Comments by Reviewer #1

Review of acp-2016-570, Alteration of the size distributions and mixing states of black carbon through transport in the boundary layer in East Asia, by T. Miyakawa et al.

The revised manuscript takes into account most of the reviewers' comments on the first version and I recommend that it be published when the items below (most of which are minor) are addressed. There are several instances where the wording is awkward; for these I have made recommendations on alternative wording.

We appreciate the reviewer’s comments on the manuscript entitled “Alteration of the size distributions and mixing states of black carbon through transport in the boundary layer in East Asia”. As the reviewers suggested, we have modified the manuscript.
(Reviewer’s comments in bold)

Major revision points

1. Terminology

The washout and rainout were rephrased by below-cloud and in-cloud scavenging, respectively, as suggested. (We used simply “wet removal” only in Abstract.)

2. More analyses of total particle diameters of BC-containing particles.

We included not only D_S/D_{core} ratio but also D_S in the results and discussion. Figure 7c modified includes the evolution of the peak diameter of number-D_S distribution as a function of the degree of the removal of BC. Removal of large BC-containing particles was clearer in the modified figure than in the previous one. The discussions on the CCN activity of BC-containing particles were included in the revised manuscript. The ACSM-derived chemical composition and physicochemical properties of fine mode aerosols were analyzed to estimate the critical supersaturation (SS_C) as a function of D_S/D_{core} ratio in Figure 8. The estimated SS_C decreases as increases in D_S/D_{core} ratio, which we can easily expect. It is indicated that the relative abundance of BC-containing particles with higher D_S/D_{core} ratio and lower SS_C decreased through the in-cloud scavenging during the observation period. The words “selective removal” in this manuscript were rephrased by simply “removal”, as the BC-containing particles with D_{core} <0.1 μm can be significantly

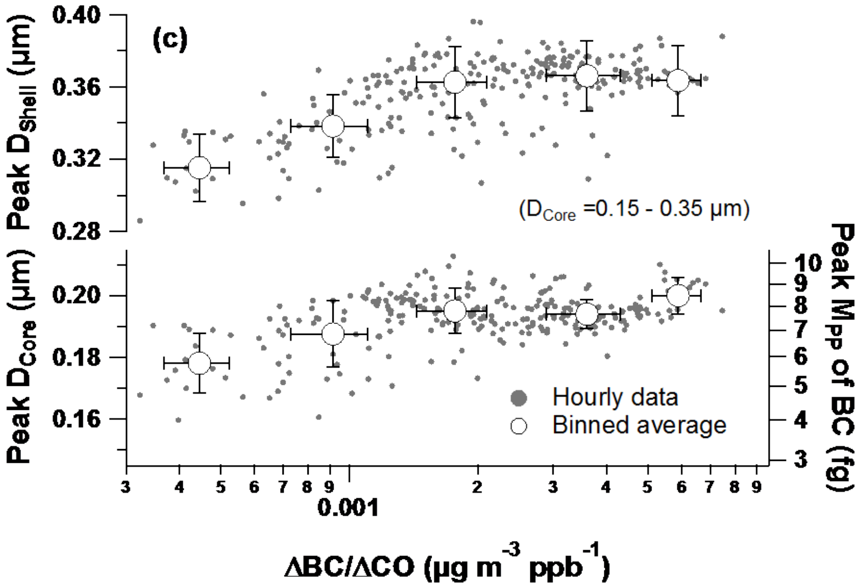


Figure 7c modified

(The evolution of D_S as a function of ΔBC/ΔCO ratios was added to the previous figure. The range of D_{core} for the calculation of D_S ranged from 0.15 to 0.35 μm)

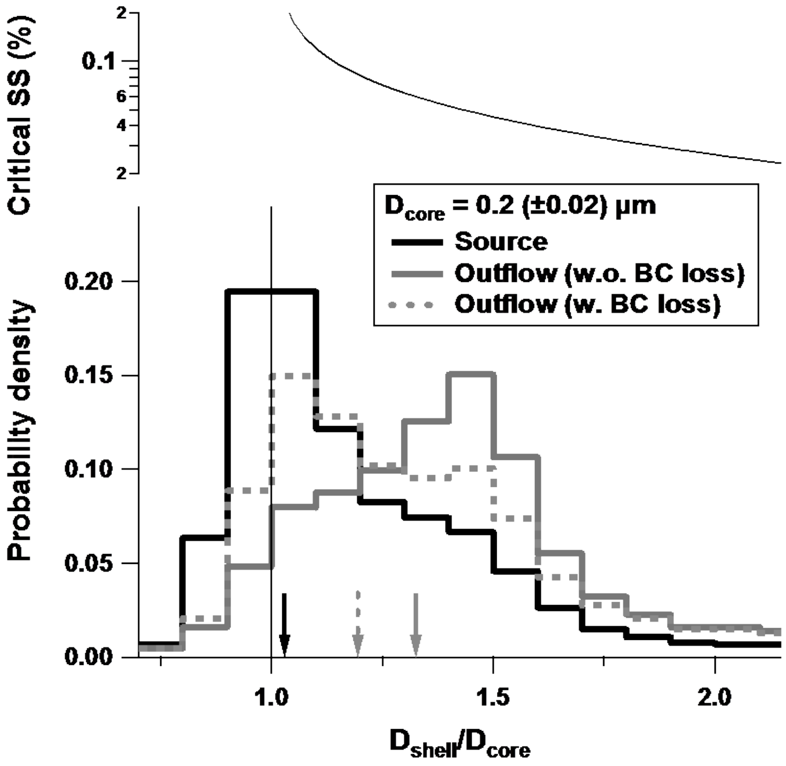


Figure 8 modified

(Median values for all distributions were plotted as vertical allows to more clearly illustrate the changes in the distributions. The estimated SS_C as a function of D_S/D_{core} ratio was plotted.)

3. Chemical composition

We modified section 3.5 as the reviewer suggested. The comparison between cases (2) and (3)/(4) is the most useful to illustrate the changes in chemical composition with the cloud processing. This comparison suggests the slight increases in ammonium sulfate and slight decreases in ammonium nitrate, OM, and BC. The cloud processing only slightly changed the chemical composition of fine aerosols. We hence modified this section based on the interpretation above. Needless to say, one the most important point is that the variations of chemical compositions were small. Therefore, we did not modified this point.

4. The process to change the size distributions and mixing state

We described the coagulation as one of candidates for the process controlling the changes in the size and mixing states without any quantitative evidences. As the reviewers suggested, the particle concentrations are a key to consider how this process is effective to change the microphysical properties of fine mode particles. In this study, we observed the BC-containing particles mainly at a remote island in Japan. We hence considered that coagulation can be expected to be minor, especially in air masses affected by wet removal. In the revised manuscript, we weakened the expression of the statements on the role of coagulation in the aging. For example, the sentence (Line 478-481) was modified into "The aging (e.g., coagulation) of aerosols particles through the transport (i.e., around ~1 day) after the wet removal events may also lead to the further modification of the shape of the particle size distributions and the mixing state distributions which have been affected by cloud processes. This factor is actually expected to be minor because the particle concentrations are too low to have high coagulation coefficients to accelerate this effect."

Comments.

Line 86: The word "control" seems a bit strong, as it could easily be argued that global- and regional-scale distributions are controlled by sources; perhaps "strongly affect" or "have a large influence upon"

We have corrected as suggested.

Line 113: define quantitatively what diameter range "fine mode" refers to

We replaced "fine mode" by "$PM_{2.5}$".

Line 140: how is Dcore different from MED? If they are the same, then this should be explicitly stated, or better yet, only use one term for this quantity.

Same. We modified the expression of the BC diameter for BC-containing particles. We only used D_{core} to represent the BC diameter.

Line 146: The statement that the particles were not so thickly coated seems at odds with the statement that the ratio was as high as 4 (line 145) or even 2.5 (line 146) – these seem like rather large coatings. Figure 8 indeed shows that Ds/Dcore is typically ~1.4 or so, but the statement as given on line 146 is unconvincing.

The D_S/D_{core} of 4 is the upper limit of the calculation. We actually never found such high D_S/D_{core} BC-containing particles. The D_S/D_{core} of ~2.5 means around the maximum levels of the retrieved values. We modified the sentences into "The upper limit of the estimation of D_S/D_{core} ratios is 4 in this study. Maximum levels of D_S/D_{core} ratios retrieved were ~2.5 at D_{core} of 0.2 μm.".

Lines 163-164: It is not the uncertainty that is minor, but rather the contribution to the mass that was outside the measured range – a very different quantity.

As the reviewer suggested, this is not uncertainty. We hence simply modified the sentence into "Note that the unmeasured fraction of rBC mass was minor (<5%) in this study.".

Line 178: This sentence is redundant to one on line 167 that stated that the average discrepancy was "comparable to the uncertainty of the COSMOS", which is not the same as "within the uncertainty." Perhaps remove one of the statements.

We modified the sentences as suggested.

Line 370: It is not clear what is meant by "lower envelopes of correlations", especially as something that can be compared to a slope.

Line 377: It appears the authors meant to state ~10 mm rather than ~1 mm.

This statement is true. We hence have not modified the sentence.

Lines 379-380: last sentence can be removed with no loss of information

We have corrected as suggested.

Line 398: The fraction of BC seems to be the same with or without rain (2.4 vs 2.5%); this seems to require some discussion.
Line 402: The statement that cloud processes affected the relative abundance of ammonium sulfate is true, but misleading, as it seemed that the only effect was a reduction in the ammonium nitrate, why would result in an increase in the relative abundance of ammonium sulfate. To focus on clouds affecting ammonium sulfate seems to misrepresent what actually occurred. Thus this statement requires a bit more discussion.
Line 403: Rather than state that the concentrations of OM increased from average in case 2, it would be better to state that OM seemed to be removed during precipitation, which attributes a physical explanation to the observation. That is, unless the authors are arguing that OM is formed during transport under dry conditions (which seems to be the statement made on lines 403-404 without supporting evidence).

We respond to the above three comments as follows.
Differences between cases (2) (i.e., w.o. precipitation and cloud impacts) and (3)/(4) (i.e., w. could impacts) are appropriate to clarify the differences in chemical compositions between with and without cloud processing. We hence added the sentences “The comparison between cases (3) or (4) and (2) is useful to elucidate the effect of the cloud processing.” and “Ammonium sulfate contribution slightly increased with the in-cloud scavenging (based on the comparison between cases (2) and (3) or (4)), while the relative contributions of ammonium nitrate, OM, and BC slightly decreased.”.
As the reviewer suggested, all components of fine aerosols were removed by the wet removal process (this feature has been discussed in Kanaya et al., 2016). We hence added the sentence “As all components of fine aerosols were removed through the in-cloud scavenging (Fig. 10 of Kanaya et al., 2016), it is expected that the relative abundance does not largely vary with the in-cloud scavenging.” after the sentence “The relative ~ 10%”. The secondary formation of OM at this site has been discussed in previous studies listed in the manuscript. We modified the last two sentences in this section into “Detailed mass spectral analyses of OM, secondary formation of OM, and cloud-phase formation of OM in East Asia are beyond the scope of this study, and they are not discussed in this study. The former two issues have been investigated by previous studies (e.g., Irei et al., 2014; Yoshino et al., 2016).”.

Line 421: I don't see where the APT values for the "outflow without BC loss" and "outflow with BC loss" are given. These criteria were selected based on delta_BC/delta-CO ratios rather than APT values.

These data sets were classified by the values of ΔBC/ΔCO. The average APT values for these two air masses are listed in Table 2.

Line 427: The size distributions of BC in Figure 7 differed among all three graphs; what the authors mean is the shape of the size distributions different primarily at BC diameters less than 0.1 micrometer.

Yes for the number size distributions. Other aspects are to show the typical size distributions of BC-containing particles at the observation sites, and to show the changes in the size distributions as a function of degree of removal.

Lines 428-430: This statement is presented without evidence; it may be true, but merely stating it as true because it is one explanation is not sufficient.

The sentences were modified into "In outflow air masses, such small BC-containing particles would be scavenged by larger particles in the coagulation process during transport. The below-cloud scavenging can also affect the BC-containing particles in the smaller size range (<0.1 μm) when the air masses were affected by the precipitation.".

Line 479: A simple calculation would give a good estimate for the amount of coagulation experienced over 1 day, which I would think would be quite low.

At this moment, we did not perform the calculation of this fraction. However, the particle concentrations after the wet removal are too low to show the large changes in the size distributions only through the coagulation. We modified the sentence into "The aging (e.g., coagulation) of aerosols particles through the transport (i.e., around ~1 day) after the wet removal events may also lead to the further modification of the shape of the particle size distributions and the mixing state distributions which have been affected by cloud processes, which is actually expected to be minor because the particle concentrations are too low to have high coagulation coefficients to accelerate this effect.".

Line 711: It should be stated that the +/- 20% is from the 1-1 line.

We have corrected as suggested.

There were a few places where the meaning was not clear, or where sentences were awkward to read, probably because of language difficulties. Suggestions are presented for how these could be reworded.

We appreciate your kindness for such proper suggestions to improve the readability of this paper.

Line 49: "exhibits on hygroscopicity" – perhaps "exhibits increased hygroscopicity"

We have corrected as suggested.

Lines 77: "… of BC during the cloud droplets formation, in air masses…: - perhaps "… of BC in air masses …"

We have corrected as suggested.

Lines 84: "the cloud processes" – perhaps "through cloud processing"

We have corrected as suggested.

Line 92: "synthetically" – meaning not clear; perhaps omit this word

We have corrected as suggested.

Lines 93-94: sentence reads awkwardly; perhaps "This study determined that the transport efficiency of BC aerosol particles through the PBL was substantially reduced by wet removal."

We have corrected as suggested.

Line 162: "distributions, to the outsides of the measurable…" – perhaps "distributions outside the measurable"

We have corrected as suggested.

Line 272: "migrating anticyclone and cyclone" – not clear what is meant; do the authors mean that both occur together, or that one of each was observed, or that either can be typically observed?

We have corrected to “The migrating anticyclone and cyclone have passed alternately over East Asia during this period, which is typically dominant in spring over East Asia (Asai et al., 1988).”.

Line 274: sentence reads awkwardly; perhaps omit.

We have removed it as suggested.

Line 320-321: perhaps "Possible uncertainties in this estimate result from inaccuracies in the parameterization of the washout rate."

We have corrected as suggested.

Lines 311-329: entire paragraph seemed repetitive and could have been stated in 3-4 sentences

We actually tried to reduce the sentences in the section 3.3. We consider that this part is a key to represent which processes (below-cloud or in-cloud scavenging) are more important as the wet removal of BC mass during the observation period. We hence could not summarize this part in 3-4 sentences as we have to include the details on the estimation of the removal rate of below-cloud scavenging (this should be included as pointed out by the co-editor). We finally reduced the number of sentences in this section from 10 to 7.

Comments by Reviewer #2 Dr. Gavin McMeeking

Rather than review the revised manuscript in full, I have focused on an evaluation of the strength of the responses to the comments raised by myself and the other reviewer, and as to whether they adequately address the comments. While many of the changes have improved the manuscript, there still remains areas where the reviewer comments have not been addressed, as detailed below.

We appreciate the reviewer's comments on the manuscript entitled "Alteration of the size distributions and mixing states of black carbon through transport in the boundary layer in East Asia". As the reviewers suggested, we have modified the manuscript.
(Reviewer's comments in bold)

Major revision points

1. Terminology

The washout and rainout were rephrased by below-cloud and in-cloud scavenging, respectively, as suggested. (We used simply "wet removal" only in Abstract.)

2. More analyses of total particle diameters of BC-containing particles.

We included not only D_S/D_{core} ratio but also D_S in the results and discussion. Figure 7c modified includes the evolution of the peak diameter of number-D_S distribution as a function of the degree of the removal of BC. Removal of large BC-containing particles was clearer in the modified figure than in the previous one. The discussions on the CCN activity of BC-containing particles were included in the revised manuscript. The ACSM-derived chemical composition and physicochemical properties of fine mode aerosols were analyzed to estimate the critical supersaturation (SS_C) as a function of D_S/D_{core} ratio in Figure 8. The estimated SS_C decreases as increases in D_S/D_{core} ratio, which we can easily expect. It is indicated that the relative abundance of BC-containing particles with higher D_S/D_{core} ratio and lower SS_C decreased through the in-cloud scavenging during the observation period.

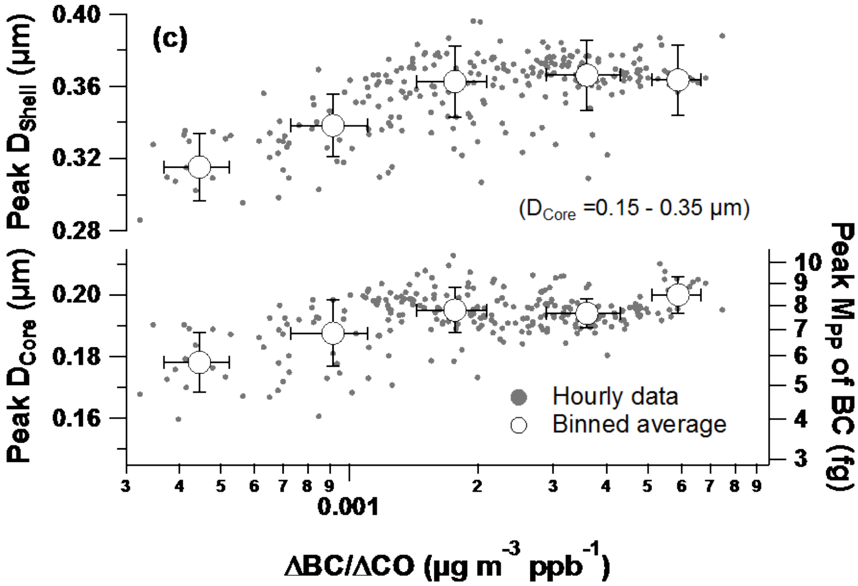


Figure 7c modified

(The evolution of D_S as a function of ΔBC/ΔCO ratios was added to the previous figure. The range of D_{core} for the calculation of D_S ranged from 0.15 to 0.35 μm)

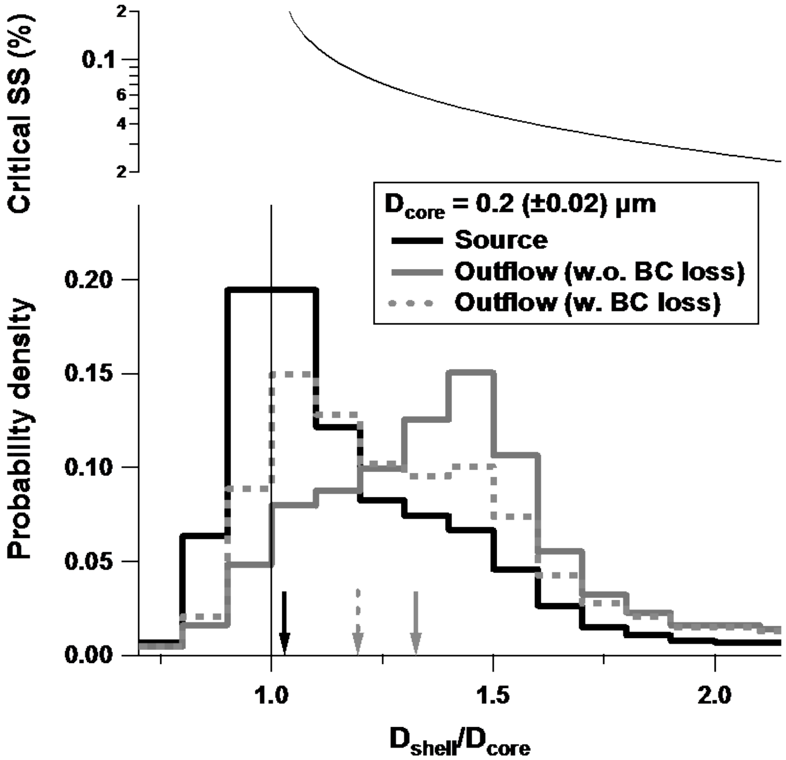


Figure 8 modified

(Median values for all distributions were plotted as vertical allows to more clearly illustrate the changes in the distributions. The estimated SS_C as a function of D_S/D_{core} ratio was plotted.)

3. Chemical composition

We modified section 3.5 as the reviewer suggested. The comparison between cases (2) and (3)/(4) is the most useful to illustrate the changes in chemical composition with the cloud processing. This comparison suggests the slight increases in ammonium sulfate and slight decreases in ammonium nitrate, OM, and BC. The cloud processing only slightly changed the chemical composition of fine aerosols. We hence modified this section based on the interpretation above. Needless to say, one the most important point is that the variations of chemical compositions were small. Therefore, we did not modified this point.

4. The process to change the size distributions and mixing state

We described the coagulation as one of candidates for the process controlling the changes in the size and mixing states without any quantitative evidences. As the reviewers suggested, the particle concentrations are a key to consider how this process is effective to change the microphysical properties of fine mode particles. In this study, we observed the BC-containing particles mainly at a remote island in Japan. We hence considered that coagulation can be expected to be minor, especially in air masses affected by wet removal. In the revised manuscript, we weakened the expression of the statements on the role of coagulation in the aging. For example, the sentence (Line 478-481) was modified into "The aging (e.g., coagulation) of aerosols particles through the transport (i.e., around ~1 day) after the wet removal events may also lead to the further modification of the shape of the particle size distributions and the mixing state distributions which have been affected by cloud processes. This factor is actually expected to be minor because the particle concentrations are too low to have high coagulation coefficients to accelerate this effect."

Responses to Reviewer #1

Response to Line 56 comment: The changes/additions to Section 3.2 are good, but I am confused by the second-to-last statement in the response: "The rainout process is a major process to reduce the loss of aerosols in wet removal". Is this just a typo, since the calculations show only a minor estimated contribution? I think the terms washout and rain out should be avoided, and instead use "in-cloud" and "below-cloud" scavenging to describe the different physical processes.

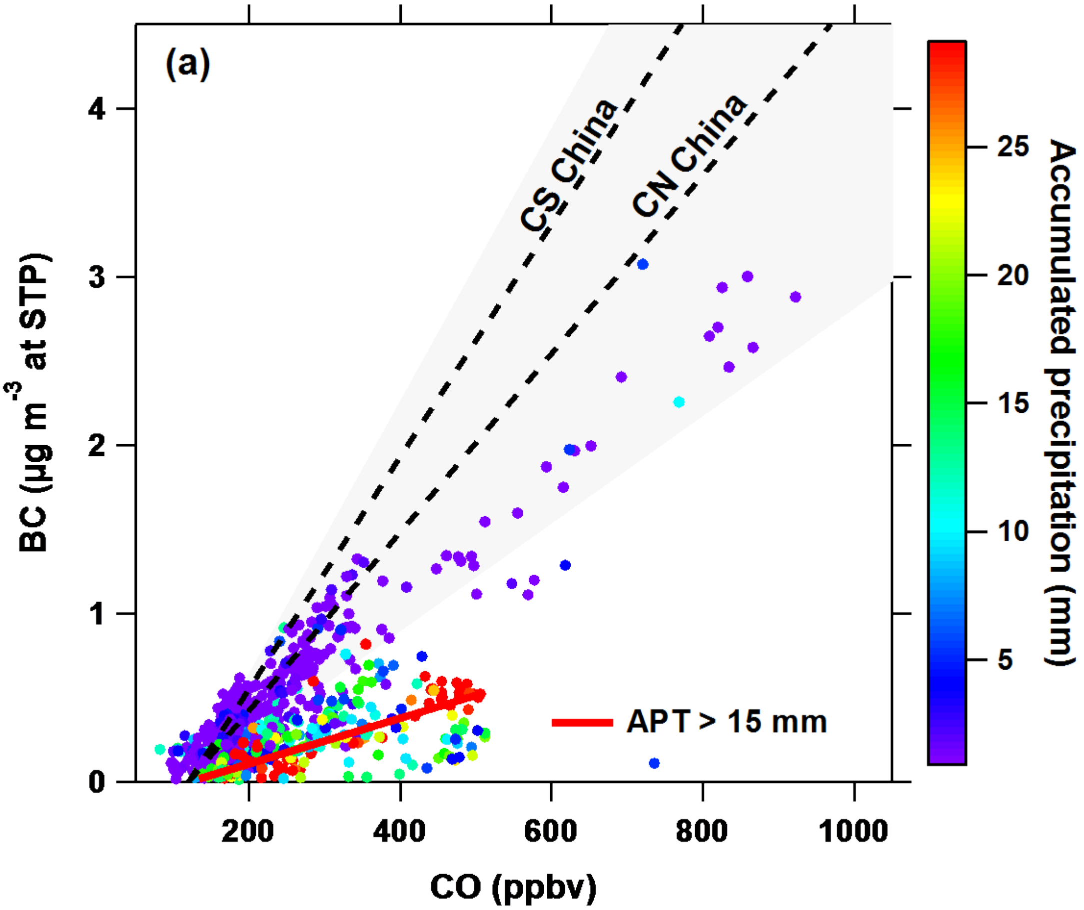
We modified the representations as suggested.

Response to Line 152-154: Also a useful addition, however change "the discrepancy can be partly attributed to …" to "the discrepancy may be partly attributed to", since it has not been established whether there is a difference in the SP2 response to BC in remote air and FS.

We have corrected as suggested.

Response to reviewer comment on line 317-319:
The final line of text in Section 3.4 states "the changes in SO4/CO correlation were largely controlled by the rainout process and weakly influenced by aqueous-phase formation during transport." The argument in the response to the reviewer is that the aim is to determine the impact of the cloud process on aqueous-phase formation of SO4. The difference in slopes in this case is also small, and neither the response nor the revised manuscript addresses the main point of the reviewer comment that questions the significance of the different relationships in the data. A stronger response, and argument in the revised text, would provide uncertainties in the regression coefficients and discussion of the significance of the differences in the relationships. The underlying reasons given by the authors (wet removal and in-cloud formation) are certainly plausible, but not proven based on the data shown here.
Additional minor point, but the range shown in the figure 6a is different from that stated in the revised text. The range shown in the plot includes the upper/lower limits associated with each of the Kanaya ranges...it may be better to give the same range in both (mean values?), whichever is most appropriate for the comparison.

We evaluated the significance of differences in the slope of SO_4^{2-}/CO correlation between with and without cloud impacts using the analysis of covariance to investigate whether linear regression slopes for two data sets are statistically different. We found that the difference was significant. Figure 6a was modified. The ranges of the emission ratios of BC to CO (ER) shown in Kanaya et al. (2016) are actually large (This is because the uncertainty in their estimation is large.). We should consider this point when we compare those with the observed ΔBC/ΔCO ratios. We hence did not remove the 1 σ range of the emission ratios (shaded region in the figure), however we added the representative values of ER for central north- and central south-china as the lines in the modified figure (see what the modified figure actually looks like in the following).



Modified figure 6 (a)

(Representative values of the emission ratios of BC to CO for central north- and central south-China shown in Kanaya et al. (2016) were plotted on the modified figure.)

Response to reviewer comment on line 343:

The inclusion of "absolute" size distributions does not directly address the main point of the reviewer comment, that there is little evidence of preferential loss of larger BC particles relative to the loss of smaller particles. The new Figure 7c is more helpful, showing a trend, though quite noisy, in the mode BC core diameter. A stronger response would also note that the more important parameter to examine here would be total particle diameter, not just that of the BC core. Just because the BC core is small does not mean that the total particle diameter, including a coating, is also small, and therefore may be as easily scavenged as a bare or weakly coated larger BC core.

We further analyzed the SP2 data sets to respond the reviewer's comment, as already described earlier (see "Major revision points"). The hourly peak values of D_S were analyzed by fitting a lognormal function to BC number size distributions. The evolution of peak D_S as a function of ΔBC/ΔCO was also plotted in Fig 7 (c). A decreasing trend of D_S with the removal of BC, which is similar to D_{core}, gave us an additional insight into the removal of BC-containing particles as suggested by the reviewers. As the larger particles have a higher CCN activity, the observed decreasing trend in D_S is consistent with our proposal, "selective removal of large BC-containing particles", which we have made in the previous manuscript. However, below-cloud scavenging can also affect such smaller BC-containing particle concentrations. We hence rephrased "selective removal" by simply "removal".

Response to reviewer comment on line 345:

The response to the reviewer is weak. It does not address the main point of the comment, that concentrations are too low for coagulation to be an important process in removal of small BC particles. Given the manuscript focuses on changes in BC size distributions it seems such a fundamental topic should be discussed, even briefly, in the manuscript.

As the reviewers suggested, the coagulation process cannot solely affect the observed changes. However, the size distributions of BC in air masses near sources can be significantly affected by the coagulation process. We modified the original sentence, to weaken the expression, into "In outflow air masses, such small BC-containing particles would be scavenged by larger particles in the coagulation process during transport." to weaken the expression. The modified manuscript include two factors, coagulation and below-cloud scavenging, as factors to affect the concentrations of sub-0.1 μm BC-containing particles.

Response to reviewer comment to line 372:

I'm not clear which uncertainty in section 2.1 is being referred to in the response to this comment, but while I would agree that the SP2 can resolve quite small differences in rBC mass (assuming constant material properties), I think the uncertainty the reviewer is talking about here is the statistical uncertainty associated with the spread in the data, and whether there is a significant difference in fg/particle for the two conditions. Note that the comparisons of log-normal fit MMDs in Table 2 is less reliable because it includes an assumed density, which might not be constant for the two cases.

We interpreted the uncertainty suggested by the reviewer #1 is related to the SP2 performance. In order to further illustrate the differences, we have tested the statistical significance. We found that the observed differences are statistically significant ($p < 0.01$). The descriptions on this point were added to support the significance of the changes. "The changes in the peak D_{core} and D_S from the highest to lowest bins of ΔBC/ΔCO ratios were 0.02 μm (2-2.5 fg) and 0.05 μm, respectively, which are statistically significant ($p < 0.01$).”

Response to reviewer comment to line 373:

The response to this comment somewhat undercuts the response to previous comments and the usefulness of Figure 7c. If size distributions change again during subsequent aging following the wet removal process, then is the apparent decrease in BC core size shown in Figure 7c meaningful or simply a random example where postwet removal aging processes happen to give a somewhat smaller average BC core size? Could a slightly different aging process following wet removal lead to a larger average size? On this basis I think any conclusions drawn regarding size dependent loss of BC should be removed or at minimum highly qualified noting the confounding factors the authors have pointed out in several of their responses.

The point we included in the previous responses was that the shape of the size distributions can be modified through aging. We interpreted the relatively small changes in BC microphysical parameters as the result of the mixing process in the PBL (i.e., mixing of BC-containing particles between in the cloud and w.o. cloud processing in the PBL). We modified this point in the manuscript to prevent misunderstanding our interpretation and to show that is might be possible but minor, as follows. “The aging (e.g., coagulation) of aerosols particles through the transport (i.e., around ~1 day) after the wet removal events may also lead to the further modification of the shape of the particle size distributions and the mixing state distributions which have been affected by cloud processes, which is actually expected to be minor because the particle concentrations are too low to have high coagulation coefficients to accelerate this effect.”

Responses to my comments:

First general comment (BC removal processes):

The additional discussion of BC removal processes is good, but suggest changing “Their” to “previous” in line 56 of the revised manuscript, and giving a very brief summary of the Kanaya et al. (2016) dry deposition results in section 3.2. For example, “The dry deposition in this region has already been evaluated by Kanaya et al. (2016), who found minimal decrease in BC/CO ratios for air masses unaffected by wet removal but with different transport times.” The addition of a quantitative examination of below cloud scavenging is good.

We have corrected as suggested.

Second general comment (BC core versus shell; SP2 operating parameters):

The inclusion of SP2 operating conditions during the study is a good addition, however I do not think the response really addresses my point about the physical meaning and impacts of the BC core size versus the diameter of the mixed particle (core + shell). The BC core diameter is not the relevant diameter for CCN activation or other in-cloud scavenging processes, unless all particles are uncoated. I feel the manuscript should more clearly address this point, as well as the implications for some of the observations. For example, if most of the particles detectable by the SP2 are coated to the point where they roughly interact and/or activate in/as cloud droplets in a similar fashion then we would not expect a strong size dependence of removal. A more thorough and quantitative treatment of the interactions of BC particles mixed to varying degrees with other material with clouds would greatly strengthen the manuscript. While a full-blown microphysical modeling study would probably be beyond the scope of the investigation, some theoretical work treating particles as a simple core-shell morphology mixed with sulfate and organic aerosol and applying this to Kohler theory could be a great addition and strengthen the science presented.

As already described earlier (see "Major revision points"), we added the evolution of the total diameter of BC-containing particles as a function of the degree of the removal of BC (modified Fig 7(c)). This figure illustrates the removal of large BC-containing particles through the in-cloud process. Furthermore, we included the estimation of critical supersaturation (SS_C) of BC-containing particles as its CCN activity in "Discussion". As an example, we added the SS_C as a function of D_S/D_{core} ratios of BC-containing particles with D_{core} of 0.2 μm on Figure 8. The changes in the distributions of D_S/D_{core} ratio can be easily connected with the CCN activity, even though the estimated SS_C was not experimentally evaluated. The modified figures 7 (c) and 8 support one of the major outcomes in this study, namely, size and mixing state distributions of BC-containing particles in the PBL were affected by the in-cloud scavenging process.