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Interactive comment on "Alteration of the microphysical properties of black carbon through transport in the boundary layer in East Asia" *by* Takuma Miyakawa et al.

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Anonymous Referee #1 Review of "Alteration of the microphysical properties of black carbon through transport in the boundary layer in East Asia" by Takuma Miyakawa et al. submitted to Atmospheric Chemistry and Physics.

We appreciate the reviewer's helpful and constructive comments on the manuscript entitled "Alteration of the microphysical properties of black carbon through transport in the boundary layer in East Asia". As the reviewers suggested, we have modified the manuscript. Major points for the revisions are listed as follows. 1) Title has been changed. 2) Supporting information (SI) has been prepared. 3) We have modified the discussion section.

The manuscript discusses ground-based measurements, with several instruments, of black carbon (BC) near an industrial source region and at a location removed from the source to study the effects of precipitation on the size distribution and properties of the BC-containing particles. The manuscript is well written and competently explains the study, but several of the arguments do not seem supported by the data. If the comments below are addressed I would recommend that the manuscript be accepted for publication. The title refers to "microphysical properties," which is true, but perhaps "size distribution and amount of associated non-BC material" would be more accurate, as the former term implies a host of properties that were not addressed.

Response>As the reviewer suggested, this study has investigated a part of the microphysical parameters of BC. Shape and chemical composition of BC-containing particles, which were not directly measured in this study, are important for considering the climatic impacts of BC-containing particles. However, chemical composition of non-refractory (non-BC) materials for both BC-free and -containing particles was measured using an Aerosol Chemical Speciation Monitor (ACSM). We addressed just simply the mixing state of BC-containing particles, and therefore revised the title slightly to "Alteration of the size distributions and mixing states of black carbon through transport in the boundary layer in East Asia".

Line 56: The sweeping statement that "washout cannot substantially affect the lifetime of atmospheric BC-containing particles," even with a reference to Seinfeld and Pandis, seems difficult to justify. Do the authors mean that because most of the BC-containing particles have diameters of several hundred nanometers, their ability to be scavenged by falling precipitation is not very large? This would seem to depend on the intensity of precipitation.

Response>As the reviewer suggested, the accumulation mode aerosols including BC are not effectively removed by the falling rain droplets. Washout process is dependent on the precipitation intensity (PI) and rain drop size as well as the particle size range. In this study, the information of rain drop size is not available. The average PIs along

a backward trajectory were calculated for the rain period in 3d-backward time (PI > 0 mm h-1). They ranged from 0.1 to 2.5 mm h-1 (median = ∼0.6 mm h-1). Using the PI value of 0.6 mm h-1, the scavenging rates of accumulation mode particles were estimated to be 6E-3 h-1 (6E-5 h-1) with the assumed rain drop diameter of 0.2 mm (2 mm). The corresponding time constants are around 7 and 694 days. These are longer than the typical transport time from the continent to the observation site. The details are described in SI.

Line 148: Rather than "lower and upper boundaries" it would be preferable to state "outside the diameter range . . ." so that it is clear what size is being referred to.

Response>We have revised as suggested.

Lines 152-154: Some discussion of why the EC and rBC concentrations differ, and especially why the rBC concentration is less, seems to be necessary. Line 168: Some justification for the selection of 0.5 as the collection efficiency for sulfate in the ACSM is required.

Response>In this study, we compared rBC with effective BC (EBC) measured using a light absorption technique (COSMOS). As we stated in the original manuscript, the difference between rBC and EBC is within the uncertainties related to both measurements. One of the unclear uncertainties, which have not well been studied, is the detection sensitivity of SP2 to the ambient rBC particles (incandescence signal intensity per rBC particle mass, SLII-mpp) in a remote atmosphere. It was found in previous studies (Moteki and Kondo, 2010; Miyakawa et al. 2016) that the SLII-mpp relationship of fullerene soot (FS) particles, which is used as a calibration standard for the SP2, is similar to that of ambient rBC particles in urban/industrial area. We hence assume the same sensitivity of SP2 to the ambient rBC in a remote atmosphere as that of FS particles and rBC particles in urban/industrial area. I added some explanations on the related uncertainties to the section 2.1 in the revised manuscript. The collection efficiency of ACSM-SO42- was derived from Yoshino et al. (2016). This paper is included

in the reference list of the revised manuscript.

Line 206: Some discussion of how sensitive the results are to different choices for the percentile (i.e., does the background value change if concentrations lower than the 10th percentile were averaged?) would be helpful, or better yet, a distribution of the CO concentrations should be shown.

Response>When we set 10th percentile of CO mixing ratio as the threshold value, the derived background CO mixing ratio was calculated to be 131 ppb, which is slightly higher than the original value (120 ppb). We prepared SI including the descriptions on the determination of the background CO mixing ratio. Please see SI for details.

Line 277: The statement that the ACSM-SO4 and the IC-SO4 "generally agreed well" is true, but from Fig. 5c there appears to be little variability in either at concurrent times when comparison could be made.

Response>The variability in IC-SO42- mass concentration was ∼9 μg m-3 at STP (min - max ∼1 - ∼10). Wider range of concentrations (<∼20 μg m-3) were observed during an intercomparison experiment in Queens/New York (Drewnick et al., 2003). To the best of our knowledge, the observed range was larger enough to discuss the intercomparison results. For example, Takegawa et al. (2005) reported the intercomparison results of SO42- mass concentration between Aerodyne AMS and PILS-IC. The range given in their study (< ∼7 μg m-3) is smaller than ours.

Line 284: It is not clear why the positive correlation of SO4 and CO suggests that the SO4 was secondary and that SO4 contributed to the BC coatings; more explanation of these assumptions/conclusions is required.

Response>Growth of BC-containing particles should be explained separately from the formation. Besides our observation results, previous studies support the description of formation and structure of the coating of BC in the original manuscript. As the reviewer suggested, we revised the related sentences and included more explanation in the

revised manuscript.

Line 290: The authors note "the small variability of SO4/CO ratios," yet Figure 6b shows that these ratios vary considerably.

Response>As the reviewer suggested, this statement and Figure 6b seem to contradict each other. We removed this sentence for the clarity.

Lines 294, 297: The two "experiments," which consisted of two brief time periods out of a month of data, were used to justify conclusions regarding flow patterns. While the results are indeed consistent with the arguments made, it seems difficult to justify such conclusions on the basis of one comparison.

Response>As the reviewer suggested, the results shown in this study are based on the observation during not-so-long time periods. We agree that it is actually difficult to draw the general conclusions. However, we still believe that this paper shows the significance in the observational studies of the relationship between removal process and the changes in the BC microphysical properties, because the observed meteorological conditions in the spring of 2015 were not special and similar to those with an average year. We added the sentences “The migrating anticyclone and cyclone were observed during this period, which is typically dominant in spring over East Asia (Asai et al., 1988). We here only briefly describe the meteorological fields (wind flow and precipitation) in the following.” behind the first sentence in section 3.1, and modified the last sentence in section 3.5 to “As the results from this study are based on observations during a limited length of time, it would be worthwhile to further investigate the possible connections of the variabilities in BC microphysical properties and meteorological conditions in this region to provide useful constraints on more accurate evaluations of climatic impacts of BC-containing particles (Matsui, 2016)”. Please see the revised manuscript for details.

Line 317: The authors refer to the SO4/CO ratio, but does this really refer to the deltaSO4/delta-CO ratio? It was unclear to me here and a number of places else-

where in the test whether the CO and SO4 values referred to delta-CO and delta-SO4 values or not. For clarity, I would recommend using "delta-" values throughout.

Response>We clearly found the lower concentrations of SO42- relative to CO for the data with the higher APT in Figure 6b of the original manuscript. Another reason not to include the ΔSO42-/ΔCO ratio is the uncertainty related to the variability in the background of SO42- in East Asia. Although the use of the same data treatment would be clear for the readers, we did not quantitatively analyze the hourly ΔSO42- and ΔCO values for considering the relative enhancements of SO42- to CO in this study. We hence added the sentences to explain why we do not analyze Δ values in the revised manuscript in section 2.2.

Lines 317-319: The difference in slopes shown in the inset to Figure 6b doesn’t seem sufficiently large, given the scatter of the data, to be significantly different, and certainly not to justify the conclusion that the controlling process is rainout.

Response>The rainout lowered the transport efficiency of SO42- as well as BC (to CO). However, the cloud process not associated with the precipitation can affect the relative increases of SO42- concentration. The major purpose to include this figure is to elucidate the impact of the cloud process on the aqueous-phase formation of SO42-, and is not to discuss the loss processes. Figure 6b is modified in the revised manuscript to clarify the data points with the APT of zero (no precipitation through the transport). These data points are highlighted by marking using cross markers. Please see the revised Figure 6b for details.

Line 343: Here and elsewhere the argument is made that aging leads to growth of BC particles, which is well accepted, but such aging can also lead to loss of larger particles through rainout, het size distributions in Figure 7 doesn’t show much of a difference between size distributions for air masses with BC loss and those without, and certainly not more of a difference for larger BC particles than for smaller ones. This discrepancy requires explanation.

Response>All the size distributions shown in Figure 7 are normalized by the number or mass integrated for the measured size range, which is described in the caption of this figure. The “absolute” size distributions show more differences between with and without BC loss. We modified the size distributions from “normalized” to “absolute” and added a new figure (fig 7c of the revised manuscript) of the relationship between BC peak diameters and ΔBC/ΔCO (i.e., degree of the removal of BC). This figure clarifies the significance of the observed changes in the peak diameter. Please see the revised figure for more details.

Line 345: The statement that "small BC-containing particles were scavenged by larger particles in the coagulation process" is a hypothesis, but stated as truth. It would seem that concentrations are too low for much coagulation over the brief period (a few days), especially for particles that are many tens of nanometers in diameter. Calculations or a simple model would be required to support this hypothesis. Line 353: It would be preferable, and less ambiguous, to rephrase "BC size of 0.2" to "BC diameter of 0.2".

Response>In the consideration of the washout process, the removal of small BC-containing particles through the washout is expected to be significant as well as the coagulation process. We hence describe the possibility of both processes in the revised manuscript. We rephrased “BC size of 0.2” to “BC diameter of 0.2”.

Line 368: The discussion focused on transport pathways of particles in the particular region of the study, but I was expecting more discussion on the results, what they mean, and so forth. There seemed to be little relevance to the second paragraph of the discussion.

Response>We reorganized the discussion part (section 3.5). We merged and reorganized the first paragraph and the half of the second paragraph into one paragraph. The latter half of the first paragraph of section 3.5 discusses the observed features and its relevance to the finding in previous studies. We consider that the relationship between transport pathways (i.e., processes during transport) and its impact on the

aerosol particles is a key and relevant to our observation results. We hence modified the sentences of the third (second in the revised manuscript) paragraph.

Line 372: The decrease in the peak diameter of the mass size distribution is very small, and within uncertainty.

Response>The change in the peak diameter is small, however, significant. Corresponded change in BC mass is $\sim$1 fg/particle. This difference can be resolved by the SP2 and beyond the uncertainty. The variabilities of the peak diameters are summarized in Table 1 in the original and revised manuscript and are smaller than those measured. As we described in the above, we added a new figure to show the tendency of the BC particle diameter as a function of the degree of BC removal (Fig 7c of the revised manuscript).

Line 373: The statement that the evidence implies selective removal of large BC containing particles is not supported by Figure 7, which shows a very slight difference in the size distribution between "with BC loss" and "without BC loss" but not apparent selective decrease of larger particles. If there were selective removal, I would expect the size distribution to not be lognormal, but to have a deficit on the large side below what a lognormal would be. Figure 3a is very difficult to read; could it be made larger? Figure 3b requires units for q_v to accompany the scale. Figure 4a should be made larger also, if possible. Figure 5b: it is difficult to distinguish the COSMOS and SP2 BC values; perhaps make one red and the other black? Figure 6a: do the axes refer to delta-CO and delta-BC? If so, they should be labeled as such. Figure 6b, inset: what does "all data" refer to? If this is to label the gray dot, then it is not clear.

Response>The activation of aerosol particles to cloud droplets has occurred during transport. We did not observe the aerosol particles below the convective cloud, because the migratory cyclone was the dominant process for the upward transport in spring in East Asia. We thus considered that SP2 detected BC-containing particles which have been aged (about a half $\sim$ a day, typical transport time) since affected by

the wet removal. The size distributions of BC-containing particles can change during transport again after the rainout process, and therefore do not always conserve the original shape. We have corrected some figures as suggested. We enlarged all figures as large as possible as suggested. Units of all parameters in Fig 3 were clarified in the modified one. The color of SP2-BC in Fig 5 was changed to red. Axes of Fig 6a do not refer to delta (so we didn't change). Fig 6b was modified, because it was not clear. All the values in Figure 6 are absolute concentrations (not delta). Fig 7c was newly added (Please see the texts for details).

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/acp-2016-570/acp-2016-570-AC1-supplement.pdf

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