

Interactive comment on “Aerosol hygroscopicity and CCN activity obtained from a combination analysis based on size-resolved CCN and aerosol chemical composition observations during the AC3Exp13 campaign” by F. Zhang et al.

Anonymous Referee #1

Received and published: 1 July 2014

General comments: The paper “Aerosol hygroscopicity and CCN activity obtained from a combination analysis based on size-resolved CCN and aerosol chemical composition observations during the AC3Exp13 campaign” by F. Zhang, et al. 2014 provide a new data set in the southeast area of Beijing, China. The authors present useful observations on chemical composition, size distribution or mixing state of aerosol, and the results are consistent with the previous studies. However, the data analysis provides only qualitative explanation, which is known by previous studies. The paper titled “a combination analysis based on size-resolved CCN and aerosol chemical composition observations”, however authors did not clearly demonstrate the advantage of using size-resolved measurements. Authors may consider providing more analysis/discussion which separates aerosol size effect with its chemical composition effect by size-resolved measurements.

Re: The reviewer made a good point. By using size-resolved CCN data, CCN activity can be investigated for aerosol particles with different size range. However, we cannot separate aerosol size effect with its chemical composition effect only based on size-resolved CCN measurements. To do this, size-resolved chemical composition data (measured by high resolution AMS) are required at least. We feel a little pity for that we are not able to do this in this paper due to the lack of such measurements and dataset (size-resolved chemical composition data) during the campaign. That’s just why we provide more qualitative explanations on impacts of chemical composition on CCN activity. However, based on the limited data in the region, we have shown some interesting results and highlighted the importance of aerosols chemical composition on determining the activation properties of aerosol particles, which was not taken into account in previous/early literatures conducted in the North China Plain. Recently, we are planning size-resolved chemical composition measurements combined with size-resolved CCN measurements in the region (probably in Beijing). Thus, some more quantitative analysis and results would be expected in our future papers.

In addition, the closure study shows that NPO test has a similar or may even better agreement between CCN_estimation and CCN_measurement than PO closure test. That is odd to reviewer.

Re: Thanks a lot for reviewer pointing this and thus let us to check and revise the data again, including multiple charge correction and transfer function which are applied for each CN size distribution spectrum as well as CCN efficiency spectrum in the revision. Then, the CCN efficiency spectrum fitted by CDF method as well as the three parameters (MAF, Da and σ) is revised. Finally, we used the revised activation ratio curve and calibrated CCN number concentrations to do the CCN closure test. Fig 5 and Fig.6 show the revised results of PO and NPO closure tests. If we just look at the closure results at SS>0.2%, although the slopes for both PO and NPO closure tests don’t show significant differences, the correlations (R^2) for NPO test is much worse than PO test at a given SS. The lower correlation in NPO test just indicated that about 30%-40% uncertainties in N_{CCN} prediction are

associated with the changes of particle composition.

At lower SS, particles will activate at larger size and it is supposed their chemical composition will be closer to ACSM measurement. Why lower correlation exhibited at lower SS?

Re: One reason for the slight worse closure between measured and estimated CCN number concentrations at lower SS lies in that size-resolved activation ratios exhibit a larger variability at low SS than that at higher SS. Also, compared to the activated CCN number concentrations at high SS, the N_{CCN} is with a less amounts at low SS, which would lead to larger uncertainties in CCN prediction.

Specific comments:

Page 6, Line 3-6: the field campaign was mainly conducted in June and July, 2013.

However, the results are presents in different periods without clearly stating the criteria for selection. For example, figure 1 is for 07/07-07/21/2013, figure 3 is for 07/07-07/19/2013, and figure 9 is for 06/19-06/24/2013. Please clarify.

Re: In the campaign, aerosol particle size distribution (10-700 nm) and bulk CCN activation were measured from 1 June to 25 June 2013. Size-resolved CCN was measured from 7 July to 21 July 2013. Aerosol chemical composition was measured from 31 May to 30 June 2013. Therefore, the CCN efficiency spectra (Fig. 1) are derived from the size-resolved CCN observation from 7 July to 21 July 2013. The aerosol particle size distribution data measured from 1 June to 25 June 2013 combing with the derived CCN efficiency spectra (Fig. 1) is used for NPO CCN closure test. We have clarified this in the revised version (see Page 7, lines 5-17). In Fig. 9, an example (or case) for temporal variations of bulk AR at SS of 0.5%, derived κ_{chem} and N_{CN} from a few days (19-24 June) during the observed periods is given.

Page 6, Line 17: what is the inlet RH for CCN?

Re: the inlet RH for CCN is <30%, which has been included (see Page 7, line 21).

Page 7, Line 10: Need more information on BC analysis, because BC probably is the main source for externally mixed inactive CCN.

Re: The campaign averaged mass concentrations of BC are $\sim 4.2 \mu\text{g m}^{-3}$, and the averaged mass fractions are about 6%, with maximum of 18% and minimum of 2%. However, after doing the revision and analyzing the data more carefully, we have derived more confident explanations and suppose on the composition and mixing state of aerosol particles during the campaign. The revised results suggest the aerosols are with fewer portions of externally mixed particles than that previously derived.

Page 7, Line 20: the criteria of clean day and pollution day is little weak. May consider include gas phase measurement and meteorology data, such as wind directions.

Re: In the revision, we have examined the synchral winds to classify the data as background and pollution conditions. Basically, the polluted conditions are with $N_{CN} > 15000 \text{ cm}^{-3}$ when the airflow came from southeast/east and the background cases are with $N_{CN} < 15000 \text{ cm}^{-3}$ always associated with the winds from west or northwest.

Page 8, line 2, page 12, section 4.1.1, and Table 1: It is expected that D_{cut} is larger than D_a . But at SS=0.079% in table 1, D_{a_POL} is larger than D_{cut_POL} . Why?

Re: thanks a lot for the reviewer's careful check. We just checked and revised the data again. In the revised version, the parameters have been recalculated in Table 1, and also the standard deviations of some parameters, e.g. Da_POL, Dcut_POL, Ka_POL, Ka_BG, etc., have also been added in Table 1.

Page 11, line 11-14: it is not true. With MAF only, you can not characterize aerosols with homogeneous composition and a core-shell structure aerosols may has MAF = 1.

Re: Yes, the reviewer is right. We just corrected this point in the revised version (see Page 15, line 23; and Page 16, lines 1-2).

Page 12, Line 1-3: With increasing SS, the aerosol particle critical activation size changes too. With ACSM measurement, authors can only get bulk chemical composition and chemical composition varies with aerosol size. The conclusion maybe ture, but cannot draw from the differences of AR. In addition, Kuwata et al. paper was published in 2007.

Re: In a new version of the paper, we have revised this.

Page 12, section 4.1.2: the discussion here is not consistent with figure 1. In figure 1, the average AR at 0.109% is around 0.6 for POL and 0.8 for BK cases. The substantial portion of externally mixed CCN-inactive particles is around 20-40%, not 14-22%. The significant increase of MAF at POL case suggests that there is a large variability in mixing state at different size particles. What do authors mean by "a higher sensitivity of particle MAF dependence on SS"?

Re: "a higher sensitivity of particle MAF dependence on SS" just means that MAF would be very different for different SS. However, the point has been revised in the paper.

Page 14: Line 23: for particles at size range of 30-60 nm, kappa for polluted particles is high than clean aerosols. Why? Is clean case supposed to have more aged aerosols? Or does that mean the fresh biomass burning aerosol has higher kappa?

Re: the reviewer makes a good point. Although we cannot figure out accurately and definitely why the kappa for polluted particles is higher than clean aerosols, it's really interesting. For background days, larger particles were on average more hygroscopic than smaller particles. This result is consistent with most of field observed results. However, κ_a at polluted cases exhibited relatively flat trend. It didn't exhibited significant increase but with larger error bars around a given D_p , suggesting the complex and diversities of particle compositions and their mixing state at polluted cases. In this case, larger particles are even less hygroscopic than the smaller particles. We think one of the possible reason for the changes of κ_a at polluted cases may be due to the high organics freshly emitted from biomass burning, which would coat on those larger particles and then lead the particles with less hygroscopic. Overall, κ for polluted aerosols are about 20% lower than that of clean aerosols for particles in accumulation size range; but for these particles in nucleation or Aitken size range, κ_a for polluted particles is slightly higher than that at background cases. Based on laboratory experiment, Petters et al., (2009) examined the hygroscopic properties of particles freshly emitted from biomass burning. They found that κ was a function of particle size, with 250 nm particles being generally weakly hygroscopic and sub-100 nm particles being more hygroscopic. During the campaign at Xianghe, the biomass burning aerosols are the lead particles for the selected polluted cases. The laboratory results,

to some extent, can thus explain our field measurements. But further investigations including laboratory experiments and field measurements of size-resolved chemical composition are needed to confirm and clarify this.

Figure 2, Is the data presented here are average of whole campaign? Please add error bar or uncertainty estimation.

Re: Yes, the data presented in Figure 2 are average of whole campaign during background and polluted conditions. The error bars (with one standard deviation) have been added in Figure 2.

[Interactive comment on Atmos. Chem. Phys. Discuss., 14, 14889, 2014.](#)

Anonymous Referee #2

Received and published: 31 July 2014

This manuscript describes a CCN activity in highly polluted location as observed at the Xianghe Atmospheric Observatory, China, and presents the analysis of the aerosol size and chemical composition effects on the CCN activity. While the data set is interesting and could provide new information, especially considering the location, the analysis and discussion is lacking clarity and thoroughness.

General comments

The fact that MAF is always significantly below 1 raises some questions, it well may be due to externally mixed hydrophobic particles as explained by the authors; however, this has to be proven. First of all, it should be shown or at least checked if MAF is equal to 1 for the calibration particles (e.g. ammonium sulphate) at high number concentrations (~25000). This would rule out effects of water depletion and system setup. Once this is proven, an evidence or indication that externally mixed fresh black carbon particles were present during these observations should be provided. Actually, black carbon is not even mentioned here, some vague explanation of "externally mixed particle composition" ((page 14901, L 19) is presented, which, to my opinion, is not enough to prove such a significant effect.

Re: the reviewer made a good point regarding our paper's revision. The comments from the reviewer just let us to check and revise the data again, including multiple charge correction and transfer function which are applied for each CN size distribution spectrum as well as CCN efficiency spectrum in the revision. Then, the CDF fit curve as well as the three parameters (MAF, D_a and σ) is revised (see Fig. 1 and Table 1). Because the effect of water depletion is so small that it can be neglected. And also MAF is actually equal to 1 for pure ammonium sulphate particles (0.05mol L^{-1}). Furthermore, the observations have indicated that particles can be able to activate to CCN completely when $D_p > 300$ nm even at $SS = 0.08\%$. Therefore, a smaller portion (1-MAF, 2-6%) (in Fig 1) is just caused by an error of CDF fit method which will lead to lower MAF than it should be.

Also, the paragraph 4.2 on κ dependency on D_p requires more details. What is D_p in this case? How the dependency is derived? I assume it is the same D_p as in Figure 4. If data

presented in figure 2 are averages of the data shown in Figure 4, then I see some inconsistency, which has to be verified: $\kappa_{\text{cut_POL}}$ at $D_p=163\text{nm}$ would average out to ~ 0.46 , which contradicts the number presented in figure 2 (<0.4), but would be in line with other kappa's at different sizes and there would be no more reduction in kappa with D_p ... I may be wrong, but this should be checked. In any case, one should be cautious by basing the conclusion on one point, which seems to be outlier. However, if you trust this point and think that it is outside a kappa uncertainty range, then it should be shown and proven in this paragraph.

Re: The D_p in the previous version of Figure 2 is D_a and D_{cut} , which we used to derive the κ_a and κ_{cut} . Thus, in Figure 2, that's just κ_a dependency on D_a , and κ_{cut} dependency on D_{cut} . We have clarified this in the revised paper. In the revised paper, Figure 4 showed the PDF of κ_a . Therefore, the PDF of κ_a in Figure 4 should be consistent with the κ_a showed in Figure 2. I

The potential of information on chemical particle composition has not been fully used here. κ_{chem} differs from other kappa's derived in this paper, which is attributed to incorrect kappa used for the organics, then why not to try different and correct kappa's? Why not to link organic kappa with f_{44} , especially that authors indicate AF dependency on f_{44} in polluted cases.

Re: In the revised paper, we used a linear function between κ_{org} and f_{44} derived by Mei et al., (2013) to estimate the κ_{org} in our study. The formula is written as $\kappa_{\text{org}} = 2.10 \times f_{44} - 0.11$ (Mei et al., ACP, 2013). By applying the function, calculated κ_{org} is 0.115 ± 0.019 during the observed period. Then we used the estimated κ_{org} to calculate κ_{chem} .

Figure 5 indicates two modes, at least for the background κ , thus two values at ~ 0.35 and 0.45 would be consistent with figure 2, which shows different kappa at different sizes. Could you check if this would be consistent with particle size distribution: if lower κ_{chem} occurs for the events dominated by smaller particle mode and vice versa – larger κ_{chem} for particle distributions dominated by larger particles (size distributions could be obtained from concurrent smps measurements).

Re: the reviewer's suppose is right. However, we just looked the data and plotted the time series of κ_{chem} and N_{CN} for Nuc., Ait and ACC modes particles (see below). No obvious correlation between κ_{chem} and particles size was observed. We think that two reasons can well explain this: Firstly, it can be seen from the Figure 2, κ_a increased with the D_p at background conditions, while they didn't change much along with the particles size under polluted events (with high N_{CN}). In other words, larger κ_{chem} is not always dominated by larger particles in such cases. Second, κ_{chem} estimated in this paper are a bulk hygroscopicity parameters, each κ_{chem} derived at every observed time indicated overall averaged hygroscopicity of the particles with particle size <1000 nm (PM1.0). Thus, the relationship between κ_{chem} and particle size is complex. Size-resolved chemical composition data can well address this issue. As we stated earlier, we are planning size-resolved chemical composition measurements combined with size-resolved CCN measurements in the region (probably in Beijing). Thus, some more quantitative analysis and results would be expected in our

future papers.

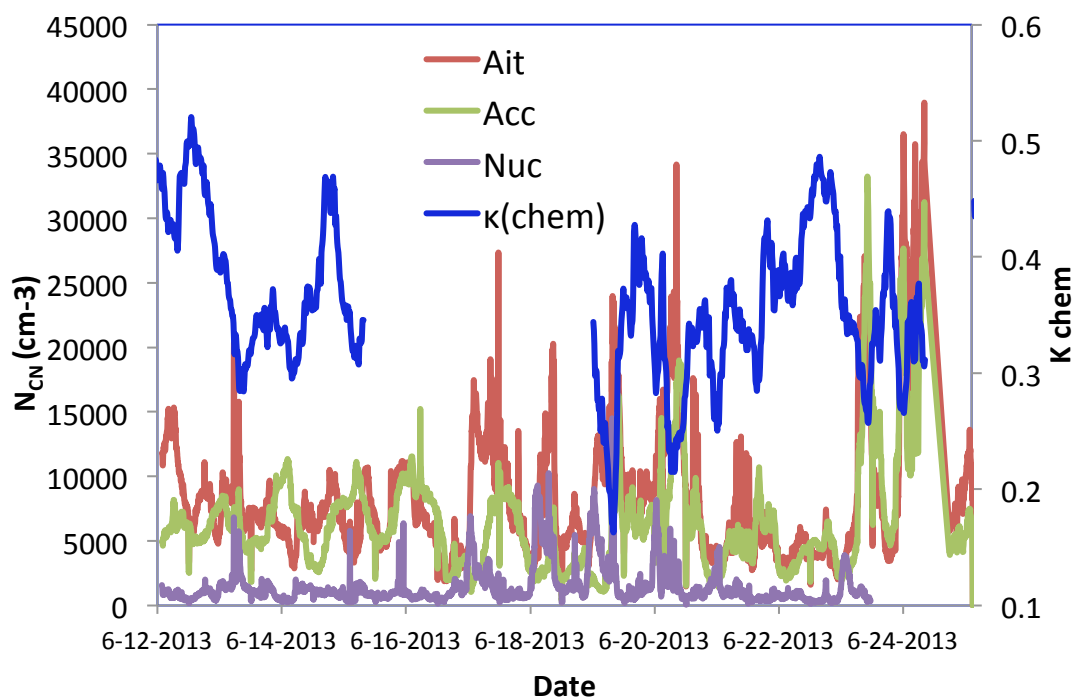


Fig 1s Time series of K_{chem} and N_{CN} for Nuc., Ait and ACC modes particles

The whole paragraph on chemical composition (4.6) is very qualitative, it requires more quantitative approach: I suggest the authors provide scatter plots with proper statistics, or at least quantify "high correlation", "well correlated", "moderate correlation". Time trends are not enough for proper analysis.

Re: Thanks for the suggestions. In the revised version, we have included a scatter plot (Fig. 8) to address the correlation of K_{chem}, f₄₄ and AR under background and polluted conditions.

Specific comments:

P14895 L3 and L13: RH range should be specified.

Re: revised (see Page 8, lines 11-12).

P14896 L1: More details on ACSM operation should be provided, e.g. collection efficiency applied in this study; information on the inlet: particles were or were not dried; calibrations.

Re: Some more details regarding the ACSM measurements have been included. (see Page 8, lines 19-25; Page 9, lines 1-15).

P14896 L11: Specify N_{cn}, what were the lowest and highest size limits?

Re: in this study, we used a SMPS to measure aerosol particle size distribution with size range of

10-700 nm. Thus, the N_{CN} is aerosol number concentrations with particle size range of 10-700 nm.

P14899 L14: Why sea salt and dust are expected to be negligible for the size range of < 500 nm? Give some more information, discussion, references.

Re: revised. (see pages 13, lines 11-15)

P14899 L15: Define size (mobility diameter, vacuum aerodynamic?) why 10-500nm if ACSM measures 50-1000 nm, I guess it is in D_m , but it should be specified.

Re: revised. Here the 10-500 nm is just a written mistake, it has been corrected. (see page 13, line 14).

P14903 L17-18: This sentence is confusing – reduction due to good activity?

Re: revised.

P14905 L17: To me the range is 0.15-0.52 as shown in Figure 5.

Figure 5: Include a description of the red line at 0.3 and fittings into the caption.

Re: Yes, the reviewer is right. But, K_{chem} estimated in this paper are a bulk hygroscopicity parameters, each K_{chem} derived at every observed time indicated overall averaged hygroscopicity of the particles with particle size <1000 nm (PM1.0). But κ_a and κ_{cut} derived from size-resolved CCN measurement refer to the particle hygroscopicity parameter at a given D_p . The comparison between κ_{chem} and κ_{CCN} (κ_a and κ_{cut}), to some extent, is thus not such reasonable. One probably can compare the campaign mean K_a averaged by all the K_a at different size diameter with the mean K_{chem} . In the revised paper, we removed the PDF of κ_{chem} in section 4.4. In section 4.6, we will focus on examining the relationship between bulk AR, f_{44} and κ_{chem} , trying to understand the impact of chemical composition and particle size on aerosol hygroscopicity and CCN activity.

P14908 L8, L11, L25, L24 and others: define goodness with R or R2.

Re: revised. (see Pages 21-22, Fig. 8)

P14910 L22-23: this sentence is confusing- smaller particles were more aged and coated than larger particles? It requires better explanation.

Re: revised. (see Pages 18-19). For these particles in nucleation or Aitken size range, κ_a for polluted particles is slightly higher than that at background cases. Based on laboratory experiment, Petters et al., (2009) examined the hygroscopic properties of particles freshly emitted from biomass burning. They found that κ was a function of particle size, with 250 nm particles being generally weakly hygroscopic and sub-100 nm particles being more hygroscopic. During the campaign at Xianghe, the biomass burning aerosols are the lead particles for the selected polluted cases. The laboratory results, to some extent, can thus explain our field measurements. But further investigations including laboratory experiments and field measurements of size-resolved chemical composition are needed to

confirm and clarify this.

P14910 L13: Provide a reference for the typical atmospheric SS of 0.4 %.

Re: in the revised version, such saying has been removed.