Anonymous Referee #1

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General comments:

The paper “Challenges of parameterizing CCN due to changes in particle physicochemical properties: implications from observations at a suburban site in China” by F. Zhang, et al. 2015 provide more surface measurement dataset in China. The authors present useful observations on CCN activation properties and the results are consistent with the previous studies. However, the paper is lack of the discussion on what affects CCN properties, such as distinguishing the effect of chemical composition from size distribution or mixing state of aerosol. Thus, the results and conclusion are not new and expected from previous studies. Authors may consider providing more analysis/discussion which separates aerosol size effect with its chemical composition effect.

Re: The reviewer made a good point. In the previous version of this paper, we mainly focus on examining the influence of extremely high volume fraction of organics on CCN prediction in polluted area of China, to our knowledge, which have not been examined in the region. However, in the revision, the sensitivity of both the volume fraction organics (x_{org}) as well as oxidation level (using f_{44}, the fraction of m/z 44 in total organics, as an indicator) of organics on estimating N_{CCN} is examined (see Section 4.4).

But as proposed by the reviewer, to separate aerosol size effect with its chemical composition effect is the key point to study the relative importance of size and composition impact on CCN activity. We are now drafting another paper and mainly concern the impacts of chemical composition and mixing state on CCN activity by using size-resolved chemical composition data measured by AMS as well as size-resolved CCN data measured by SMPS-CCNc. In the paper, we will distinguish the effect of chemical composition from size distribution or mixing state of aerosol.

In addition, the figure 1 shows the maximum activation fraction is around 0.9 for both sites, but in the paper by Zhang et al. 2014, the table 1 shows that MAF is larger than 0.94%. Please explain the inconsistency.

Re: there are two reasons can explain the inconsistency: firstly, the CCN spectra here are plotted by the observed campaign averaged values, but in the paper published previously, we plotted the fitted curve by using CDF method at both background and polluted cases; secondly, a further calibration and correction method was applied to the data, which forced the AR values to 1 if it is higher than 1when the Dp>300 nm, and thus leading to slight lower MAF. This treatment we think is more reasonable for that the large particles should be activated but the AR would never be larger than 1.

Specific comments:

P16143, Line 10-15, P16154, section 4.3.2: When author mentioned PSD effect was examined, how does author exclude the chemical effect/mixing state effects? If you cannot separate those effects, it is impossible to exam the influence of the PSD on Nccn estimation.

Re: This section is with the aim to examine the impact of variation of PSD on the CCN number concentration. Thus, the campaign averaged PSD (not changed along with the time) is used for calculating CCN number concentrations by multiplying the time dependent CCN spectra (changing of CCN spectra can indicate the variation of chemical composition and mixing state).

P16146, section 2, line 14: what do you mean "relatively little"? Is it occasionally local interference? If so, was the data screened? What percentage of the data is screened? Do they happen in the same pattern? Such as all in the morning?

Re: here it means that the site is with very little influence from the local vehicles and industries. The data points, which are probably due to the local vehicle or industrial emissions, account for <1% during the campaign. Here, we focus on the chemical and physical impacts on the CCN activity but the variations of CCN and aerosol particles, thus we didn't distinguish the data as like local influenced or regional background. However, the invalid data, which are due to the instrumental problems, were removed. We do observed diurnal cycles of N_{CN} during the observed periods showing high level of N_{CN} usually presenting at about 11:00-12:00, which we think was closely related to the new particle formation events. We are drafting another paper mainly concerning the impacts of new particle formation on CCN activity.

P16148, line 7: what the mass concentration from ACSM? Is the BC concentration significant comparing the rest of chemical compositions?

Re: the campaign averaged mass concentration of PM1 by ACSM is 31.6 μg m^{-3}.The mass concentration of BC, which was measured by a seven-wavelength aethalometer (Model AE31), was ~2.5 μg m^{-3} during the campaign. Thus, compared with the other chemical composition measured by ACSM, BC mass concentration is much lower.

P16148, line 16-20, What is the percentage of valid data? Is there a time pattern for the invalid data appearance?

Re: the valid data account for about 80% during the whole campaign. We didn't observe an apparent time pattern for the invalid data.

P16149-150, section 3, it is almost identical with the paper published in Zhang et al. 2014. Please consider remove it and refer to the paper.

Re: thanks for the comments, some corrections have been made in the section and the paper Zhang et al., 2014 is referred to.

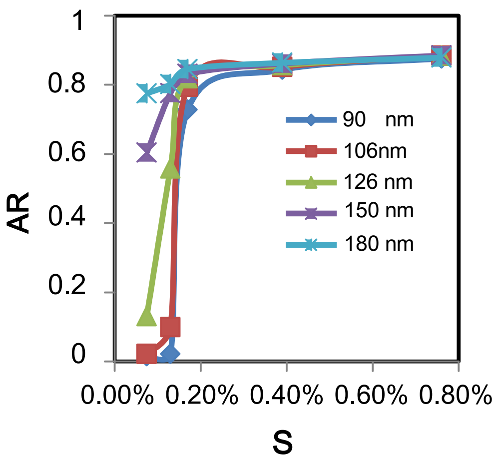
P16151, line 7, because the maximum activation fraction is around 90%, should the cut-off diameter at AR=50% represent the critical activation size?

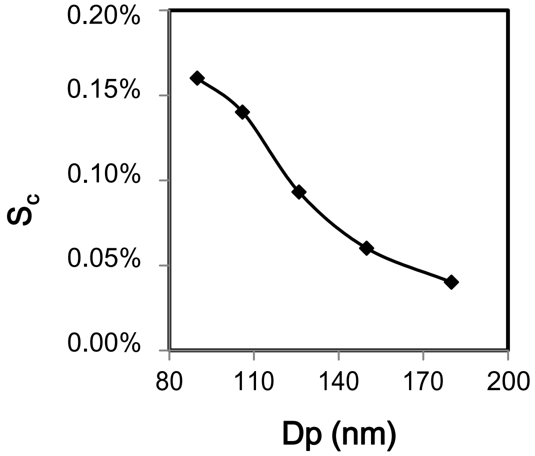
Re: here, we just refer to an ideal case, when all CCN-active particles have the same composition and size, a steep change in AR from 0 to 1 would be observed as D_p reached D_{cut} when AR=50%. However, just as proposed by the reviewer, the actual observed maximum activation fraction (MAF) is around 90%. At the real cases, the $\mathrm{D_{cut}}$ is usually defined as when AR=MAF/2.

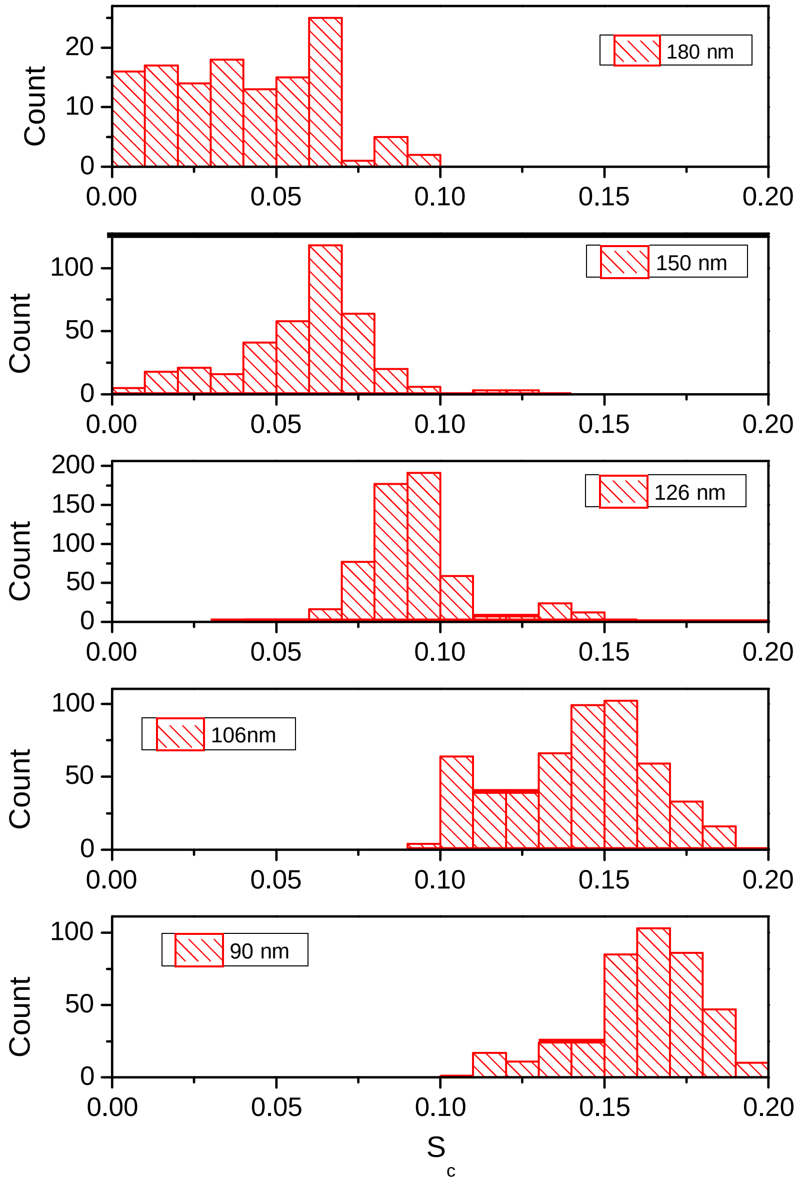
P16151, line 10-15, To discuss the heterogeneous of hygroscopicity of aerosol, it is better to analyze data using supersaturation vs activation fraction. Here is an ex-ample of such discussion:

http://www.atmos-chem-phys.net/13/12155/2013/acp-13-12155-2013-supplement.pdf

Re: thank you very much for the suggestion and giving the example. We just plot data using supersaturation vs activation according to the method in the pdf file. The probability distribution functions (PDFs) of the $\mathrm{S_c}$ for the particles with $\mathrm{D_p}$ of 90 nm, 106 nm, 126 nm, 150 nm and 180 nm are showed in the following figure. PDFs for each $\mathrm{D_p}$ have a wider distribution, suggesting heterogeneous of hygroscopicity of aerosol. But considering the major concern of this paper, we decide not to address this in this paper.


AR
1
0.8
0.6
0.4
0.2
0
0.00%
0.20%
0.40%
0.60%
0.80%
S
90 nm
106nm
126 nm
150 nm
180 nm


S_c
0.20%
0.15%
0.10%
0.05%
0.00%
80
110
140
170
200
Dp (nm)


Count
20
10
0
180 nm
0.00
0.05
0.10
0.15
0.20
Count
100
50
0
150 nm
0.00
0.05
0.10
0.15
0.20
Count
200
150
100
50
0
126 nm
0.00
0.05
0.10
0.15
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Count
100
50
0
106nm
0.00
0.05
0.10
0.15
0.20
Count
100
50
0
90 nm
0.00
0.05
0.10
0.15
0.20
S_c

P16152, line 4-5, what is the height of the back-trajectory running at?

Re: the height is 10 m from the ground.

P16154, section 4.3.2, it is well know that the size effect of aerosol on CCN concentration. If author wants to discuss that, please add more qualitative analysis.

Re: according to the comments from the reviewers, this section was removed in the revised manuscript.

Reviwer#2

Overview -

The authors report measurements relevant to the problem of CCN activation. Their data set contains activated ratios (AR(D)) at six supersaturations (S ~ 0.07, 0.1, 0.2, 0.4 and 0.8%), an assessment of organic aerosol mass fraction (integrated over all particle sizes), ambient aerosol particle size distribution (PSD), and ambient CCN concentration. Comparing measurements made at two locations (Xinzhou in 2014 and Xianghe in 2013), the authors find a difference in the shape of the AR(D) and a difference in the 50% activation dry diameter. Some of the Xinzhou AR's plateau at a value that is significantly less than unity.

What I have summarized (these results are in Figures 1 and 2) is compelling, easy to understand and worthy of publication. However, the presentation that follows (Figures 4, 5, 6, 7 and 8) is difficult to understand. Most perplexing is the use of terminology "estimated Nccn", “calculated Nccn”, “predicted Nccn” and “modeled Nccn” to describe quantities derived from the measurements. As I discuss below, these things need to be described.

Re: the terminologies like “estimated, calculated or predicted ...” in the paper has been unified.

There another issue:

I am surprised the two methods (estimated and observed in Figure 5) do not agree better. I note that there is a bias and that the correlation coefficients (R2) is rather small. Is it possible that coincidence in either the SMPS/CN or in the CCN contribute to this poor agreement? Related to this, Rose et al. (2008) say: “For the calibration experiments, the number concentration of monodisperse aerosol particles was kept below 3×10^{3} cm^{-3} to avoid counting errors caused by coincidence.” The other possibility is that using a campaign-averaged AR(D) may have contributed the discrepancy. Perhaps there are other reasons. The authors should address why the two methods compared in Figure 5 correlate so poorly.

Re: the Figure 5 was with the aim to investigate the influence of the variation in size distribution on N_{CCN}, the actual measured CCN efficiency spectrum is multiplied by a campaign averaged particle number size distribution (PSD) (assuming not changed along with the time), which yields the CCN size distribution. This is then integrated over the whole size range (14-600 nm) to estimate N_{CCN}. But actually, the PSD changed significantly and showed temporal variations, which is the main reason for the poor correlations exhibited in Figure 5. That shouldn't be caused by the instruments. However, after careful reconsideration and revision of the paper, this section just was removed (as proposed by the first reviewer), and the new version will be focused on detection the sensitivity of fraction of organics as well as the oxidization level of organics on estimating N_{CCN}.

Summary -

The manuscript needs to be reworked.

Specific Comments -

Abstract

Isn't there is a contradiction between the statements 1) variation with PSD showed a poor correlation and 2) the PSD played a dominant role?

Re: revised. Please see the above response.

P16146L13-16

Here you say there is little pollution from cars or industry, but in the next sentence there is mention of plumes from Xinzhou. This needs clarification.

Re: thanks for the comments. It has been clarified in the revised version. (Page 6-7, Lines 81-89)

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)?

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.

P16147L29

2.5 mm ?

Re: 2.5 um, 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?

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 ~1.7x10^4 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).

P16148L27

Since Figure 1 shows efficiency curves for both sites, I don't understand why the "campaign-averaged" efficiency was used for this. Do you mean the campaign-average for the Xianghe site? To me it is unclear what the campaign is (both Xinzhou in 2014 and Xianghe in 2013; or just Xinzhou in 2014)?

Re: in Figure 1, the campaign averaged CCN efficiency spectra observed at Xianghe in summer 2013 are showed with black lines, and the campaign averaged CCN efficiency spectra observed at Xinzhou site in summer 2014 are showed with red lines.

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.

P16153L2

Transportation -> transport

Re: corrected.

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.

P16154L9-9

I don’t agree with your statement that the Ji and Shaw (1998) and/or the Twomey (1959) (Nccn = CSk) parameterizations assume uniform aerosol composition. I also do not agree with your assertion that these parameterizations do not take into account variation in CCN loading. For example, you could have taken an _observed_ CCN spectrum (Nccn versus S) and fitted that as a function if S (e.g., Nccn = CSk). That spectrum accounts for the PSD and composition. The issue you mention is relevant only if you do not have a measured CCN spectrum and you proceed, in a model, with a generic “C” and a generic “k”.

Re: yes, the reviewer is right. The paragraph has been rewritten. Some new discussion has been revised and added (see Section 4.3, Page14-15, Lines 268-284).

Figure 1

Symbols and line color (black and gray) are used to designate results obtained at the two locations (Xinzhou and Xianghe). The plot would be much more easily understood if you present with a better scheme for delineating the two stratifications (location and supersaturation).

Re: revised. Thanks for the comments.

Figure 2 – Case #1

Isn’t the behavior seen here (AR < 1 at large diameter) indicative of an externally-mixed aerosol, for example one containing pure soot and hygroscopic particles? Isn’t that worth mentioning/discussing? Isn’t external mixing a complicating factor when it comes to converting the measurements to a CCN spectrum?

Re: Yes, the reviewer proposed the point exactly. We have mentioned this thing in the revision (see Page 13, lines 244-247), but because we didn't measure the mixing state of the particles, we say the low maximum activation fraction (<1) is just an indication of externally-mixed particle, as the reviewer suggested. Of course, the mixing state of the particles would greatly impact the CCN activation. We are now working on a paper, which will concentrate on discussing this issue by using the size-resolved chemical composition data measured by AMS.

P15154L7

What are "bulk ARs"?

Re: bulk ARs means the ratio of N_{CCN} to N_{CN}, 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."

P16154L8

Reference to the specific section of Pruppacher and Klett is needed. Pruppacher and Klett is a huge book.

Re: revised.

P16154L23

In Figure 4 *t*here is no obvious indication of negative correlation in the plotted data, or in the fit lines (all of these have positive slope). If you provided the "R", not R2 (text) and if you defined the "R" (Pearson product moment), that would solve this problem. Also, the Figure legend shows R2 < 0, which is mathematically impossible. All of this needs work.

Re: the Figure 4 has been replotted. For the cases with $R^2<0$, that is because that we used the lognormal axis here.

P16154L25-26

I find this statement of a "CN size distribution" confusing. Isn't this the PSD define earlier. If that is the case you should use a consistent definition throughout. If a distinction is needed, you shoulddefine/distinguish these early in the manuscript.

Re: "CN size distribution" here is just the PSD. Thanks a lot for the comments. This issue has been revised.

P16155L1

This is confusing. If you multiply the CCN efficiency spectrum by the (CN) size distribution, you get a "CCN distribution", but that is only valid for the selected S. I feel more clarity is needed here.

Re: revised. (see Pages 16, lines 306-313 and see Pages 18, lines 358-364)

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 N_{CCN}, 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 N_{CCN} 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 N_{CCN}.

Thanks for the explanation. In the revision, do you explain what you mean by the "observed N_{CCN}"?

P16155L5-6

This is a big jump. Why the would the predicted CCN (you meant estimated, or is "predicted" different?) be influenced by PSD more than it is already? I note that the estimated is the summed product of AR(D) and PSD(D)?

Re: in the early version, we discussed the influence of variations of PSD on CCN estimation. However, the part in the revised manuscript has been removed. (See above comments and response)

P16155L8

Here you are using "calculated" CCN? Is this different from "estimated" CCN and "predicted" CCN? If you mean "estimated CCN", it is not clear how the organic mass fraction is being used in these calculations.

Re: all of them have been changed to "estimated" CCN. The section was revised and some more details regarding to how the organic fraction is being used in these calculations have been included. (see Pages 15-16, lines 292-305)

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 f_{44}, the fraction of m/z 44 in total organics, as an indicator) of organics to estimatimation of N_{CCN} 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 N_{CCN} 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 (N_{CCN}) 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."

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 N_{CCN} is sensitive to aerosol chemical composition, not the other way around.

Another example is L294 (revision).

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

Another example is L396 (revision)

Figure 5

These are single-parameter (slope) fits, I think. Hence, the “linear” used here is a special case of linear. This comment applies to Figures 6 and 8 too.

Re: revised.

P16158L24

Mr. Mcribb’s. Isn’t this Maureen Cribb?

Re: yes. Thanks a lot for the careful check.The sentence in acknowledgement was removed.

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.

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

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

L345 (revision) – misspelled word “usully”)

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

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