

Reply to RC2

Based on a field campaign conducted in Xingtai in the central North China Plain, the authors discussed about the chemical composition, hygroscopicity and CCN activity of aerosol particles. There have been a number of studies talked about the north part of NCP but very few about the central part. And it was found that aerosol mixing state and hygroscopicity in Xingtai largely differs from that in the north part of NCP. My major concerns are:

- 1) Xingtai locates at the western boundary of NCP and is heavily affected by the mountain-valley wind (L126). Can the measurement well represent the background aerosol in the central NCP?

Re: The influence of mountain-valley wind is regional. Figure 1 in this reply shows pollution in the NCP is rather non-uniform, the central region is more serious than that in northern and southern regions. Our sampling site (Xingtai) is located in one of the pollution centers and thus represents the condition near an emission source region. The average $\text{PM}_{2.5}$ mass concentration at this station was $45.2 \mu\text{g m}^{-3}$ in this campaign, which was only 15% lower than that ($53.3 \mu\text{g m}^{-3}$) measured at the urban site in Xingtai. In addition, OOA and sulfate were the most important organic and inorganic species respectively. Figure 2 in this reply shows that the diurnal cycle of OOA was flat and the diurnal cycle of sulfate was also smoother compared with nitrate, also reflecting the regional characteristics of the main pollutants. All these suggest that the influence of mountain-valley wind is limited and this site is a good representative in this region. Detailed discussion about gas precursors and aerosol chemical species in this region can be found in Zhang et al., (2018).

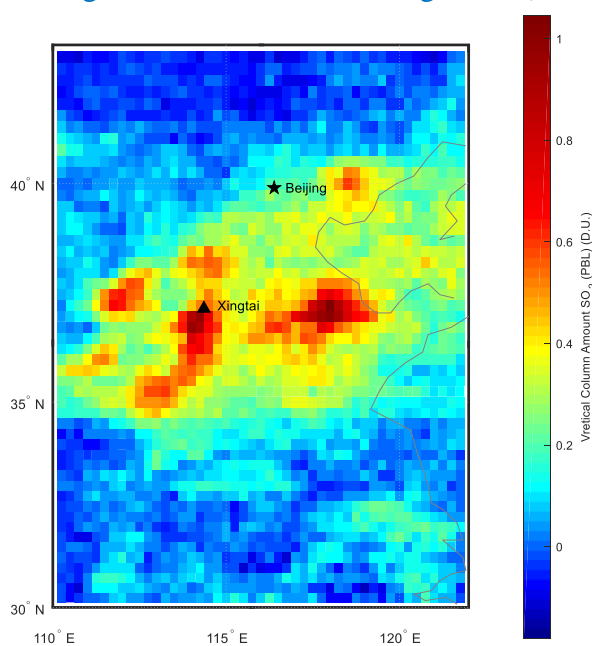


Figure 1. The distribution of mean SO_2 concentrations of May from 2012 to 2016. The map of NCP can refer to Fig. 4 in this reply.

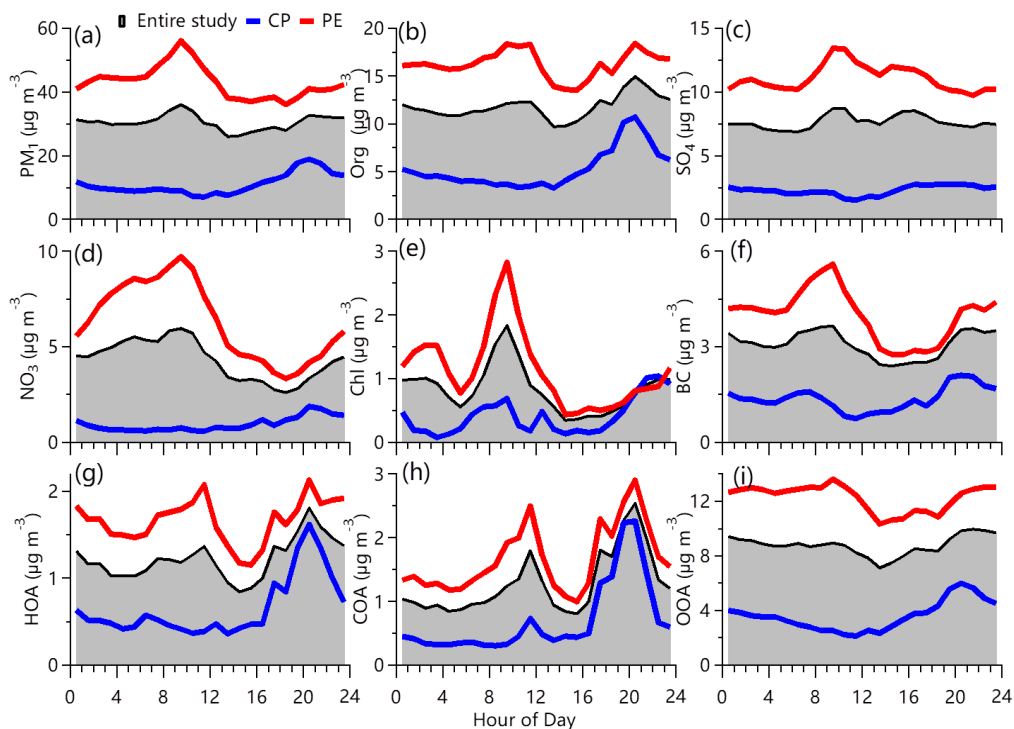


Figure 2. Diurnal cycles of chemical species of PM₁ and OA factors during entire study, PE (polluted events) and CP (clean periods). The figure is from Zhang et al., (2018).

2) I did not find a strong connection between the sections of CCN (section 4.3.3 and 4.4) and HTDMA (section 4.1 to 4.3.2). They look like two independent works but each of them a too weak to be an individual study.

Re: Aerosol mixing state is one of three factors influencing aerosol activation ability. In this campaign, we only measured bulk CCN data rather than size-resolved CCN data. The bulk CCN data cannot provide the information about aerosol mixing state but HTDMA data can. HTDMA data in this campaign suggests the aerosol is highly internal-mixed and aged, which is the base to do CCN closure studies in this paper. In addition, the HTDMA data are very useful for the analysis of the activation rate diurnal variations. These are important links between the sections of HTDMA and CCN.

Specific comments:

L51: defined as the mixture of solid and liquid particles suspended in air,

Re: Good suggestion, we have corrected.

L79: I did not see any causal relationship between L72-78 and L79-81

Re: L79-81 had been corrected as “aerosol hygroscopicity and CCN activity are very different in different regions due to different chemical compositions”.

L113: the author need to give more detailed information of the station. Does it locate in urban, sub-urban or rural environment? What about the surroundings, any roads, industrial or residential activities nearby?

Re: This suburban site is situated ~17 km northwest of Xingtai urban area in southern Hebei Province. A provincial road is ~400 m southeast of the sample site, a school adjoins the east, and a town is ~600 m in the northwest (Fig. 3 in this reply). There are many industrial manufacturers in this region including coal-based power plants, steel and iron works, glassworks, and cement mills. We have added more environment information about the sample site in the manuscript.



Figure 3. The surroundings at the sample site.

L114: how do the authors define the NCP? From the map in Fig. 1 it seems the station locates at the southern boundary of the plain. In L126 the authors also state the station is “heavily affected by the mountain-valley wind”.

Re: NCP is one of the largest plains in China. It covers an area of about 0.3 million square kilometers. The Fig.1 in the manuscript only shows a part of NCP, a full image can refer to Fig. 4 in this reply. This figure shows the observation site is in the central NCP although it is not far away from the Taihang Mountains. This station is still a good representative site in this region although it is affected by the mountain-valley wind (c.f. response to the Question 1).

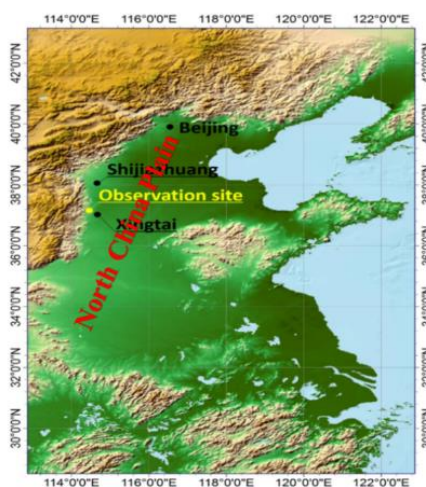


Figure 4. Map showing the observation site and the scale of North China Plain (NCP). The original figure is from Wang et al., (2018).

L138: are then passed – pass

Re: Yes, we have corrected it.

L144: Normally the RH of the HTDMA should be calibrated with ammonium sulfate, especially for high RH measurement. Did the authors calibrate the system during the campaign?

Re: Yes, the RH calibration is important for HTDMA running. Figure 5 in this reply shows the calibration result with ammonium sulfate during our campaign. It shows the deliquescence point of ammonium sulfate is $78 \pm 1\%$, this is consistent with previous studies (Badger et al., 2006; Tan et al., 2013).

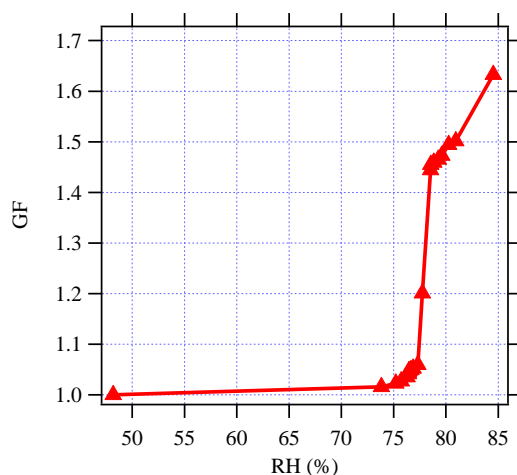


Figure 5. Humidogram of ammonium sulfate for 150-nm particles measured with the HTDMA.

L147: I suggest to use single letter for variables, for example, $f_{\{g\}}$ for growth factor.

Re: It's a good suggestion, but we tried to follow the conventional acronyms such as "GF" or " gf " that has been used in most previous papers. " f_g " is a good suggestion but it's easily confused with the expression of the aerosol scattering enhancement factor (f_{RH}). Therefore, we'd prefer to continue the use of "GF" in this manuscript.

L154: An Aerosol Chemical. . .

Re: Corrected per the comment.

L156: Is the cyclone for all the aerosol instruments or only for the ACSM?

Re: ACSM and AE33 had their separate cyclones. SMPS had an impactor in the inlet, which can also remove the most particles larger than its measurement range. HTDMA had no cyclone which has a minor effect on its measurement. CCNc had not also a cyclone because it needed to measure the bulk CCN number concentration in this campaign.

L164: Is there a separate inlet line with PM₁ size cut for the aethalometer? I think the authors need to give a clear description of the inlets and sampling line for all the instruments. Now I am a bit confused.

Re: Yes, aethalometer had a separate inlet headed by a PM₁ for filtering particle size great than 1 μm . CCNc and HTDMA shared the same inlet. During this campaign, all sampling instruments were placed in two containers at ground level and two air conditioners were used to maintain the temperature at 20–25 °C inside containers. All stainless tube inlets were 1.5 m above the top of containers.

L181: I do not know why the SS needs to be corrected. Normally after applying the calibration parameters to the system, the set SS is the true effective SS in the chamber. No more correction is needed. Is the SS corrected with the first or second calibration result? Is there any large difference between the two calibrations?

Re: Actually, the SS is influenced by flow rates and the temperature gradient in the cloud column. Therefore, the flow and temperature calibrations are also needed, which had been conducted before this campaign and the corresponding parameters were applied in the system. However, the SS maybe changed if the CCNc runs unsteadily, so we did two SS campaigns before and after the campaign instead of using the SS parameters from a single calibration. Figure 6 in this reply shows the results of the SS calibrations, the calibration method is the same as Rose et al., (2008). The results show CCNc run well and steadily during this campaign. The calibrated SS used in this paper was from the mean SS of two calibration results.

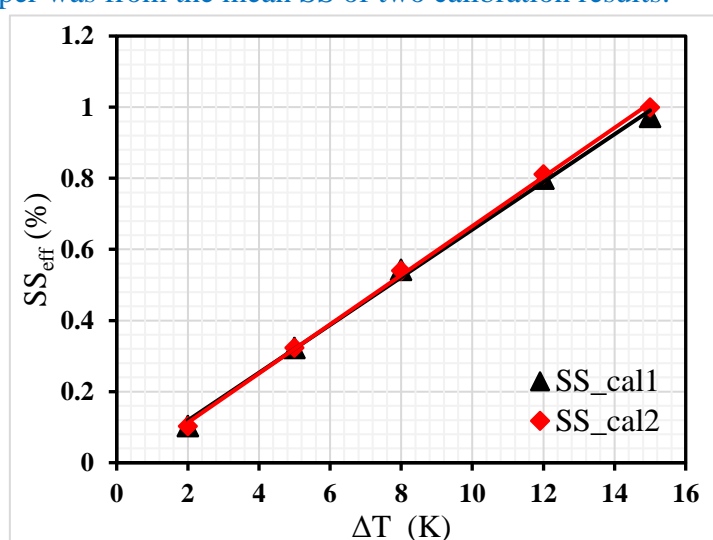


Figure 6. The results of SS calibration experiments with ammonium sulfate: CCN efficiency spectra measured at 5 different temperature gradient (ΔT). SS_cal1 and SS_cal2 are the calibration results before and after the campaign respectively.

L183: AR defined in the manuscript is determined both on chemical composition and PNSD. I suggest using critical diameter.

Re: The critical diameter ($D_{0,crit}$) used in this study was derived from the hygroscopicity parameter (κ_{chem}), not measured directly. AR is used for a preliminary analysis of its relationships with nucleation events and PBL height. In the further campaigns, we will conduct the size-resolved CCN measurements through connecting DMA and CCNc. The critical diameter will be retrieved from size-CCN data, which can study the relationships in detail.

L235: I guess here the authors mean the kappa- S_c relationship.

Re: The relationships of κ , S_c ($S_c = s_c - 1$) and D_d is shown in Fig.1 in Petters et al. (2007). Actually, the D_d is the critical diameter corresponding to the critical supersaturation when κ is known. Therefore, here we first establish the s_c - D_d relationship, not κ - s_c relationship.

L246: How do the authors define the mean diameter.

Re: Here the mean diameter is the geometric mean diameter (D_m). It is defined as:

$$D_m = \frac{\int_{15\text{nm}}^{685\text{nm}} n(\log D_p) D_p d\log D_p}{\int_{15\text{nm}}^{685\text{nm}} n(\log D_p) d\log D_p}$$

We found a mistake in its calculation previously, now it has been corrected in the revised manuscript for which we are very grateful to the reviewer.

L261: Is there undefined species? Maybe the authors can do a simple mass closure between ACSM and SMPS data by assuming a typical aerosol density in that region, to check if there is anything missing in the aerosol mass defined by ACSM. This is important since the authors use this data later to estimate kappa.

Re: The mass closure between ACSM and SMPS is hard to realize because aerosol density and morphology are unknown during this campaign. Even so, we try to do a simple mass closure according to the suggestion of the reviewer. Here we assume aerosol particles are spherical and the density is 1.6 g/cm^3 . The closure result (Fig. 8 in this reply) shows the two masses are related dependent on time. For most of the time, their correlation is good although the SMPS mass was always lower than that of ACSM+BC. The biases are likely caused by different measurement size range, and the variations of aerosol density and morphology.

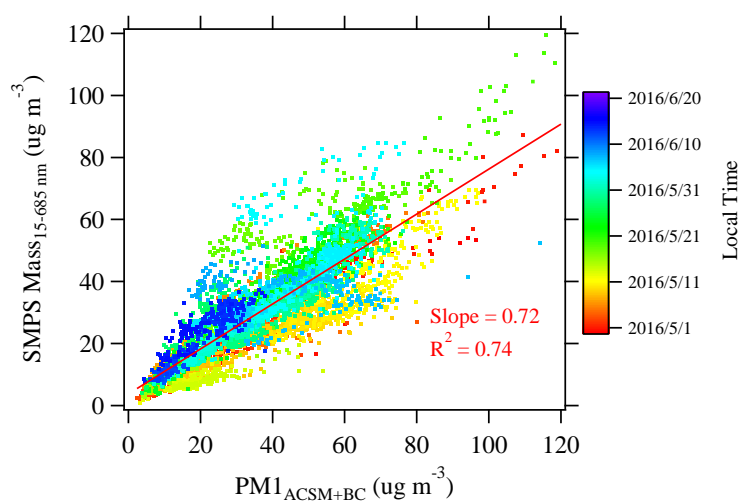


Figure 7. Comparison of the mass concentrations of PM₁ (=NR-PM₁+BC) with those derived from SMPS measurements ($D_p = 15\text{-}685 \text{ nm}$).

L267: How did the authors assume the kappa for HOA, SOA and OOA?

Re: The gravimetric densities (ρ) and hygroscopicity parameters (κ) of all species used in this study for CCN closure (note: POA = HOA+COA, SOA = OOA).

Species	NH_4NO_3	$(\text{NH}_4)_2\text{SO}_4$	NH_4HSO_4	H_2SO_4	POA	SOA	BC
$\rho \text{ (kg m}^{-3}\text{)}$	1720	1769	1780	1830	1000	1400	1700
K	0.67	0.61	0.61	0.9	0	0.1	0

L277: the hydrophobic mode locates at kappa of 0.05 for Dd of 40 nm, and shift towards 0 for large particles. Do the authors have any explanation on this?

Re: The direct comparison of the κ -PDF is depicted in Fig. 9 in this reply. There is an obvious difference of the hydrophobic mode as the reviewer found. This is related to the different chemical compositions. The hydrophobic mode of 40-nm particles is mainly caused by organics, while that of the larger particles is mainly caused by BC. BC is fully hydrophobic but some organics has a limited water uptake ability. This can be verified from previous studies, Wu et al., (2017) reported the fresh emitted BC are mainly in the accumulation mode.

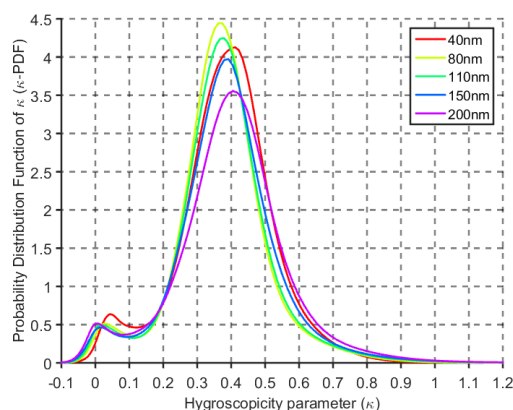


Figure 8. Comparison of κ -PDF of different size particles.

L305: the difference decreases with increasing size because most of the larger particles are well aged.

Re: Good point. We have added the corresponding expression.

L316: of precursors

Re: We have corrected.

L316: is there trace gas (SO₂, NO_x etc.) measurement during the campaign to support the hypothesis here?

Re: Yes. Figure 10 in this reply shows the diurnal variations of trace gases and meteorological variables (T and RH) in this campaign. Affected by the mountain-valley wind, prevailing winds shifted from the northwest to the southeast in the early morning. There are more industrial emissions to the southeast of the measurement site than to the northwest. Therefore, the CO, SO₂ concentrations increased sharply in the morning after the wind shift. The increased CO suggests the increase of VOCs because of their similar sources. The O₃ concentration increased gradually after sunrise during the day, reflecting the enhancement of atmospheric oxidation capacity. The ample supply of effluent SO₂ and VOCs precursors and the strong atmospheric oxidation capacity under high RH and low T conditions made plenty of sulfate and SOA produce (Wang et al., 2016; Wang et al., 2017). This is the reason in the frequent occurrence of NPF events and the enhancement of aerosol hygroscopicity during the daytime at XT.

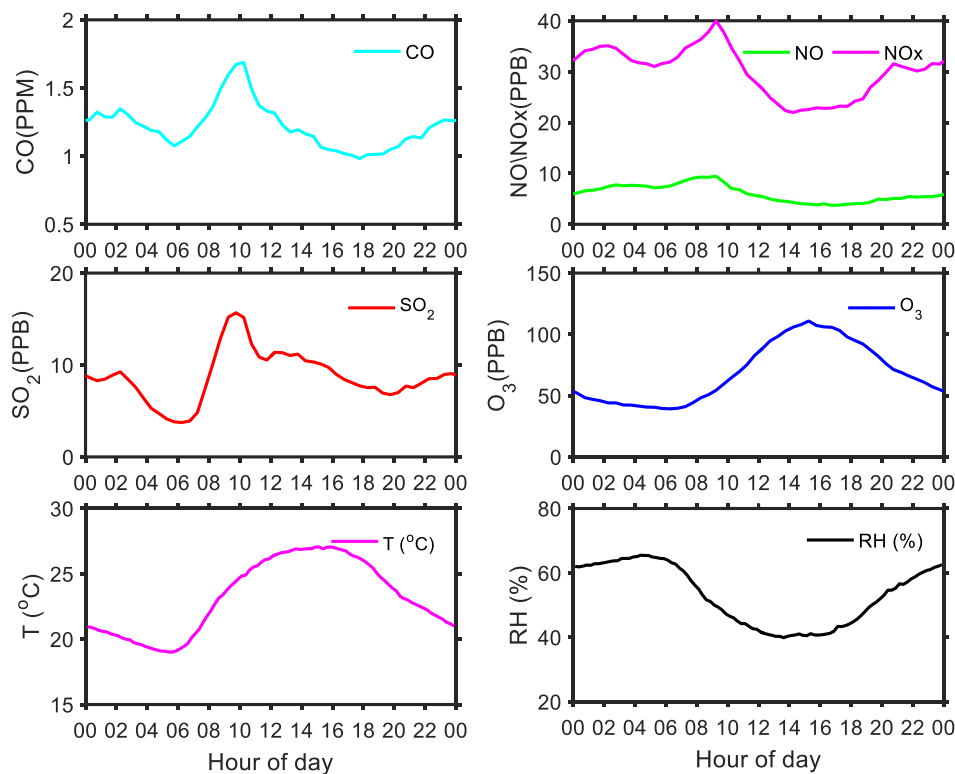


Figure 9. Diurnal variations in trace gases (CO, NO_x/NO, SO₂ and O₃) and meteorological variables (*T* and RH).

L346: 100 nm is too much for nucleation mode.

Re: It has been corrected as “small Aitken mode particles (< 50 nm)”.

L359: From Fig. 6 it seems kappa already starts decrease at 12:00. The secondary aerosol production is also active in the afternoon (Fig. 7b). Why does kappa for larger particles decrease?

Re: This is related with the local emissions, especially the emitted organics. As is shown in the diurnal variations (Fig.2 in this reply), the primary organics (COA and HOA) increase sharply near noon. This is the reason why κ has a short-time decrease at near 12:00.

L360: in Fig. 6c, kappa of larger particles also reaches ~ 0.4 around noon, which is also very close to that of pure AS. But from Fig. 6d we can see there is still a large fraction of hydrophobic and less-hygroscopic species.

Re: As discussed in section 4.2, aerosol particles in this site were highly internal-mixed and aged. κ -PDF for all size particles showed only one hydrophilic mode during daytime although there was still a large fraction of hydrophobic and less-hygroscopic species. This is because the condensation of sulfuric acid on organics or BC can greatly enhance their hygroscopicity (Peng et al., 2016; Zhang et al., 2017).

L370: the growth of the newly formed particles is also driven by condensation of sulfate and organics.

Re: Yes, we have corrected.

L374: why does the PM1 composition differs largely from 40-200 nm particles? 200 nm is in the accumulation mode which is the main contributor of PM1 mass. So I

would not expect a large difference between κ_{chem} and $\kappa_{\text{gf},200\text{nm}}$.

Re: The reviewer is right. We have deleted the expression “the bulk chemical compositions of PM₁ and of 40–200 nm particles differ greatly” in the manuscript. The difference was mainly induced by the simple ZSR mixing rule. This feature was stronger at noon when atmospheric oxidation and the aging process were more rapid. We have studied this phenomenon deeply in another paper (Zhang et al., 2017).

L387: Use critical diameter in stead of AR in this section.

Re: As mentioned above, we did not take size-resolved CCN measurement in this campaign, so critical diameter cannot be got directly. We will do the work in the future campaigns.

L394: the number concentration of fine particles. . .

Re: We have corrected.

L400: I do not think one can get this conclusion based on the discussion in this section. The result is in consistent with it but can not directly prove it. Also I think the paper of Dusek et al., (2006) should be cited here. Dusek U, Frank G P, Hildebrandt L, et al. Size matters more than chemistry for cloud-nucleating ability of aerosol particles[J]. Science, 2006, 312(5778):1375.

Re: Figure 11 in this reply depicts the sensibility tests of aerosol size distribution and chemical composition to the CCN number concentration estimation, which are similar with that of Dusek et al., (2006). The figure shows the closure correlation using mean NASD (normalized aerosol size distribution) is weaker than that using mean κ_{chem} , reflecting the more important effect of particle size for aerosol CCN activity than chemical composition. We have added the figure in the supplement and cited this paper in the revised manuscript.

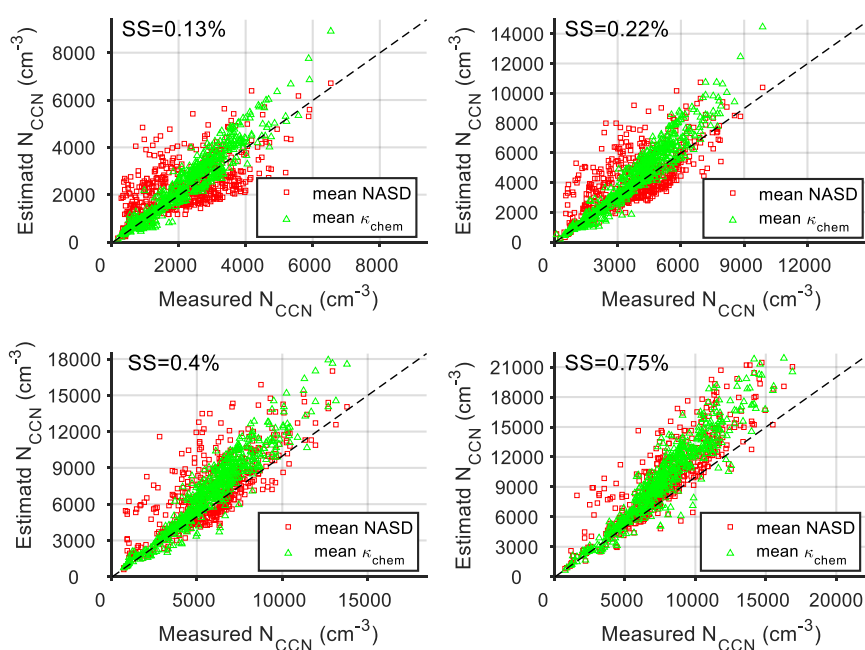


Figure 10. Correlation between the measured and estimated CCN number concentration. The later was from the mean NASD (normalized aerosol size distribution) but variable composition (κ_{chem}) or using the mean κ_{chem} but variable NASD.

L407: the critical diameters of aerosol for SS from 0.07% to 0.80% range from about 30 nm to 200 nm. As shown in Fig.6, there is a large difference between κ_{chem} and κ_{gf} and the authors claimed that PM1 composition “differ greatly from 40-200 nm particles” (L374). It means one can not use the PM1 composition in the CCN closure. I think a better way might be to compare the κ obtained from HTDMA and CCN measurements. Although some species may exhibit different κ in sub- and super-saturation, at least the two measurements are in the same size range.

Re: The related expression “PM₁ composition differ greatly from 40-200 nm particles” is not appropriate, which has been deleted in this manuscript. The κ closure from HTDMA and CCN data is useful to analyze the aerosol hygroscopicity in detail. However, it cannot be realized in this campaign because no size-resolved CCN data. It will be done in the future campaigns.

L434: From this paragraph what I understand is, 0.31 is the average κ_{chem} and calculated N_{CCN} is not sensitive on the variation of κ_{chem} . But how can you make sure that 0.31 is a good proxy for the calculation of N_{CCN} in XT? You found some discrepancies between the calculated and measured N_{CCN} and claimed that there are some biases in measured N_{CCN} . So, there is no reference to check which κ value is appropriate. Normally, water depletion effect can be neglected if $N_{\text{CCN}} < 1e4$. Maybe you can try to do the fit for data points $< 1e4$ and $> 1e4$ separately.

Re: Figure 8 in the manuscript shows there is a limited difference for the CCN closure using variable or mean κ_{chem} , so N_{CCN} is not sensitive on the variation of κ_{chem} . 0.31 is only a reference value for people who need to calculate the CCN concentration in this region in their models. As the reviewer says, the CCN closure can be categorized according to N_{CCN} . Actually, the measured N_{CCN} is biased when $N_{\text{CCN}} > 5500 \text{ cm}^{-3}$ (Fig. 12 in this reply), this is coincident with the report from DMT-CCNC manual. Figure 12 in this reply also shows the CCN closure is very good when $N_{\text{CCN}} < 5500 \text{ cm}^{-3}$, reflecting the validation of the closure method used in this study.

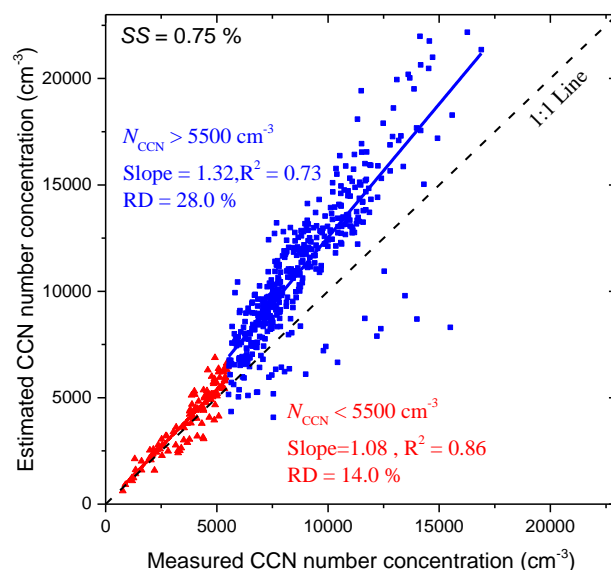


Figure 11. Estimated versus measured CCN number concentrations at SS = 0.75 %. The N_{CCN} is estimated based on κ -Köhler theory, using the real-time κ_{chem} . Here, the critical value of $N_{\text{CCN}} = 5500 \text{ cm}^{-3}$ is used to separate the points into two groups. A separate linear regression analysis is done on each group. The slopes, correlation coefficients (R^2), and relative deviations (RD) are shown in the figure.

L437: the sensitivity of Nccn on aerosol mixing state is not examined in this section.

Re: According to the HTDMA measurement results, aerosols in this region are highly internal-mixed and aged. Therefore, we directly assume aerosols are internally mixed when calculating the CCN number concentration as description in section 3.2.

Another work of our group have suggested the mixing state had a minor effect for the CCN estimation in Beijing (Ren et al., 2017).

References:

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