of low organics (e.g. x_{org}<40%), the effect caused by the f_{44} was quite insignificant both at high and low supersaturations. This is due to that the overall hygroscopicity of the particles is dominated by inorganics such as sulfate and nitrate, which are more hygroscopic than organic compounds. Our results indicated that it would ~~decrease the uncertainties in estimating N_{CCN} and~~ lead to a more accurate estimation of N_{CCN} to increase the proportion of secondary organics, especially when the composition of the aerosols is dominated by organics.

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The applicability of the CCN efficiency spectrum measured at the Xinzhou site to the Xianghe site was examined and a good agreement was found when the supersaturation level was > 0.2%. However, N_{CCN} at the Xianghe site was overestimated by 19-23% when the supersaturation level was < 0.1%. Because of the similar mass fractions of inorganics and organics measured at the two sites, we conclude that this overestimation was mainly caused by the smaller proportion of aged and oxidized organic aerosols at Xianghe compared with aerosols at Xinzhou.

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455 measurements).

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Figures

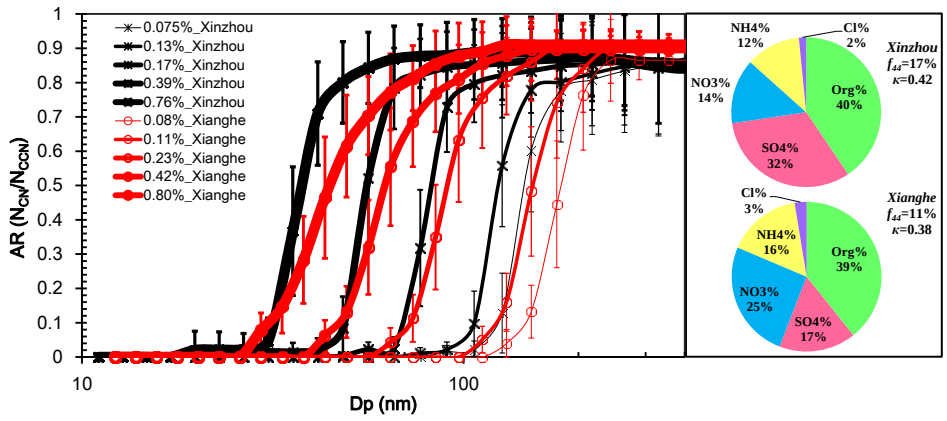

Fig. 1. Mean CCN efficiency spectra at the Xinzhou site (black lines with asterisks) measured from 22 July-26 August 2014 and at the Xianghe site (red lines with circles) site measured from 7-21 July 2013 for different supersaturation levels. Error bars representing one standard deviation are shown. Right panels show particle chemical composition in terms of mass concentration fractions at Xinzhou (top panel) and Xianghe (bottom panel) during their respective observation periods. The campaign average mass concentration of PM_1 is 31.6 μg m^{-3} and 72.4 μg m^{-3} at Xinzhou and Xianghe respectively. Note that the preset supersaturation levels were 0.07%, 0.1%, 0.2%, 0.4% and 0.8% at both sites, but effective supersaturation levels showed slightly different after calibration.

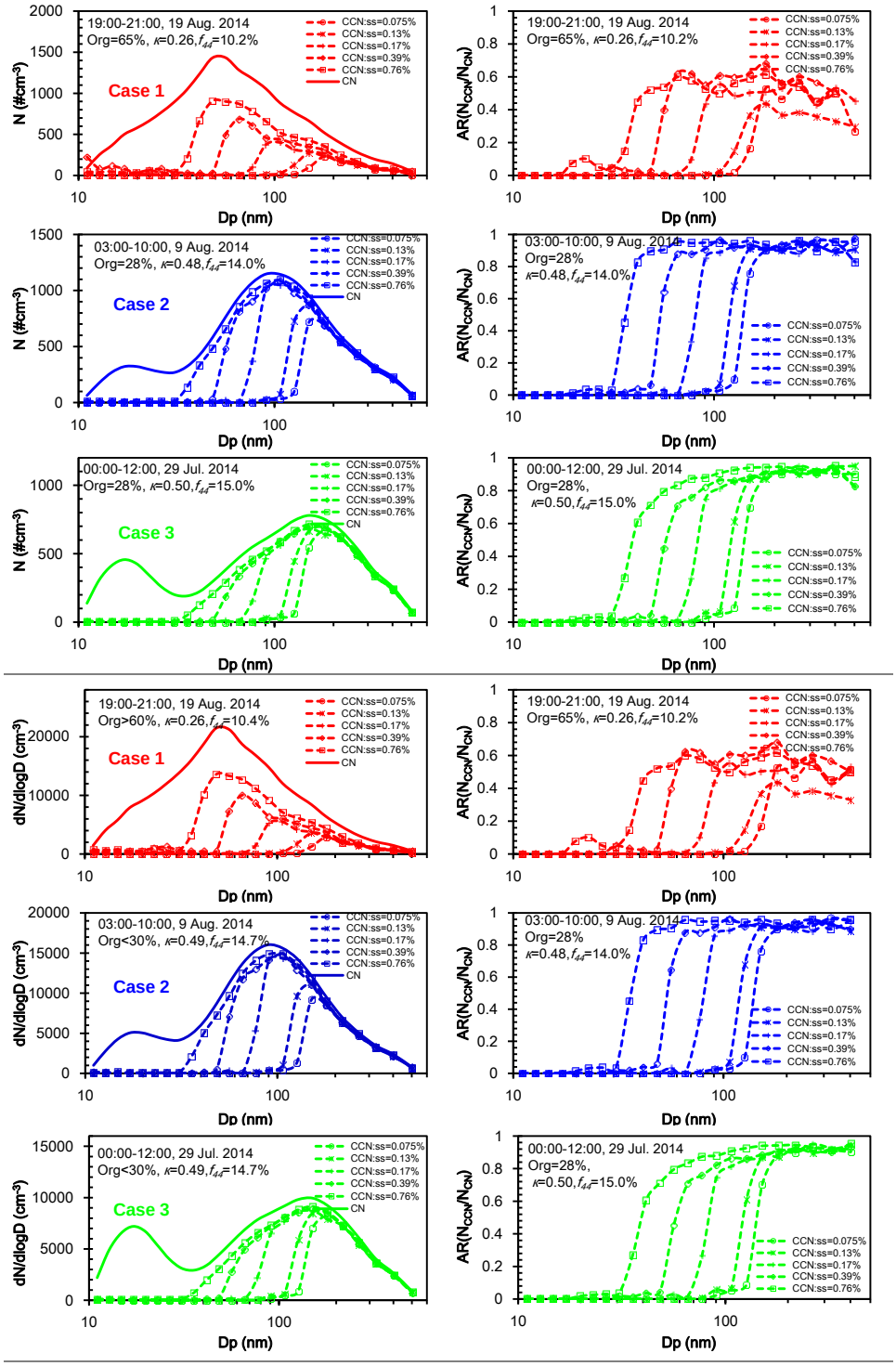

Fig. 2. Particle number size distribution (PSD) and CCN size distributions (left panels) and CCN efficiency spectra (right panels) at different supersaturation levels for Case 1 (upper panels, 19 August 2014, 19:00-21:00 LT), Case 2 (middle panels, 9 August

2014, 03:00-10:00 LT), and Case 3 (bottom panels, 29 July 2014, 00:00-12:00 LT). Total CN number concentrations are 16671 cm^{-3}, 12869 cm^{-3}, and 10134 cm^{-3} for Case 1, Case 2, and Case 3, respectively. Mass concentrations of PM_1 are 28.36 μg m^{-3}, 81.45 μg m^{-3}, and 78.73 μg m^{-3} for Case 1, Case 2 and Case 3, respectively.

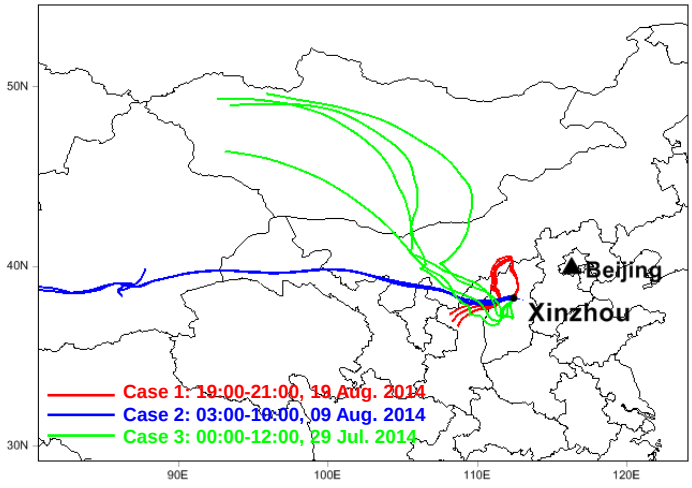

Fig. 3. Five-day back trajectories for Case 1 (in red), Case 2 (in blue), and Case 3 (in green) calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory model with National Centers for Environmental Prediction reanalysis data. The arrival height of the trajectories at the Xinzhou site was at the surface.

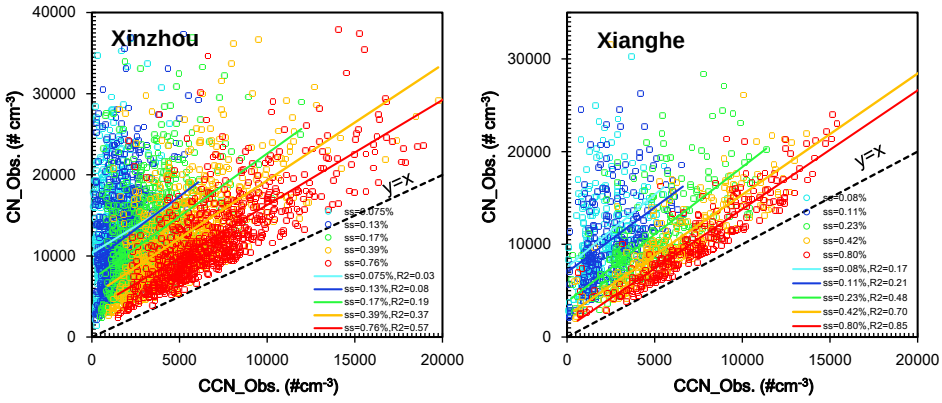

Fig. 4. Measured N_{CN} as a function of measured N_{CCN} for different supersaturation levels at the Xinzhou (left panel) and Xianghe (right panel) sites. The scatterplot between $CCN_{\_Obs}$ and CN_Obs. were fitted with a linear function (in colored lines) and R^2 refer to the correlations of them. .

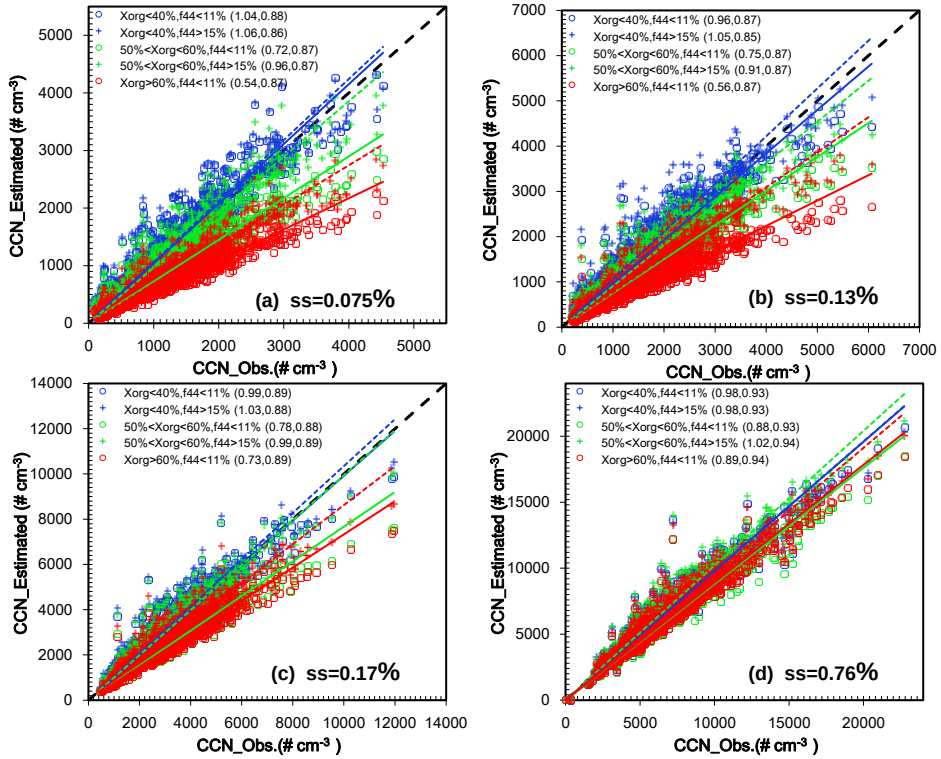

Fig. 5. The sensitivity of N_{CCN} to both organics volume fraction (x_{org}) ~~as well as~~and oxidation level (using f_{44}, the fraction of m/z 44 in ~~total organics, as an indicator~~aerosol organic material) of organics ~~to estimation of N_{CCN}~~ at supersaturation

levels of (a) 0.075%, (b) 0.13%, (c) 0.17% and (d) 0.76%.% for cases when x_{org} = 35% (blue circles), 52% (green circles), and 66% (red circles)). The size-resolved CCN data were sorted when the x_{org} >60 %, 50%<x_{org} <60 %, 40%<x_{org} <50 % and x_{org} <40 % respectively to do the sensitivity examination. The results of 40%<x_{org} <50 % was not plotted here. Mean values of the hygroscopic parameter κ_{chem} at f_{44}<11% when x_{org} >60 %, 50%<x_{org} <60 %, 40%<x_{org} <50 % and x_{org} <40 % are 0.27, 0.34, 0.40 and 0.46, respectively; while at f_{44}>15% the value increased to 0.36, 0.42, 0.46 and 0.50 respectively. Linear best-fit lines through each group of points are shown. Slopes and R^2 values are given in parentheses.

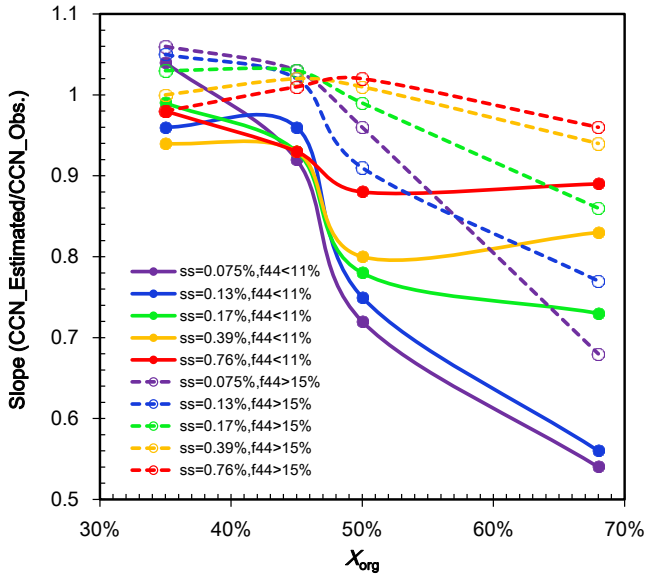

Fig. 6. Slopes of the linear fit of estimated and observed N_{CCN} dependence on volume fraction of organics (x_{org}) at f_{44}<11% and f_{44}>15% for different supersaturation levels. Mean values of the hygroscopic parameter κ_{chem} at f_{44}≤11% when x_{org} >60 %, 50%<x_{org} <60 %, 40%<x_{org} <50 % and x_{org} <40 % are 0.27, 0.34, 0.40 and 0.46, respectively; while at f_{44}>15% the value increased to 0.36, 0.42, 0.46 and 0.50 respectively.

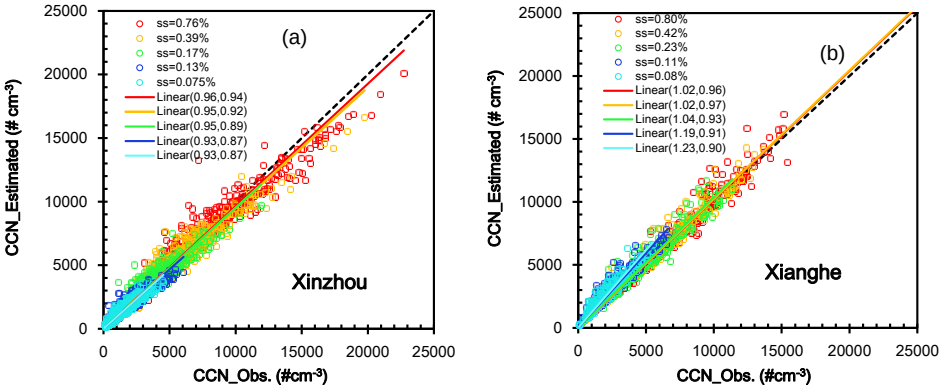

Fig. 7. Estimated N_{CCN} as a function of observed N_{CCN} for different supersaturation levels at (a) Xinzhou and (b) Xianghe. Note that the campaign mean CCN efficiency spectra at Xinzhou are used for estimating N_{CCN} at Xianghe. Linear best-fit lines

873 through each group of points are shown. Slopes and R^2 values are given in
874 parentheses.
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