Responses to the reviewers' comment

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) Relative importance of washout and rainout has been quantitatively discussed in a section that we newly produced (section 3.2 in the revised manuscript).
3) We have added a new section (section 3.5 in the revised manuscript) focusing the changes in chemical compositions of fine aerosols measured using an Aerosol Chemical Speciation Monitor.
4) We have modified the discussion section especially to clarify our speculations based on the observed results.
5) We have modified the size of figures for visible clarity.

*Note the reviewers' comments in **bold**.

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.

>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.

>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 raindrop size as well as the particle size range. Using a parameterization (Wang et al., GMD, 2014) including the raindrop size information, we estimated the removal rate of aerosol particles via below-cloud-scavenging. The precipitation intensity along trajectories and the parameterization suggests that the removal rate is estimated to be 1×10^{-3} h^{-1} on average, and be ranging from 0.5×10^{-3} to 2×10^{-3} h^{-1} in the submicron size range. The temporal duration in rain along the trajectory was also calculated. The combination of their estimations enables us to estimate the fraction of the accumulation mode particles removed through the rainout. The fraction removed was estimated to be only 1.0% on average (+2.59%/-0.9%). The rainout process is a major process to reduce the loss of aerosols in wet removal.

We added a new section to describe the above explanations (section 3.2 in the revised manuscript) as follows.

“3.2 Removal processes of fine aerosol particles

In this study, the removal processes including dry deposition and washout were considered to be minor. The dry deposition in this region has already been evaluated by Kanaya et al. (2016). The washout is dependent on the precipitation intensity and rain drop size as well as the particle size range. We quantitatively investigated the relative importance of rainout to washout in this study. The removal rates of submicron accumulation mode particles through the washout (Λ_{accum}) was estimated to be ~1×10^{-3} h^{-1} ($0.5\text{-}2 \times 10^{-3}$ h^{-1}) using a parametrization given by Wang et al. (2014) and the average precipitation intensity along the trajectories (0.78 ± 0.6 mm h^{-1}) as an input to the parameterization. The possible uncertainties in this estimation are derived

from the discrepancies in Λ_{accum} the removal rates between the parameterization and some experimental results (Wang et al., 2014). The values of Λ_{accum} can be underestimated by an order of magnitude by using the parameterization, which is however overly pessimistic. The temporal duration in rain along trajectories for air masses with the APT greater than 0 mm was 10 (±8) hours on average. These values can be used for the estimation of the removed fraction of submicron aerosols through the washout process. The average fraction of submicron aerosols removed was 1% (+2.59%/-0.9%). Even though we took into account the uncertainties for estimating Λ_{accum}, it was found that the washout process did not play a major role in the removal of BC in East Asian outflow."

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.

>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.

>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, S_{LII}-m_{pp}) in a remote atmosphere. It was found in previous studies (Moteki and Kondo, 2011; Miyakawa et al. 2016) that the S_{LII}-m_{pp} 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.

We inserted the sentences in the second paragraph of section 2.1 as follows.

"Fullerene soot (FS, stock 40971, lot L20W054, Alfa Aesar, USA) particles were used as a calibration standard for the SP2. A differential mobility analyzer (Model 3081, TSI Inc., USA) was used for preparing the monodisperse FS particles."

We also added the sentences in the second paragraph of section 2.1 as follows.
“While the validity of the calibration standard, FS particles, has been evaluated only near source regions (Moteki and Kondo, 2011; Miyakawa et al., 2016), the discrepancy can be partly attributed to the differences in physicochemical properties between ambient BC in remote air and FS particles.”

The collection efficiency of ACSM-SO_4^{2-} was derived from Yoshino et al. (2016). This study is referred in 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.
>When we set 10^{th} percentile of CO mixing ratio as the threshold value, the derived background CO mixing ratio was calculated to be 131 ppb, which is very slightly higher than the original value (120 ppb). We have prepared SI including the descriptions on the determination of the background CO mixing ratio as follows.

“S1. Determination of the background mixing ratio of carbon monoxide (CO)
We assume the 5th percentile value of CO mixing ratio (138 ppb) as a threshold value to extract its background level (CO_{bg}). CO_{bg} is defined as the average of CO mixing ratios below the 5th percentile in this study, and is calculated to be 120 ppb. When we change the threshold from 5th to 10th percentiles (146 ppb), derived CO_{bg} increases from 120 ppb to 131 ppb. Figure S1 depicts the probability density function of the observed CO mixing ratio with the assumed threshold. It is suggested that the assumption of the threshold value very slightly affected the estimation of CO_{bg}.

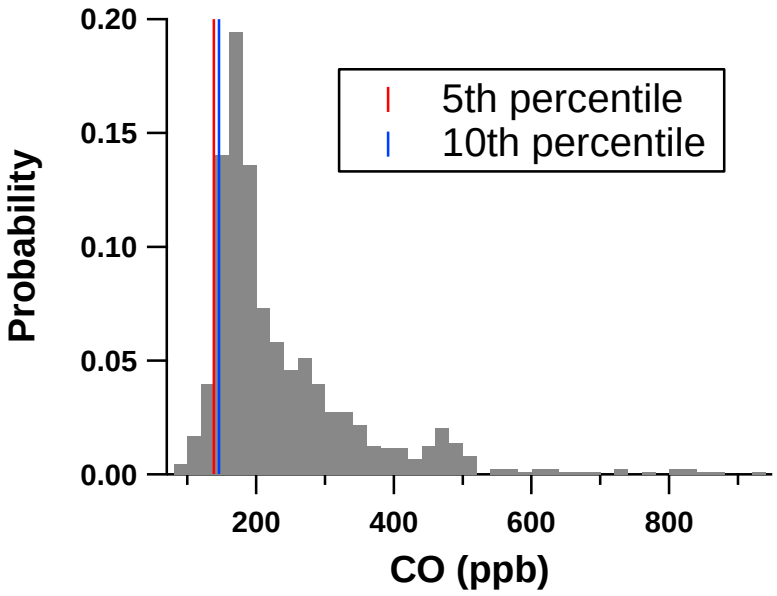

Figure S1. Probability density of measured CO mixing ratio (shaded bars). Red and blue vertical lines correspond to the 5th and 10th percentile values of the observed CO mixing ratios."

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.

>The variability in IC-SO_4^{2-} 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 SO_4^{2-} 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.

>Air masses are well mixed and diluted through transport before sampling in outflow regions. The effects of differences in the source types can be cancelled by the transport process when the spatial distributions are similar. Anthropogenic SO4, which is abundant in this region, is produced from SO2 oxidation in atmosphere. SO2 does not always share the emission sources with CO, because power generation sector

has a great contribution to SO2 emission but not to CO. Actually, the spatial distribution of SO2 emissions in East Asia is similar to that of CO emissions (Koike et al., JGR, 2003; Kurokawa et al., ACP, 2013). For clarifying this fact, we referred in the revised manuscript the previous studies where CO is used as a tracer to investigate the transport and transformation of sulfur compounds in East Asian region (Koike et al., JGR, 2003; Sahu et al., JGR, 2009). We added more explanations on this point in section 2.2 in the revised manuscript as follows

"Relative changes in SO_4^{2-} to CO were also analyzed using the linear regression slopes of their correlation in this study. We did not calculate of their hourly values, because it was difficult to determine the background concentration of SO_4^{2-}. The ues of CO as a tracer of sulfur compounds in East Asia was validated by Koike et al. (2003). Although sulfur dioxide (SO_2), which is a major precursor of anthropogenic SO_4^{2-}, does not always share the emission sources with CO, the special distributions of SO_2 emissions is similar to those of CO emissions in East Asia (Koike et al., 2003; Kurokawa et al., 2013). Analyzing the increase or decrease in the slopes of the SO_4^{2-}-CO correlation is beneficial to the investigation of the formation and removal processes for SO_4^{2-}. Especially, the aqueous-phase reaction of SO_4^{2-} in clouds is discussed using this parameter."

Growth of BC-containing particles should be explained separately because the coating material was not directly measured in this study. The ACSM measurements supported the interpretation of chemical composition of non-BC components. It is found that the major components of non-BC materials were ammonium sulfate and organic matter (OM) as summarized in Table 1 newly added in the revised manuscript. We suggested that the major coating materials of BC were ammonium sulfate and OM. Besides our observation results, a previous study (Takami et al., JGR., 2013) supports our suggestions.

"Table 1. Mean chemical composition of fine aerosols during the observation period

Componnents	Period average	APT			
		0 mm	0 mm RH_{max} <50%	0 mm RH_{max} >80%	>15 mm
Ammonium sulfate	44.9%	41.8%	34.0%	48.9%	50.4%
Ammonium nitrate	11.7%	15.7%	10.7%	8.0%	5.0%
OM	40.9%	40.1%	52.0%	40.4%	42.0%
BC	2.5%	2.4%	3.2%	2.6%	2.5%

”

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

We 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)”.

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 elsewhere 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.

>We clearly found the lower concentrations of SO_4^{2-} relative to CO for the data with the higher APT in Figure 6b of the original manuscript. Another reason not to include the $\Delta SO_4^{2-}/\Delta CO$ ratio is the uncertainty related to the variability in the background of SO_4^{2-} in East Asia. Although the use of the same data treatment would be clear for the readers, we did not quantitatively analyze the hourly ΔSO_4^{2-} and ΔCO values for considering the relative enhancements of SO_4^{2-} to CO in this study. We hence added the sentences to explain why we do not analyze Δ values in section 2.2 in the revised manuscript as follows.

"Relative changes in SO_4^{2-} to CO were also analyzed by using the linear regression slopes of their correlation in this study. We did not calculate the hourly $\Delta SO_4^{2-}/\Delta CO$ values, because it was difficult to determine the background concentration of SO_4^{2-}. Analyzing the slope of the SO_4^{2-}-CO correlation is beneficial to the investigation of the formation processes as well as the removal processes for SO_4^{2-}. Especially, the aqueous-phase formation of SO_4^{2-} in clouds is discussed by using this parameter."

We modified the section 3.4 in the revised manuscript. The slopes of SO_4^{2-}-CO correlation were more systematically investigated. We selected three cases. In the original manuscript, we have already analyzed the data points with the APT of zero and higher and lower RH_{max} (i.e., no precipitation with and without cloud impacts, respectively). In addition to these cases, we added a case for the data points with the APT >15 mm which represent the data points heavily affected by the wet removal. The linear regression slopes for three cases were added to Figure 6b in the revised manuscript. It is very clear to investigate the enhancement ratios.

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.
>The rainout lowered the transport efficiency of SO_4^{2-} as well as BC (to CO). However, the cloud process not associated with the precipitation can affect the relative increases of SO_4^{2-} concentration. The major purpose to include this figure is to elucidate the impact of the cloud process on the aqueous-phase formation of SO_4^{2-}, and is not to discuss the loss processes. Figure 6b is modified in the revised manuscript to clarify the data points with the higher values of APT and with the APT value of zero (no precipitation through the transport). These data points are analyzed by the linear regression. Please see the revised Figure 6b for details. In section 3.3, we added the

descriptions on the changes in regression slopes associated depending on the air mass histories.

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.

>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). Please see the revised figure for more details. The air mass mixing in the PBL as well as partial experience of can also change the shape of particle size distributions. Furthermore, we could not perform quantitative evaluations for these effects. We believe that these complicated processes can be evaluated by a model study. We added the sentences to the last part of the first paragraph in "Discussion" section (section 3.7 in the revised manuscript) as follows.

"The coagulation of aerosols particles through the transport after the wet removal events can lead to the modification of the particle size and mixing state distributions affected by cloud processes. The suppression of changes in the microphysical properties of BC-containing particles during transport in the PBL can be related to these factors. More quantitative assessments of the impacts of these factors should be performed using a model which has a function to resolve the mixing state of aerosol particles (e.g., Matsui et al., 2013)."

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".

>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.

>We reorganized the discussion part (section 3.7 in the revised manuscript). We merged and reorganized the first paragraph and the half of the second paragraph into one paragraph. We added the explanations to interpret the observed results and to show the limitation at this moment as follows.

“The coagulation of aerosols particles through the transport after the wet removal events can lead to the modification of the particle size and mixing state distributions affected by cloud processes. The suppression of changes in the microphysical properties of BC-containing particles during transport in the PBL can be related to these factors. More quantitative assessments of the impacts of these factors should be performed using a model which has a function to resolve the mixing state of aerosol particles (e.g., Matsui et al., 2013).”

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 did not removed this part and 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.

>The change in the peak diameter in Fig 7b is small (corresponded change in BC mass is 1 fg/particle). 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). Fig 7c indicates 2-2.5 fg/particle decrease from the higher (~6 ng m^{-3} ppb^{-1}) to lower values (0.4-0.5 ng m^{-3} ppb^{-1}) of $\Delta BC/\Delta CO$. This difference shown in Figure 7c can be resolved by the SP2 (beyond the uncertainty as described in

section 2.1 of the revised manuscript.). The variabilities of the peak diameters are summarized in Table 2 in the revised manuscript and are smaller than those measured.

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.

>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 ~ 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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Referee #2 Dr. Gavin McMeeking
Review of Miyakawa et al.

We appreciate your 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 two reviewers suggested, we have modified the manuscript. Major points for the revisions are listed as follows.

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2) Relative importance of washout and rainout has been quantitatively discussed in a section that we newly produced (section 3.2 in the revised manuscript).
3) We have added a new section (section 3.5 in the revised manuscript) focusing the changes in chemical compositions of fine aerosols measured using an Aerosol Chemical Speciation Monitor.
4) We have modified the discussion section especially to clarify our speculations based on the observed results.
5) We have modified the size of figures for visible clarity.

*Note the reviewers' comments in **bold**.

The authors present a one month case study examining measurements of black carbon properties at a remote island site, using co-located measurements of CO and sub-micron aerosol composition and reanalysis data to evaluate precipitation impacts on the observed properties. The manuscript focuses on contrasting observed properties during periods with differing accumulated precipitation along backward trajectories. The paper is well prepared and well organized and the subject is well within the topic area for ACP. There are several areas where minor revisions are needed, however, before the paper can be recommended for publication. I agree with the points raised by Reviewer #1, so have tried to not repeat too much of what has been already raised. The comments should be addressed in a revised manuscript. In addition:

+ Given the focus of the manuscript, the introduction would benefit from a more thorough discussion of the various BC removal mechanisms, with more mechanistic details given as to why various processes may or may not be important in the study area. Distinction should be made between in-cloud processes (nucleation scavenging versus scavenging by pre-existing droplets), below-cloud (washout) and dry deposition.

We added the sentence describing the removal processes of BC to the second

paragraph of section “Introduction”. Relate to this, as the reviewer #1 suggested, we have modified the descriptions on the relative importance of the washout (to the rainout) (in section 3.3 of the original manuscript). We made a new section for the explanation as follows.

“3.2. Removal processes of fine aerosol particles

In this study, the removal processes including dry deposition and washout were considered to be minor. The dry deposition in this region has already been evaluated by Kanaya et al. (2016). The washout is dependent on the precipitation intensity and rain drop size as well as the particle size range. We quantitatively investigated the relative importance of rainout to washout in this study. The removal rates of submicron accumulation mode particles through the washout was estimated to be ~1 × 10^{-3} h^{-1} (0.5-2 × 10^{-3} h^{-1}) using a parametrization given by Wang et al. (2014) and the average precipitation intensity along the trajectories (0.78 ± 0.6 mm h^{-1}) as an input to the parameterization. The temporal duration in rain along trajectories for air masses with the APT greater than 0 mm was 10 (±8) hours on average. These values can be used for the estimation of the removed fraction of submicron aerosols through the washout process. The average fraction of submicron aerosols removed was 1% (+2.59%/-0.9%), indicating that the washout process played a minor role in the removal of BC in East Asian outflow.”

+ Two points regarding reported SP2-measured BC number/mass distributions. First, the manuscript needs to make it more clear when BC core versus shell diameters are being discussed, especially when linking the observations to theory. For example, while it is true we would expect larger particles to be removed in air masses heavily impacted by precipitation, the effects on BC core distributions will be confounded by other material mixed with the cores. Related to this, the diameter range for which the optical sizing of the BC particles should be provided in the methods section. Second, small changes in the detection efficiency of the SP2 at its lower limit due to changes in cavity laser power can look like changes in BC core number distribution. A short statement regarding any checks on cavity laser power or other approaches used to ensure consistent behavior at lower size limits for the instrument would be useful.

As the reviewer suggested, we added explanations on these SP2 data analyses and working conditions in section 2.1 as follows.

- Estimation of shell to core diameter ratios of BC-containing particles

We added the following sentences to describe the diameter range of BC-containing particles.

"In this study, we analyzed the D_S of BC-containing particles with a D_{core} range between 0.15 and 0.35 μm. The maximum value of D_S/D_{core} ratios analyzed is 4 in this study. Retrieved results suggest that almost all BC-containing particles were not so thickly coated (for example, D_S/D_{core} ratios of 2.5 at highest at D_{core} of 0.2 μm)."

- Laser power and lower BC diameter limit

We added the following sentence to describe that the variations in the housekeeping parameters of SP2 cannot change the main conclusions in this study.

"The variations in the laser power were within ±3% during the observation period, thus indicating that the fluctuations of laser power did not largely affect the lower limit of the detectable BC size of the SP2."

+ Potentially useful additional information provided by the ACSM is being ignored by examining only sulfate. Is there a reason for this?

>We analyzed the concentration of SO_4^{2-} measured using the ACSM for the reasons, (1) "its precursor gas (sulfur dioxide) shares the emission sources and locations with CO", and (2) "its formation process in the aqueous phase reaction is useful for analyzing the effect of a possible cloud processing through air parcel transport". We analyzed the chemical composition of fine aerosols measured using the ACSM and made a new section (section 3.5 in the revised manuscript). To show the results for the analyses, we made a new Table (Table 1 in the revised manuscript.). Figure 5 was modified by adding the temporal variations in the mass concentrations of nitrate and organic matter (OM). Sulfate and OM were the major components for fine aerosol particles in this study.

"Table 1. Mean chemical composition of fine aerosols during the observation period

Componnents	Period average	APT			
		0 mm	0 mm RH_{max} <50%	0 mm RH_{max} >80%	>15 mm
Ammonium sulfate	44.9%	41.8%	34.0%	48.9%	50.4%
Ammonium nitrate	11.7%	15.7%	10.7%	8.0%	5.0%
OM	40.9%	40.1%	52.0%	40.4%	42.0%
BC	2.5%	2.4%	3.2%	2.6%	2.5%

"

“3.5. Changes in fine aerosol compositions

Chemical compositions of fine aerosols were investigated in terms of the APT and RH_{max}. Four cases are selected here, namely (1) APT of zero (no precipitation), (2) APT of zero with RH_{max} <50% (no precipitation without cloud impacts), (3) APT of zero with RH_{max} >80% (no precipitation with cloud impacts), and (4) APT >15 mm (heavily affected by wet removal). The results are summarized in **Table 1**. Ammonium sulfate and OM were dominant in all cases. The relative contributions of ammonium sulfate in the cases (3) and (4) increased from the average, indicating that cloud processes affected the relative abundance of ammonium sulfate. The contributions of OM in the case (2) increased from the average. The formation of secondary OM can be significant under dry conditions during transport. Detailed mass spectral analyses of OM and formation of OM in cloud are beyond the scope of this study, and they are not discussed in this study. The relative changes in chemical compositions were within around 10%.”

References

Kanaya, Y., X. Pan, T. Miyakawa, Y. Komazaki, F. Taketani, I. Uno, and Y. Kondo (2016), Long-term observations of black carbon mass concentrations at Fukue Island, western Japan, during 2009-2015: Constraining wet removal rates and emission strengths from East Asia, Atmos. Phys. Chem., 16, 10689-10705, doi:10.5194/acp-16-10689-2016.

Wang, X, Zhang, L., and M. D. Moran (2014), Development of a new semi-empirical parameterization for below-cloud scavenging of size-resolved aerosol particles by both rain and snow, Geosci. Model Dev., 7, 799-819, doi :10.5194/gmd-7-799-2014.

Responses to the co-editor's comments

Takuma Miyakawa, Japan Agency for Marine Earth Science and Technology, Japan
(miyakawat@jamstec.go.jp)

Comments to the Author:
Dear Authors,

Thank you for submitting your revised manuscript. Unfortunately, you have not adequately addressed the many comments and concerns raised by the Referees in your Response to the Referees, nor have you significantly revised your manuscript to consider the Referee comments. In many cases your response to the Referee does not actually directly address the question being raised. Instead you focus on another aspect loosely related to the question raised by the Referee, instead of directly answering the question. In some other cases, your response to the Referee involved just deleting the section/sentence in your manuscript in question. This does not properly address the question or concern under discussion, and further weakens the quality of the science and strength of your arguments presented in your paper. Some more specific comments follow below.

(Note that I looked at the Track Changes version of the manuscript submitted with the Author's Response when making my decision, and therefore the incorrect version of the manuscript originally submitted and then updated on Nov. 8th did not affect my decision.)

>We appreciate your efforts to suggest the further revisions of our manuscript for the improvement. We have modified the manuscript as follows.

In order to proceed with peer review, you will need to further revise your manuscript to properly address the many important and valuable points and concerns raised by the Referees. Please note that the 2nd Referee echoed the comments raised by Referee #1, highlighting the importance of these comments. As part of your revisions, you must also produce a new more comprehensive Response to the Referees that properly responds to the specific comments being raised. In your point-by-point response please paste the section of the manuscript text that has been changed to address that point, so it is immediately clear how the manuscript has been revised to address that question. Your revised manuscript submitted actually contains only a few substantial revisions. The manuscript must be revised to properly address the major comments raised during peer-review. Be sure to address the specific question that was raised by the Referee,

instead of side-stepping the issue by discussing a different but related issue.

In your revisions please refrain from making small numerous changes to the manuscript text, correcting typos and grammar, etc. These distract from focusing on what revisions were made to the actual science, results, and arguments of the paper. It is not appropriate to make so many extensive changes to the manuscript's language and wording while it is undergoing peer review.

>We have ordered a proofreading service upon the resubmission of the revised manuscript, because we are not non-native speakers and need some helps to improve the quality of English-writing. Small changes to the main text were raised in this process. We would like you to understand that we hope to improve the readability of the manuscript by reducing mistakes in typos and grammer. We minimized the corrections to such mistakes. We tried to further revise the manuscript again by focusing the scientific issues raised from the peer review process.

In your Response summary a major revision you listed in your bulleted list was revision of the manuscript's Discussion section, yet this was in fact barely changed. Only the final paragraph was significantly modified, and this did not change the central points raised in the Discussion.

>We considered that the major points previously raised in "Discussion" are important and should not be removed and corrected without any clear reasons. In this revision, we modified the former part of this section which discusses the interpretation of the observed evidences. In the revised manuscript, the degree of changes in the size and mixing state distributions was interpreted with the complex processes in the PBL (compared to the uplifting from the PBL to the FT). Further quantitative assessments of the proposed explanation to the observed changes in the SP2-derived BC microsphysics should be performed using a model, for example, chemical transport model with a module to resolve particle mixing states (e.g., Matsui et al., JGR, 2013).

I agree that the focus only on the sulfate concentrations measured by the ACSM is odd and seems inappropriate. At other points in the paper the importance of organic components mixed with BC are discussed. The ACSM measurements should be presented, so the contributions of all the major species measured at these sites is known (e.g. sulfate, nitrate, organics, others).

>Why we focused the data analyses of and discussion on sulfate in the original manuscript is that sulfate is one of the major components of fine aerosols in this region and that it is useful to connect its formation process with cloud process, as we have already insisted. Because we still believe that the discussion on sulfate is valuable and insightful in the main context of this paper, we did not delete this point.

In the revised manuscript, we included the data analyses of chemical composition variations in non-BC materials measured by using the ACSM. In section 3.2, the temporal variations of nitrate, ammonium, and organic material (OM) are shown in Fig 5, and the average relative abundance of them is discussed. Ion balance was investigated to consider the chemical form of inorganic ions. Sulfate and nitrate were almost fully neutralized by ammonium. We found that the major components of fine aerosols were ammonium sulfate and organic material. We made a new section (section 3.4 in the revised manuscript) of the discussion on the changes in the composition of aerosols in air masses depending upon their histories (e.g., w. or w.o. precipitation). The contribution of ammonium sulfate increased with the cloud processing through the transport. The contribution of OM is significant in all cases, especially for air masses with no precipitation and no cloud impacts. Relative changes in compositions against the air mass histories were not so large and were around ~10%. These two components, ammonium sulfate and OM, are the most important contributors to the non-BC materials in fine aerosol masses. Detailed speciation of OM based on the mass spectral analyses in East Asian outflow is beyond the scope of this study and has been discussed in previous studies (e.g., Irei et al., EST, 2011). Aqueous phase formation of OM is also beyond the scope of this study. We therefore did not include these topics in the manuscript.

The response regarding the proposed small contribution from washout is not clear. This should be discussed more clearly and quantitatively in the main text, with citations to key references, instead of just putting all the details in the SI. Please provide a much more detailed response regarding this calculation and the inherent assumptions and uncertainties in your response to Referee #1. The calculated washout lifetimes seem to be unrealistically long.

>We included the descriptions on the washout process in East Asia in this period in the main text. The reason why the lifetime estimated in the previous revision is long is that we oversimplified the input parameters, especially sizes of rain drops, in calculating the scavenging rates. Using a parameterization (Wang et al., GMD, 2014) including the raindrop size information, we estimated the removal rate of aerosol particles via below-cloud-scavenging. The precipitation intensity (PI) along trajectories and the parameterization suggests that the

removal rate is estimated to be 1×10^{-3} h^{-1} on average, and be ranging from 0.5×10^{-3} to 2×10^{-3} h^{-1} (depending upon the PI value) in the submicron size range. The temporal duration in raining along the trajectories was also calculated. The combination of their estimations enables us to estimate the fraction of the accumulation mode particles removed through the rainout. The fraction removed was estimated to be only 1.0% on average (+2.59%/-0.9%). The possible uncertainties raised in this section cannot change the major conclusion that the washout process did not played a major role in the removal of fine aerosol particles.

Referee #1 Comment on Line 284: Your response and revisions do not adequately address the questions raised regarding the appropriateness of using the correlation between CO and SO4 to conclude that the SO4 was secondary and coated the BC particles. While SO4 and its precursors are co-emitted with CO, there are many other possible combustion sources that emit CO but emit much less SO2/SO4. Assuming that most or all of the SO4 and CO measured were co-emitted is not a justifiable assumption.

>Air masses are well mixed and diluted through transport before sampling in outflow regions. The effects of differences in the source types can be cancelled by these processes when the emission spatial distributions are similar among species. Anthropogenic sulfate (SO_4^{2-}) is secondarily produced from sulfur dioxide (SO_2) in atmosphere. As the co-editor suggested, SO_2 does not always share the emission sources with CO, because power generation sector has a great contribution to SO_2 emission but not to CO. However, the spatial distribution of SO_2 emissions in East Asia is similar to that of CO emissions (Koike et al., JGR, 2003; Kurokawa et al., ACP, 2013). For clarifying this fact, we should refer these previous studies where CO is used as a tracer to investigate the transport and transformation of sulfur compounds in East Asian region (Koike et al., JGR, 2003). We hence suggested by referring Koike et al. (2003) that SO_2 and CO emissions have similar spatial distributions over China and that CO can be used as a tracer of sulfur compounds as used in the previous studies.

Referee #1 Comment on Line 317-319: Your response does not actually address the point raised regarding how the slopes in Fig. 6b do not appear to be different enough to justify your conclusion that the controlling removal process is rainout.

>The scatter plots of BC, SO_4^{2-}, and CO were altered in association with the accumulated precipitation along the trajectory (APT) as seen in Fig 6a and 6b. To clarify this, we selected the data points for air masses significantly affected by precipitation (APT >15 mm) and applied the linear regression analyses to the selected data. Both the slopes for the selected data points

of BC-CO and SO_4^{2-}-CO correlations were significantly lower than the upper envelopes of the scatter plots, and were close to the lower envelope. The wet removal is a key to reduce the abundance of BC and SO_4^{2-} relative to CO. The washout process was reassessed in the main text (described in the above), and found to be not so important during the observation period. Indirectly, we found that only the rainout can account for the removal of the accumulation mode particles in this study.

Referee #1 Comment on Line 372 regarding the BC peak diameter from the SP2: You state that a difference in ~1 fg BC can be resolved within the SP2's uncertainties, but do not state these uncertainties. Your response is too vague and requires more specific quantitative details to adequately respond to the Referee.

>We included the technical descriptions of SP2 performance on the resolving power of incandescence intensity (proportional to mass per particle, mpp) in section 2.1. The values of the changes in mass per particle were quantitatively evaluated. 1 fg BC around 1 fg of BC can be resolved, however the resolution is dependent on the signal levels. Figure 7c which is newly added shows the systematic change in peak diameter or mpp as a function of the degree of BC loss. The observed change in mpp is as large as 2-2.5 fg, which is larger than the uncertainties.

Referee #1 Comment on Line 373: You have not addressed the main concern raised regarding the supposed evidence for the selective removal of large BC particles, and how this evidence is not clear in the presented size distributions.

>As discussed in the second paragraph of section 3.6 (3.5 in the original manuscript), turbulent mixing in the PBL leads partial experience of the in-cloud scavenging for aerosol particles suspended within the PBL. This indicates that a certain fraction of aerosol particles in the PBL does not experience. The degree of changes in the shape as well as peak diameter of size distributions can be reduced by this effect. The air mass aging leads to the redistribution of the particle size distribution through the coagulation. The aging process after the wet removal process as well as the mixing process can qualitatively account for why the evidence is not clear in the observed data sets. Quantitative assessments of these effects should be performed using a chemical transport model which can resolve the mixing state of aerosol particles (Matsui et al., JGR, 2013). We included these points in "Discussion" section in the revised manuscript.

Referee #2 comment on SP2 BC mass/number distributions: The Referee's question

regarding the need for more details on when BC core vs. shell diameters are being discussed has not been addressed.

>In the revised manuscript, (1) the shell and core diameter range, and (2) the effect of laser power fluctuation to the lower limit of measurable diameter of BC-containing particles are clarified in section 2.1.

(1) The range of diameters of BC-core was from 150 to 350 nm. The maximum value of shell to core (S/C) ratio of these BC-containing particles analyzed was 4. Retrieved results in this study suggest that almost all particles had no such high S/C ratios (~2.5 at the highest for 200 nm core BC-containing particles).
(2) We diagnosed the housekeeping data to check the stability of the detection efficiency of BC-containing particles. The variations of the laser power were within 3% throughout the observation period. It is found that this factor does not largely affect the lower size limit of detection.

Referee #2 comment on ACSM data: The focus only on the sulfate measurements is not appropriate. You need to expand the results presented to discuss the full set of measurements from the ACSM. Your response regarding this question did not satisfactorily answer the Referee's question. Discussing how SO2 and CO share the same emission sources (which as discussed above is not a great assumption) does not actually explain why you don't present ACSM measurements of other aerosol components such as organics, ammonium, or nitrate. If you are going to assume that sulfate is the only major secondary aerosol component mixed with the BC (line 195), you must justify this assumption based on the measurements available. I would be surprised if there were not significant contributions from other secondary species such as organic carbon. On Page 343 you discuss another study that did observe organic coatings on BC particles in East Asian outflow.

>As described the above, we included in the revisions the data analyses of chemical composition variations in non-BC materials measured by using the ACSM. The temporal variations of nitrate, ammonium, and OM are shown in Fig 5 of section 3.2, and the average relative abundance of them is discussed. Ion balance was investigated to consider the chemical form of inorganic ions. Sulfate and nitrate were almost fully neutralized by ammonium. We found that the major components of fine aerosols were ammonium sulfate and organic material. We made a new section (section 3.4 in the revised manuscript) of the discussion on the changes in the composition of aerosols in air masses depending upon their histories. The contribution

of ammonium sulfate increased with the cloud processing through the transport. The contribution of OM is significant in all cases, especially for air masses with no precipitation and no cloud impacts. Relative changes in compositions against the air mass histories were not so large and were around ~10%. The two components, ammonium sulfate and OM, are the most important contributors to the non-BC materials in fine aerosol masses. Detailed speciation of OM based on the mass spectral analyses in East Asian outflow is beyond the scope of this study and has been discussed in previous studies (e.g., Irei et al., EST, 2011). We therefore did not include this topic in the manuscript. We refer a previous paper to present the chemical and structural feature of BC-containing particles in East Asian outflow air masses (Takami et al., JGR, 2013) as a great example of the mixing state of BC at the observation site. The major components, ammonium sulfate and OM, revealed by the ACSM measurements in this study were same as their study.

Ryan Sullivan
ACP Co-Editor

We again appreciate your efforts. The revisions will improve our manuscripts. We hope our paper contribute the significance of the Atmospheric Chemistry and Physics.

Alteration of the ~~microphysical properties~~size distributions and mixing states of black carbon through transport in the boundary layer in East Asia

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Abstract. Ground-based measurements of black carbon (BC) were performed near an industrial source region in the early summer of 2014 and at a remote island in Japan in the spring of 2015. Here, ~~We~~ we report the temporal variations in the transport, size distributions, and mixing states of the BC-containing particles. These particles

were ~~measured~~ characterized using a continuous soot monitoring system, a single particle soot photometer, and an aerosol chemical speciation monitor. The effects of aging on the growth of BC-containing particles were examined by comparing the ground-based observations between the near-source and remote island sites. Secondary formation of sulfate aerosols through gas- and cloud-phase reactions strongly affected the increases in BC coating (i.e., enhancement of cloud condensation nuclei activity) with air mass aging from the source to the outflow regions. The effects of ~~the~~ wet removal on ~~the~~ BC microphysics were elucidated by classifying the continental outflow air masses depending on the enhancement ratios of BC to CO (ΔBC/ΔCO) ratios, which was used as an indicator of the transport efficiency of BC. It was found that ΔBC/ΔCO ratios were controlled mainly by the rainout process during transport in the planetary boundary layer (PBL) on the timescale of 1-2 days. The meteorological conditions and backward trajectory analyses suggested that air masses strongly affected by rainout originated mainly from a region in South~~ern~~ China ~~region~~ (20º-35ºN) ~~during this season~~in the spring of 2015. Selective removal of large and thickly-coated BC-containing particles was detected~~found~~ in the air masses that were substantially affected by the rainout in the PBL, as predicted by Köhler theory. The size and water-solubility of BC-containing particles in the PBL can be altered by the rainout process as well as the condensation of non-BC materials.

1. Introduction

Black carbon (BC)-containing particles in atmosphere can significantly affect the radiative budget of the Earth through two effects; direct (light absorption and scattering) and indirect (aerosol-cloud interactions) effects (Bond et al., 2013; references therein). The difficulty in the estimation of these effects in the atmosphere

results from both the short lifetime relative to other greenhouse gases and the variable physicochemical properties of BC-containing particles. The BC itself is water-insoluble immediately after emission, but it subsequently exhibits~~takes~~ on hygroscopicity (McMeeking et al., 2011) and cloud condensation nuclei (CCN) activity (Kuwata et al., 2007) through atmospheric transport and aging. Only small amounts of water-soluble materials on BC particles are needed to cause their activation to form cloud droplets under moderate supersaturation conditions (Kuwata et al., 2007; 2009). It is considered that BC-containing particles are removed from the atmosphere mainly by ~~the rainout process. This is because other removal processes such as gravitational settling, dry deposition, and washout cannot substantially affect the lifetime of atmospheric BC-containing particles~~wet deposition (Seinfeld and Pandis, 2006).

The horizontal and vertical distributions of aerosols can be substantially altered by their atmospheric lifetimes (e.g., Lawrence et al., 2007). Moreover, their studies suggested that the removal processes of BC such as dry deposition, below-cloud (i.e., washout), and in-cloud (i.e., rainout) can greatly change the atmospheric lifetimes. The in-cloud processes include nucleation scavenging and scavenging by the preexisting cloud droplets. Precipitation followed by in-cloud processes leads to the irreversible removal of BC-containing particles. Samset et al. (2014), using multiple global model data sets constrained by aircraft observations, suggested that the atmospheric lifetime of BC largely affects its distribution, especially in the northern hemisphere, and this ~~resulting~~ results in significant variations in global direct radiative forcing values. The removal of BC has been considered as an important issue for the geochemical carbon cycle as well as for climate science~~s~~. The BC-containing

particles deposited onto the ocean surface can affect ocean surface particles, dissolved organic carbon (DOC), and microbial processes, by absorbing DOC, stimulating particle aggregation, and changing the size distribution of suspended particles (Mari et al., 2014).

Previous modeling studies have dealt with ~~the~~ BC aging processes (condensational growth and coagulation) ~~for~~ in box and regional-scale models, and parameterized timescales for the conversion of BC-containing particles from water-insoluble to -soluble ~~for~~ in global models (Oshima et al., 2009; Liu et al., 2011; Oshima and Koike, 2013). However, ~~Quantitative~~ quantitative knowledge of the variability of microphysical parameters of BC-containing particles and the timescale of their aging processes is still limited, and thus more investigation ~~is~~ are needed for near-source and remote regions (Samset et al., 2014). Moteki et al. (2012) reported the first observational evidence of the size-dependent activation of BC ~~to form~~during the cloud droplets formation, in air masses uplifting from the planetary boundary layer (PBL) to the free troposphere (FT) in East Asia in the spring of 2009, ~~during~~ as the part of the Aerosol Radiative Forcing in East Asia (A-FORCE) aircraft campaigns (Oshima et al., 2012). ~~The~~ A similar altitude dependence of the BC size distribution and similarity in the BC mixing state were observed in other aircraft measurements conducted in East Asia in winter (Kondo et al., 2016). Selective removal of larger BC-containing particles though the cloud process, which is predicted by Köhler theory, was qualitatively observed in the atmosphere. This observational evidence indicates that the size distributions and mixing states of BC-containing particles control the global- and regional-scale spatial distributions of BC through their upward transport from the PBL to the FT associated with rainout processes. Despite the importance of the size

distributions and mixing states of BC-containing particles in the PBL, the ~~continuous~~ measurements of their microphysical properties are still limited around the source regions in East Asia.

Kanaya et al. (2016) have conducted long-term measurements of BC for 6 years (2009-2015) at Fukue Island, and they synthetically reported the emission and removal of BC in East Asia using these data sets. It was found in their study that wet removal through transport in the PBL substantially reduced the transport efficiency of BC aerosols. Here we examine the effects of aging and wet removal during transport on the changes in BC size distributions and mixing state, as well as concentrations, based on ground-based measurements conducted at the same site in the spring of 2015 using a single particle soot photometer (SP2) and an Aerosol Chemical Speciation Monitor (ACSM). We first ~~show~~ describe the meteorological characteristics of the East Asian region in the spring of 2015. Then, we discuss the relative importance of the washout and rainout processes for the removal of BC as well as the transport patterns of the East Asian outflow air masses in spring. T~~hen, t~~he loss of BC-containing particles for that period is investigated using a similar approach to that used by Kanaya et al. (2016), and this is performed in connection with the associated changes in BC microphysics and their relevance to the transport pathways.

2. Experimental and data analysis

2.1. Atmospheric observations

~~The c~~Continuous measurements of $PM_{2.5}$ and BC aerosols ~~has~~ have been conducted at a remote island, Fukue Island, since February 2009 (Kanaya et al., 2013; Ikeda et al., 2014). The observation site is located at the Fukue Island Atmospheric Environment Monitoring Station (32.75°N, 128.68°E, **Fig. 1**). The site is located in the northwest

122 portion of Fukue Island, approximately 20 km from the main residential area in the
123 southeast. The fine mode aerosols sampled at the site are mostly transported from
124 areas beyond the island. The enhanced concentrations of BC aerosols in Fukue Island
125 ~~are~~ can be mainly attributed to long-range transport from the Asian continent,
126 according to a previous study (Shiraiwa et al., 2008) and an emission inventory work
127 (**Fig. 1**, REAS ver. 2.1, Kurokawa et al., 2013).
128 We deployed an SP2 (Droplet Measurement Technologies, Inc., USA) for the
129 analysis of microphysical parameters of refractory BC (rBC, Petzold et al., 2013) from
130 March 26, 2015 to April 14, 2015. The SP2 was calibrated before starting the
131 ambient measurements. The calibration protocol for our SP2 is described in
132 Miyakawa et al. (2016). Fullerene soot (FS, stock 40971, lot L20W054, Alfa Aesar,
133 USA) particles were used as a calibration standard for the SP2. A differential
134 mobility analyzer (Model 3081, TSI Inc., USA) was used for preparing the
135 monodisperse FS particles. The analysis of the calibration results suggests that the
136 full width of half maxima (FWHM) was typically 30% of the modal incandescence
137 signal intensity (S_{LII}) for the diameter range studied. Note that the FWHM can be
138 regarded as an upper limit to describe the resolving power of rBC mass per particle
139 using our SP2, because the combination of polydisperse size distribution of FS
140 particles and the transfer function of the DMA can broaden the distributions of S_{LII} for
141 the prepared FS particles. The variations in the laser power were within ±3% during
142 the observation period, thus indicating that the fluctuations of laser power did not
143 largely affect the lower limit of the detectable rBC size using the SP2. Mass
144 equivalent diameter (MED) was derived from the rBC mass per particle (m_{pp}) with ~~the~~
145 an assumed particle density ~~of~~ for BC (1800 kg m^{-3}, Bond and Bergstrom, 2006). A

large diameter Nafion dryer (MD-700, Perma Pure, Inc., USA) was placed in front of the SP2 for drying the sample air without significant loss of the aerosol particles greater than 50 nm. The dry air for MD-700 was generated by a heatless dryer (HD-2000, Perma Pure, Inc., USA) and a compressor (2AH-23-M222X, MFG Corp., USA). The relative humidity of the sample air was less than 20% during the observation period. The hourly number/mass size distributions and hourly median values of shell (D_S) to rBC diameter (D_{core}) ratios (D_S/D_{core}) for the selected D_{core} ranges were calculated. The retrievals of D_S from the light scattering signals measured by an avalanche photodiode and a position sensitive detector (Gao et al., 2007) were performed using a time-resolved scattering cross section method given by Laborde et al. (2012). In this study, we quantified the D_S/D_{core} ratios with a D_{core} range between 0.15 and 0.35 μm. The maximum value of D_S/D_{core} ratios analyzed is 4 in this study. Retrived results suggest that almost all rBC particles were not so thickly coated (for example, D_S/D_{core} ratios of ~2.5 at highest at D_{core} of 0.2 μm). We also analyzed the microphysical parameters of rBC particles measured using the SP2 in the early summer of 2014 at Yokosuka (35.32°N, 139.65°E, **Fig. 1**), located near industrial sources ~~beside~~ along Tokyo Bay (Miyakawa et al., 2016). These data sets were used as a reference for the BC-containing particles in air masses strongly affected by combustion sources.

Equivalent BC (EBC, Petzold et al., 2013) mass concentrations are continuously measured at Fukue Island using two instruments; a continuous soot-monitoring system (COSMOS; model 3130, Kanomax, Japan), and a multi-angle absorption photometer (MAAP; MAAP5012, Thermo Scientific, Inc., USA). The details of the air sampling and intercomparisons for EBC measurements at Fukue Island have been described

elsewhere (Kanaya et al., 2013; 2016). In this study, mass concentrations of EBC measured using the COSMOS were evaluated by comparison with those of SP2-derived rBC. The intercomparison between SP2 and COSMOS will be briefly discussed ~~in the following~~below.

Figure 2 depicts the correlation between COSMOS-EBC and SP2-rBC hourly mass concentrations. The unmeasured fraction of the rBC mass was corrected by extrapolation of the lognormal fit for the measured mass size distributions, to the outsides of the ~~lower and upper boundaries~~measurable D_{core} range (0.08~~ and ~~0.5 μm~~, respectively~~). Note that the uncertainty with respect to the unmeasured fraction of rBC mass was minor (<5%) in this study. The linear regression slope of the correlation between EBC and rBC was 0.88 (±0.03). Uncertainty with respect to the calibration was examined in an industrial region and found to be within around 3% (Miyakawa et al., 2016). The average discrepancy between EBC and rBC was beyond the uncertainty of the calibration and was comparable to the uncertainty of COSMOS (10%) as evaluated by Kondo et al. (2009). While the validity of the calibration standard, FS particles, has been evaluated only near source regions (Moteki and Kondo, 2011; Miyakawa et al., 2016), the discrepancy can be partly attributed to the differences in physicochemical properties between ambient BC in remote air and FS particles. Onsite calibration of the SP2 using ambient BC particles prepared by a thermal denuder and particle mass classifier, such as an aerosol particle mass analyzer (APM), is desirable for better quantification of the rBC mass based on the laser-induced incandescence technique in remote areas. Although we need to make further attempts to evaluate SP2 in remote areas, this study ~~suggested~~ indicated that SP2-rBC mass concentrations agreed well with COSMOS-EBC within the uncertainty

194 of COSMOS. Therefore we simply use "BC", instead of the EBC and rBC defined
195 depending upon the measurement techniques. We analyzed the COSMOS data for
196 the BC mass concentrations, and the SP2 data for the BC microphysics.
197 The chemical composition of non-refractory submicron aerosols was measured
198 using an Aerodyne Aerosol Chemical Speciation Monitor (ACSM, Aerodyne, Inc.,
199 USA.) placed in an observatory container at Fukue Island during the observation
200 period. The details of the ACSM at Fukue Island have been described in Irei et al.
201 (2014). The collection efficiency (CE) of the ACSM was assumed to be 0.5 for this
202 period (Yoshino et al., 2016). We considered sulfate (SO_4^{2-}) ions as a major non-BC
203 material and one of the most important secondary aerosols in East Asia (Takami et al.,
204 2007) for the data interpretation. The fact that SO_4^{2-} is produced in the cloud phase as
205 well as in the gas phase is beneficial for interpreting temporal changes in SO_4^{2-}
206 concentration associated with the wet removal processes. We also analyzed other
207 non-refractory components such as nitrate (NO_3^-), ammonium (NH_4^+), and organic
208 matter (OM). During the period April 1 -7, 2015, the critical orifice of the inlet
209 assembly of the ACSM ~~was~~ became clogged. ACSM-derived SO_4^{2-}, NO_3^-, NH_4^+, and
210 OM (ACSM- SO_4^{2-}, -NO_3^-, -NH_4^+, and -OM) for this period was not used in the
211 analysis.
212 Two high volume air samplers (HV500F, Sibata Scientific Technology, Ltd., Japan)
213 were deployed on the rooftop of the observatory container. The sampling flow rate
214 for both samplers was 500 liters per minute (lpm). Air sampling was carried out for
215 21 h (from 10:00 AM to 7:00 AM) on a 110-mm pre-combusted (900°C for 3 h) quartz
216 filter (QR-100, Advantec Toyo Kaisha Ltd., Japan). Both have a $PM_{2.5}$ impactor for
217 classifying the particle size. One impaction plate was coated with vacuum grease

(HIVAC-G, Shin-Etsu Chemical Co., Ltd., Japan) to minimize the impact of coarse mode particles on the chemical analysis of fine mode particles such as radiocarbon analysis, and a pre-combusted quartz fiber filter with slits was set on another impaction plate to collect the coarse particles. Water soluble ions were analyzed using ion chromatography (IC, Dionex ICS1000, Thermo Fisher Scientific K.K., Japan). The results from the chemical analysis of filter samples are not ~~included~~ discussed in this study in detail. We only used the mass concentration of SO_4^{2-} (IC-SO_4^{2-}) in this study to evaluate the uncertainty in relation to CE of the ACSM, and to analyze the temporal variations during the period when the ACSM-SO_4^{2-} data were not available (April 1-7, 2015).

The carbon monoxide (CO) mixing ratio was also continuously measured using a nondispersive infrared (NDIR) CO monitor (model 48C, Thermo Scientific, Inc., USA). Details of the CO measurements including the long-term variations in sensitivity and zero level are discussed elsewhere (Kanaya et al., 2016).

2.2. Enhancement ratio of BC and SO_4^{2-} to CO as an indicator of the ~~BC removal~~transport and transformation of aerosol particles

In order to quantify the extent of the removal of BC, we calculated the hourly enhancement ratio of BC mass concentrations to CO mixing ratios (ΔBC/ΔCO) against the East Asian background air concentrations as follows:

$$\frac{\Delta BC}{\Delta CO} = \frac{[BC] - [BC]_{bg}}{[CO] - [CO]_{bg}}, \quad (1)$$

where [BC] and [CO] are measured hourly concentrations of the BC and CO respectively, and $[BC]_{bg}$ and $[CO]_{bg}$ are their estimated background concentrations. Here we assumed that $[BC]_{bg}$ is zero (Oshima et al., 2012). The background concentration of CO during the analysis period (March 11 – April 14, 2015) was calculated by averaging the concentrations lower than the 5th percentile (120 ppb). The validity of this value is discussed in the supporting information (S.I.).

Relative changes in SO_4^{2-} to CO were also analyzed using the linear regression slopes of their correlation in this study. We did not calculate their hourly values, because it was difficult to determine the background concentration of SO_4^{2-}. The use of CO as a tracer of sulfur compounds in East Asia was validated by Koike et al. (2003). Although sulfur dioxide (SO_2), which is a major precursor of anthropogenic SO_4^{2-}, does not always share the emission sources with CO, the special distributions of SO_2 emissions is similar to those of CO emissions in East Asia (Koike et al., 2003; Kurokawa et al., 2013). Analyzing the increase or decrease in the slopes of the SO_4^{2-}-CO correlation is beneficial to the investigation of the formation and removal processes for SO_4^{2-}. Especially, the aqueous-phase reaction of SO_4^{2-} in clouds is discussed using this parameter.

2.3. Meteorological field analysis

We used the 6-hourly meteorological data, with a resolution of 1° in terms of the latitude and longitude, from the National Centers for Environmental Prediction (NCEP) Final (FNL) operational global analysis; and daily precipitation data, with a resolution of 1° in terms of the latitude and longitude, from the Global Precipitation Climatology Project (GPCP) data set (Huffman et al., 2001). We analyzed these data

sets to investigate the general features of the meteorological field in East Asia during the observation period.

2.4. Backward trajectory analysis

We calculated backward trajectories from the observation site to elucidate the impact of the Asian outflow. ~~3~~Three-day backward trajectories from the observation site (the starting altitude was 0.5 km) were calculated every hour using the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory model (Draxler and Rolph, 2012; Rolph, 2012) with the meteorological data sets (NCEP's Global Data Assimilation system, GDAS). In this study, the residence time over specific source regions was used as an indicator of their impacts on the observed air masses. We defined five domains for assessing the impact over the Asian continent; Northeast China (NE), Korea (KR), Central North China (CN), Central South China (CS), and Japan (JP) (**Fig. 1**). The period when air masses passed over the domains NE, KR, CN, and CS at least for one hour is defined as that of "continental outflow". The impacts of precipitation on the observed air masses were assessed by a parameter referred to as the "Accumulated Precipitation along Trajectory" (APT, Oshima et al., 2012). In this study, we calculated the APT values by integrating the amount of hourly precipitation in the Lagrangian sense along each 3-day back trajectory of the sampled air masses. The hourly variations of APT were merged into the observed gas and aerosol data sets.

3. Results and discussion

3.1. The meteorological field in the spring of 2015

The mean meteorological field during the observation period (March 11–April 14,

2015) is discussed for the purpose of characterizing the general features of the wind flow and precipitation in this region. 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. **Figure 3a** shows the mean sea level pressure (SLP) and mean horizontal winds at the 850 hPa level in East Asia during the observation period. The mean equivalent potential temperature (θe) and the meridional moisture transport at the 850 hPa level during the same period are also shown in **Figure 3b**. The mid-latitude region (35-50°N, 120-140°E) was under the influence of a modest monsoonal northwesterly flow, which advected cold, dry air from the continent to the observation area. The subtropical region (20°-30°N, 110°-130°E) was under the influence of a persistent southwesterly flow, part of which was conversing into the observation area (30°-35°N), and this flow was~~being~~ confluent with the northwesterlies from the continent. The low-level southerly flow advected warm, moist air into the observation area to sustain a large amount of precipitation (**Fig. 4a**).

Figure 3c shows the temporal variations in surface pressure and precipitable water at the observation site. The surface pressure is well anti-correlated with the precipitable water. During the observation period, migratory cyclones and anticyclones occurred occasionally (3 times each). The occurrence of migratory cyclones advected moist air, which could have contributed to the wet removal of BC during transport in the PBL. In contrast, the occurrence of anticyclones advected dry air, which could have contributed to the efficient transport of BC from the source regions.

Figure 4a depicts the mean precipitation over East Asia during the observation

period. Mean precipitation showed a latitudinal gradient over eastern China and the Yellow Sea and East China Sea region (i.e., increasing precipitation from south to north), and these results suggest~~ing~~ that transport pathways can greatly affect the wet removal of aerosols. The APT was compared with the averaged latitude of each trajectory for 48 h backwardly from the time of -24 h (Lat_{ORIG}) (**Fig. 4b**), which can be interpreted as an indicator of the latitudinal origin of the air masses arriving at Fukue Island. The high APT values corresponded to the air masses that originated from the southern regions (20º-40ºN). The data points are colored according to the maximum RH values along each backward trajectory (RH_{max}). The lower relative humidty (RH_{max}) were observed in the air masses with low APT values that originated from northern regions (30º-50ºN). These air mass characteristics were consistent with the mean precipitation field (**Fig. 4a**). Some of the data points showed high values of RH_{max} (~100%) when their APT was almost zero. These data ~~would~~ probably correspond to the air masses that experienced cloud processes not associated with precipitation. Possible effects of cloud processes without precipitation on the removal of aerosol particles during transport will be discussed using these data points in the following section.

3.2. Removal processes of fine aerosol particles

~~3.2.~~ In this study, the removal processes including dry deposition and washout were considered to be minor. The dry deposition in this region has already been evaluated by Kanaya et al. (2016). The washout is dependent on the precipitation intensity and rain drop size as well as the particle size range. We quantitatively investigated the relative importance of rainout to washout in this study. The removal

rates of submicron accumulation mode particles through the washout (Λ_{accum}) was estimated to be ~1 × 10^{-3} h^{-1} (0.5-2 × 10^{-3} h^{-1}) using a parametrization given by Wang et al. (2014) and the average precipitation intensity along the trajectories (0.78 ± 0.6 mm h^{-1}) as an input to the parameterization. The possible uncertainties in this estimation are derived from the discrepancies in Λ_{accum} the removal rates between the parameterization and some experimental results (Wang et al., 2014). The values of Λ_{accum} can be underestimated by an order of magnitude by using the parameterization, which is however overly pessimistic. The temporal duration in rain along trajectories for air masses with the APT greater than 0 mm was 10 (±8) hours on average. These values can be used for the estimation of the removed fraction of submicron aerosols through the washout process. The average fraction of submicron aerosols removed was 1% (+2.59%/-0.9%). Even though we took into account the uncertainties for estimating Λ_{accum}, it was found that the washout process did not play a major role in the removal of BC in East Asian outflow.

3.3. Temporal variations in ~~BC, SO_4^{2-},~~ aerosols and CO

Temporal variations in the concentrations of BC (measured using COSMOS and SP2), SO_4^{2-} (measured using ACSM and IC), NO_3^-, OM, and CO are shown in **Figure 5**. ACSM-SO_4^{2-} generally agreed well with IC-SO4, thus indicating that the assumed CE (0.5) was valid for the observation period. As NO_3^- and SO_4^{2-} were almost fully neutralized by NH_4^+, we assumed their chemical forms were ammonium salts. In general, BC, ~~and~~ SO_4^{2-}, and OM were positively correlated with CO at Fukue Island, and these results illustrate~~showing~~ the impact of continental outflow affected by incomplete combustion sources ~~for~~ on aerosol mass concentrations. The mean

chemical composition of fine aerosols during the observation period was listed in **Table 1**. Ammonium sulfate and OM were abundant components. **Figure 5** also includes the temporal variations in the fractional residence time over the selected region defined in section 2.4 (top panel). The CO concentrations were typically enhanced for the period with the higher contributions of CN and CS. ~~The positive correlation of SO_4^{2-} and CO suggests that the secondary formation of SO_4^{2-} through transport was significant during the observation period, and that SO_4^{2-} contributed to the coating of BC-containing particles.~~ A previous study suggested that the majority of SO_4^{2-} aerosols were formed in less than around 1.5 days after the air masses left the Chinese continent (Sahu et al., 2009). Kanaya et al. (2016) showed that the typical transport time of continental outflow air masses at Fukue Island was around 1-2 days in spring. The positive correlation of SO_4^{2-} and CO suggests that the secondary formation of SO_4^{2-} through transport was significant during the observation period~~, and that SO_4^{2-} contributed to the coating of BC-containing particles~~. The structure and composition of fine aerosols in East Asian outflow were analyzed by using a secondary ion mass spectrometer in a previous study (Takami et al., 2013). They suggest that SO_4^{2-} and OM are constituents in the coating of almost all BC-containing particles. Hence we concluded that ammonium sulfate and OM contributed to the growth of BC-containing particles. ~~The small variability of SO_4^{2-}/CO ratios is consistent with these facts.~~ The period with the APT > 3 mm is highlighted by light blue in **Figure 5** to show the impact of wet removal on the transport of BC and SO_4^{2-} aerosols. The maximum concentrations of ~~BC, SO_4^{2-},~~aerosols and CO were observed on the morning of March 22 (Ep.1) under the influence of the anticyclone (corresponding to the trajectories colored red in **Fig. 4a**) when the APT values were almost zero. In

contrast, ~~BC and SO_4^{2-}~~ aerosol concentrations did not increase with CO in the period from the evening of April 5 to the morning of April 6 (Ep.2) under the influence of the migratory cyclone (corresponding to the trajectories colored black in **Fig. 4a**), when the APT was greater than 10 mm.

3.4. Correlation of BC, SO_4^{2-}, and CO ~~as an indicator of the removal of aerosols~~

Figures 6a and **6b** show scatter plots of CO with BC and SO_4^{2-}, respectively. Positive correlation of BC and SO_4^{2-} with CO was clearly found in air masses with low APT values. The linear regression was performed to the data points with the APT higher than 15 mm for BC-CO and SO_4^{2-}-CO. Note that the linear regression slope for BC-CO was determined by forcing through the background concentrations of BC (0 μg m^{-3}) and CO (120 ppb). The slopes of the fitted lines were 1.4 and 9.8 ng m^{-3} ppb^{-1} for BC-CO and SO_4^{2-}-CO, respectively, were close to the lower envelopes of the correlations. It is evident from these scatter plots that the ~~correlations~~ relative enhancements of BC~~/CO~~ and SO_4^{2-}~~/~~ to CO wea~~s~~re mainly affected by the APT. ~~The cloud processes of aerosol particles not associated with precipitation can also reduce the slope of their correlation. However, no decreasing tendency of BC/CO and SO_4^{2-}/CO against RH_{max} when APT was zero was found during the observation period (data not shown).~~Kanaya et al. (2016) found that the estimated emission ratios of BC to CO over the East Asian continent ranged from 5.3 (±2.1) to 6.9 (±1.2) ng m^{-3} ppb^{-1}, slightly depending on the origin of the air masses (this range is overlaid on **Fig. 6a**). ΔBC/ΔCO observed in the PBL over the Yellow Sea during the same season was 6.2 ng m^{-3} ppb^{-1} (Kondo et al., 2016). The data points with ΔBC/ΔCO in these ranges show low APT values (less than or ~1 mm). Wet removal (rainout) was one of the most

410 important controlling factors on the transport efficiency of BC in this region during the
411 observation period. The use of the ΔBC/ΔCO ratios is feasible for examining the wet
412 removal of BC during the observation period.
413 The cloud processes of aerosol particles not associated with precipitation can also
414 reduce the slope of their correlation. However, no decreasing tendency of BC/CO
415 and SO_4^{2-}/CO slopes against RH_{max} when APT was zero was found during the
416 observation period (data not shown). The SO_4^{2-}/CO slopes with the APT values of
417 zero were analyzed as a function RH_{max} (**Figure 6b**), and these varied from 30.7 to
418 44.1 ng m^{-3} ppb^{-1} under the conditions without (RH_{max} <50%) and with (RH_{max} >80%)
419 cloud impacts, respectively. The SO_4^{2-}/CO slope ~~slightly~~ increased with RH_{max}
420 ~~increasing~~ when the APT was zero, ~~as indicated in the subset of **Figure 6b**,~~ thus
421 suggesting that aqueous phase formation and subsequent droplet evaporation partly
422 contributed to the mass concentrations of SO_4^{2-} observed at Fukue Island. Therefore,
423 the changes in the SO_4^{2-}/CO correlation were controlled largely by the rainout process
424 and weakly by aqueous-phase formation during transport.
425
426 **3.5. Changes in fine aerosol compositions**
427 Chemical compositions of fine aerosols were investigated in terms of the APT and
428 RH_{max}. Four cases are selected here, namely (1) APT of zero (no precipitation), (2)
429 APT of zero with RH_{max} <50% (no precipitation without cloud impacts), (3) APT of
430 zero with RH_{max} >80% (no precipitation with cloud impacts), and (4) APT >15 mm
431 (heavily affected by wet removal). The results are summarized in **Table 1**.
432 Ammonium sulfate and OM were dominant in all cases. The relative changes in
433 chemical compositions of fine aerosol particles were within around 10%. The

relative contributions of ammonium sulfate in the cases (3) and (4) increased from the average, indicating that cloud processes affected the relative abundance of ammonium sulfate. The contributions of OM in the case (2) increased from the average. The formation of secondary OM can be significant under dry conditions during transport. Detailed mass spectral analyses 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 issue has been investigated by previous studies (e.g., Irei et al., 2014; Yoshino et al., 2016).

3.6. Changes in microphysical parameters of BC-containing particles associated with wet removal

Number and mass size distributions of BC classified by the values of ΔBC/ΔCO are shown in **Figures 7a** and **7b**, respectively. When ΔBC/ΔCO values in continental outflow air masses were greater than 3 ng m^{-3} ppb^{-1} (within the range of the BC/CO emission ratios given by Kanaya et al. 2016), these air masses are defined as "outflow without BC loss". These air masses originated mainly from CN via KR and NE. When ΔBC/ΔCO values of continental outflow air masses are less than 1 ng m^{-3} ppb^{-1}, the air masses were defined as "outflow with BC loss". Considering the typical emission ratios of BC to CO (6-7 ng m^{-3} ppb^{-1}; Kanaya et al., 2016), transport efficiency for the "outflow with BC loss" air masses can be estimated to be less than ~17%. These air masses originated mainly in CS. The low and high APT values for "outflow without BC loss" and "outflow with BC loss" air masses, respectively, gave us confidence in the validity of our classification as discussed in the previous section. As a reference for emission sources ("source"), the average size distributions of BC in a Japanese industrial area (see section 2.1, Miyakawa et al., 2016) are shown in **Figure**

7. The statistics of the size distributions are summarized in **Table ~~1~~2**. Observed differences in the size distributions between source and outflow were generally consistent with previous studies (Schwarz et al., 2010). Air mass aging leads to the growth of BC-containing particles. Number-size distributions of BC largely varied in the size range less than 0.1 μm (**Fig. 7a**). In outflow air masses, such small BC-containing particles were scavenged by larger particles in the coagulation process during transport. The washout process can also affect the BC-containing particles in the smaller size range (<0.1 μm). The peak diameter of mass (number) size distributions of BC became larger, from 0.16 (0.06) μm to 0.18-0.2 (0.09-0.1) μm, between source and outflow. The BC-containing particles have systematically different size distributions in outflow air masses with and without BC loss, indicating that the BC loss process also affected the size distributions. The peak diameter of BC number and mass size distributions in outflow air masses with BC loss was slightly lower than that for air masses without BC loss. The changes in the peak diameter as a function of ΔBC/ΔCO ratios are shown in **Figure 7c**. The observed changes in the diameter or mass per particle were clear and were beyond the uncertainties (see section 2.1).

Figure 8 depicts the probability density of the D_S/D_{core} ratio for the BC size of 0.2 (±0.02) μm for source and outflow air masses. The modal values of the D_S/D_{core} ratio were systematically changed with air mass aging and BC loss (wet removal). The condensation of inorganic and organic vapors on BC-containing particles during transport can account for the increase in the D_S/D_{core} ratio, as discussed in previous studies (e.g., Shiraiwa et al., 2008; Subramanian et al. 2010). As discussed earlier, the results of this study suggested that SO_4^{2-} and OM substantially contributed to the

increase in the D_S/D_{core} ratio. In outflow air masses with BC loss, modal values of the D_S/D_{core} ratio were clearly lower than those in outflow without BC loss. Furthermore, ~~It~~ it is indicated that the wet removal process also affected the coating thickness distributions for the BC sizes in the range 0.15-0.35 μm (**Table ~~1~~2**). It should be noted that the coating of BC-containing particles is not always thick in remote regions, and that the D_S/D_{core} ratio distributions, as well as size distributions, can be affected by the wet removal process during transport in the PBL.

3.7. Discussion

Not only in-cloud scavenging of BC-containing particles but also subsequent precipitation (i.e., the rainout process) can account for the changes in the microphysical parameters of BC detected in this study. Our results show a decrease of both the peak diameter of the BC mass size distribution, and the modal value of the D_S/D_{core} ratios in relation to the rainout. The observed evidence implies that there can be the selective removal of large and water-soluble BC-containing particles during transport in the PBL. The Köhler theory suggests that a lower super saturation is needed for the large and highly water-soluble particles, and this can qualitatively account~~s~~ for the observed changes in the BC microphysics.

Note that the magnitude of the change in the BC size distributions in the PBL (~~0.01~~ ~0.02 μm (~~1~~ 2-2.5 fg)) shown in **Figure 7c**~~this study~~ is smaller than that observed in air masses uplifted from the PBL to the FT, in association with wet removal (~0.04 μm (~3 fg), Fig 2 of Moteki et al., 2012) at a similar level of transport efficiency (<~20%). Although the shape of mass size distributions soon after the rainout processes can be distorted by the droplet activation of larger aerosol particles,

the observed mass size distributions were well fitted by a log-normal function (**Fig. 7b**). **Figure 8** showed the existence of BC-containing particles with the D_S/D_{core} ratios higher than 1.2 even in outflow air masses with BC loss that are expected to readily act as CCN. Air masses sampled at the ground level would be affected by turbulent mixing of those near the clouds around the top of the PBL and those in cloud-free conditions at below-cloud levels. On the other hand, most air masses sampled by aircraft measurements in the FT would experience the cloud processes during upward transport from the PBL. Mixing of air masses in the PBL suggests that they partially experience the in-cloud scavenging processes. The aging (e.g., coagulation) of aerosols particles through the transport (i.e., around ~1 day) after the wet removal events can also lead to the further modification of the particle size and mixing state distributions which have been affected by cloud processes. ~~and therefore the~~ The suppression of changes in the microphysical properties of BC-containing particles during transport in the PBL can be related to these factors. More quantitative assessments of the impacts of these factors on the observed features should be performed using a model which has a function to resolve the mixing state of aerosol particles (e.g., Matsui et al., 2013).

The transport pathways of the continental outflow air masses are horizontally and vertically variable in spring in East Asia because of the frequent alternate cyclone/anticyclone activities in spring (Asai et al., 1988). Oshima et al. (2013) examined the three-dimensional transport pathways of BC over East Asia in spring and showed that the PBL outflow through which BC originating from China was advected by the low-level westerlies without uplifting out of the PBL was one of the major pathways for BC export from continental East Asia to the Pacific, thus supporting the

general features of microphysical properties of BC in continental outflow obtained by this study. Mori et al. (2014) measured the seasonal variations in BC wet deposition fluxes at another remote island in Japan (Okinawa, ~500 km south of Fukue Island), and revealed their maxima in spring, which were consistent with the seasonal variations in the cyclone frequencies. It has been suggested that BC-containing particles were efficiently activated to form cloud droplets in the continental outflow air masses, especially from the CS region, and can affect the cloud physicochemical properties in spring in East Asia, as indicated by Koike et al. (2012). As the results from this study are based on the observations during a limited length of time, it would be worthwhile to further investigate the possible connections of the variabilities in BC microphysical properties with meteorological conditions to provide useful constraints on more accurate evaluations climatic impacts of BC-containing particles in this region (Matsui, 2016). ~~To further understand the possible connections of the variabilities in BC microphysical properties and meteorological conditions in this region can provide useful constraints on the better prediction of climatic impacts of BC-containing particles (Matsui, 2016).~~

4. Conclusions

Ground-based measurements of BC were performed near an industrial source region and at a remote island in Japan. We have reported the temporal variations in the transport and the microphysics of the BC-containing particles, measured using COSMOS, SP2, and ACSM. The impacts of air mass aging upon the growth of BC-containing particles were examined by comparing the ground-based observations between the near-source and remote island sites. $\Delta BC/\Delta CO$ was used as an indicator

of the transport efficiency of BC, because it was controlled mainly by rainout during transport in the PBL. The BC size and coating increased during transport from the near-source to the outflow regions on the timescale of 1-2 days when the rainout during transport was negligible. SO_4^{2-} aerosol was secondarily formed both in the gas- and cloud-phase during transport, and it contributed to the significant increase in the coating materials of BC (i.e., it enhanced the whole size and water-solubility of BC-containing particles). Decreases in the peak diameter of mass size distributions (~0.01 μm) and modal D_S/D_{core} ratios (~0.4 for BC of 0.2 μm) of BC-containing particles were observed in air masses substantially affected by rainout. The observed evidences~~,~~ for the selective removal of large and water-soluble BC-containing particles~~,~~ was qualitatively consistent with the Köhler theory; however ~~they~~ the values ~~are~~ were not as large as those found in air masses uplifted from the PBL to the FT in East Asia associated with precipitation. The mixing of below-cloud and in-cloud air masses in the PBL would result in suppression of the degree of changes in BC microphysical parameters by cloud processes. This study indicates (1) that the changes (sign and degree) in BC microphysics can be affected by how the air masses are transported and (2) that the observed selective removal of large and water-soluble BC-containing particles in East Asia ~~are~~ can be expected to be significant in the PBL as well as in the FT in East Asia.

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742

Figures

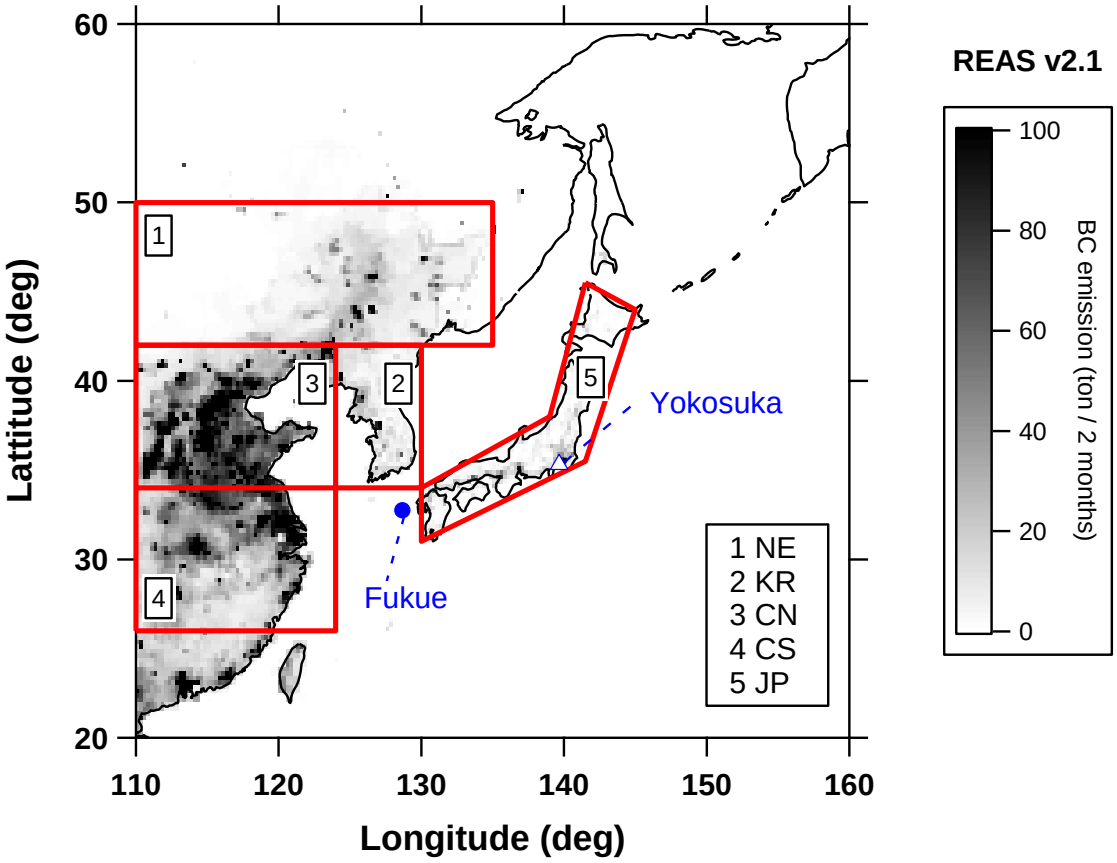
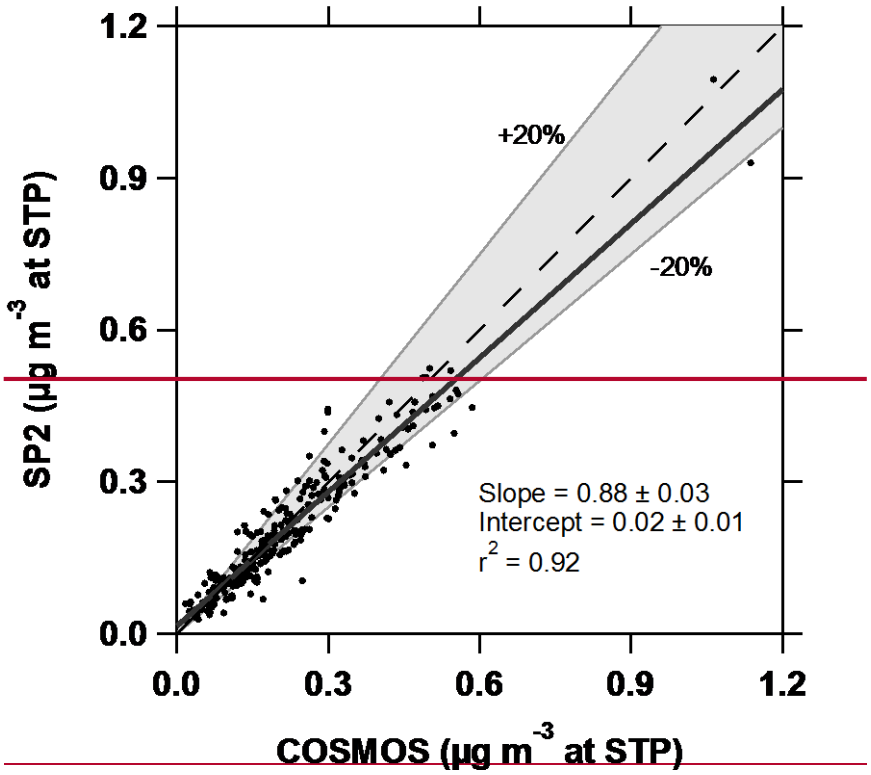


Figure 1. Map of the investigated region with two observation sites (Yokosuka, open triangle; Fukue Island, closed circle) and five defined areas (1 Northeast China; 2 Korea; 3 Central North China; 4 Central South China; 5 Japan). The bimonthly mean BC emission rate (March-April) in 2008 is overlaid on the map (REAS ver. 2.1, Kurokawa et al., 2013).


1.2
0.9
0.6
0.3
0.0
0.0
0.3
0.6
0.9
1.2
SP2 (µg m-3 at STP)
COSMOS (µg m-3 at STP)
+20%
-20%
Slope = 0.88 ± 0.03
Intercept = 0.02 ± 0.01
r2 = 0.92

752

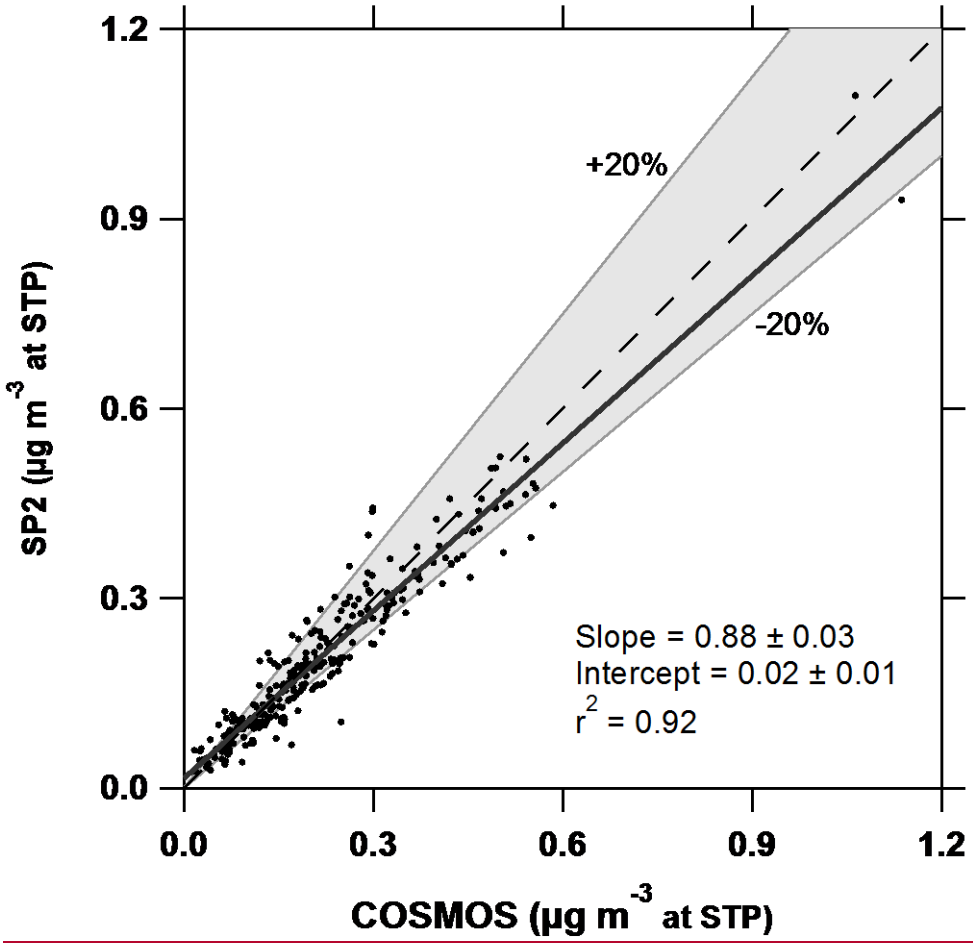
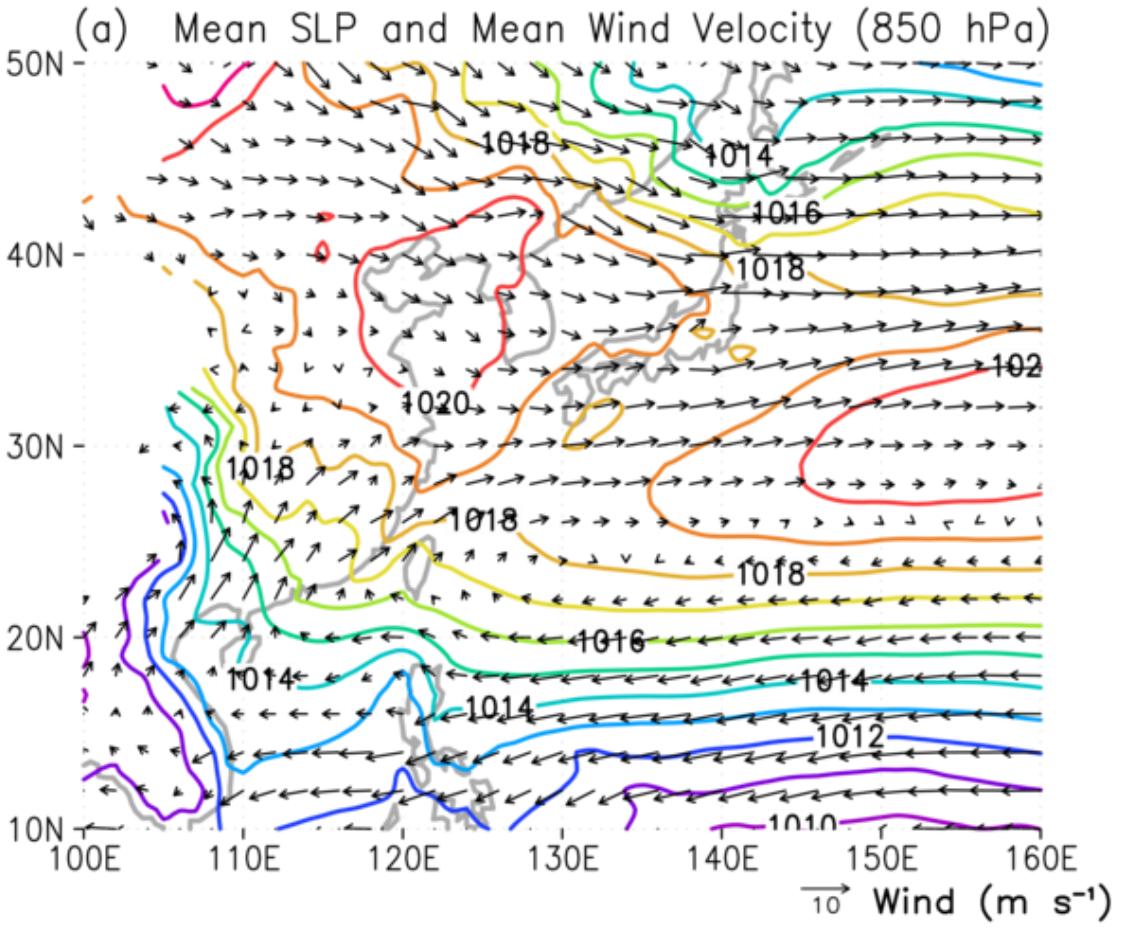
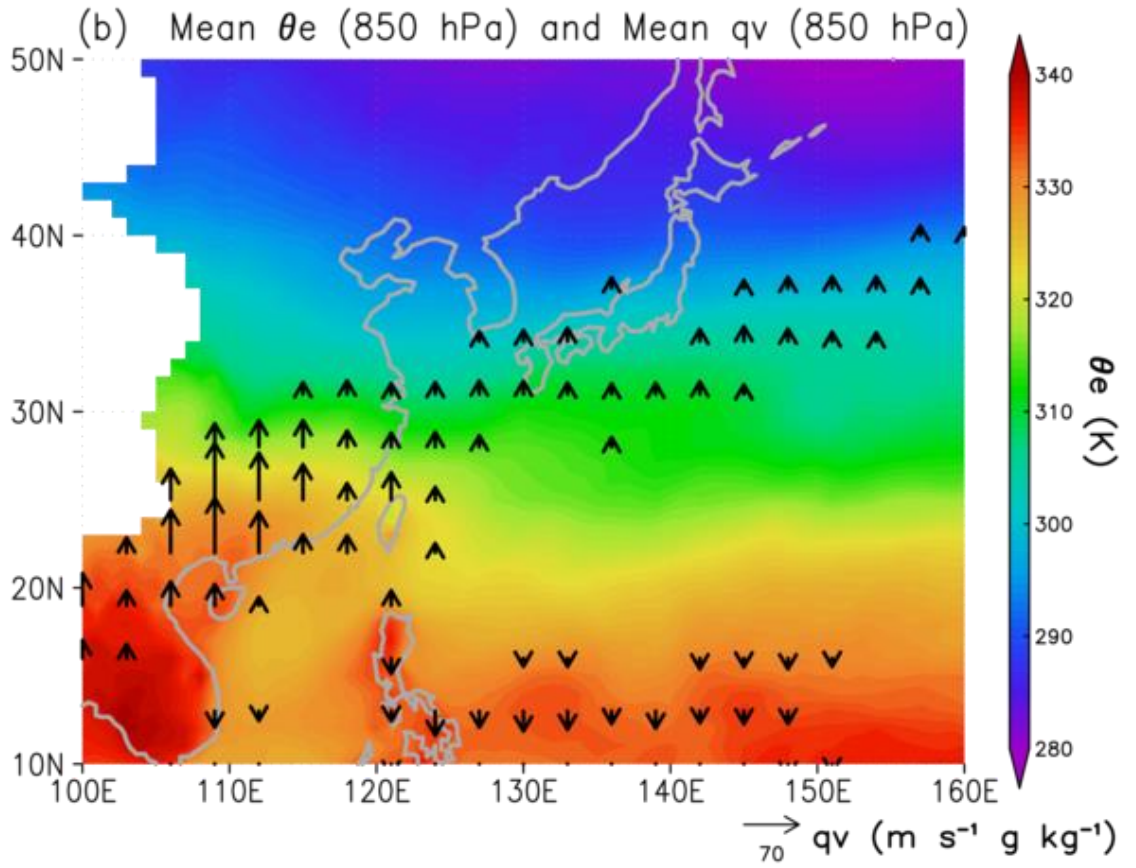


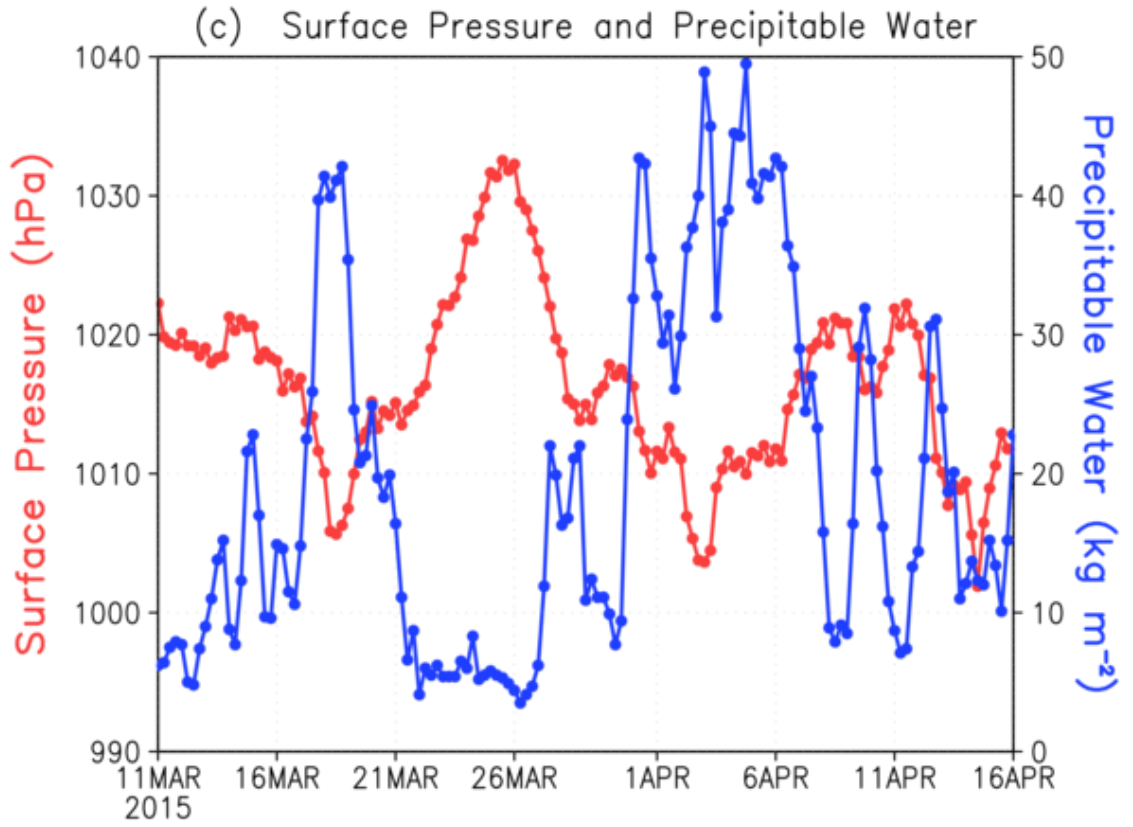
Figure 2. Correlation plot of SP2-rBC and COSMOS-EBC mass concentrations (at standard temperature and pressure). The shaded region corresponds to within ±20%.


(a) Mean SLP and Mean Wind Velocity (850 hPa)
50N
40N
30N
20N
10N
100E
110E
120E
130E
140E
150E
160E
1018
1014
1016
1018
1020
1018
1018
1018
1016
1014
1014
1012
1010
10
Wind (m s⁻¹)

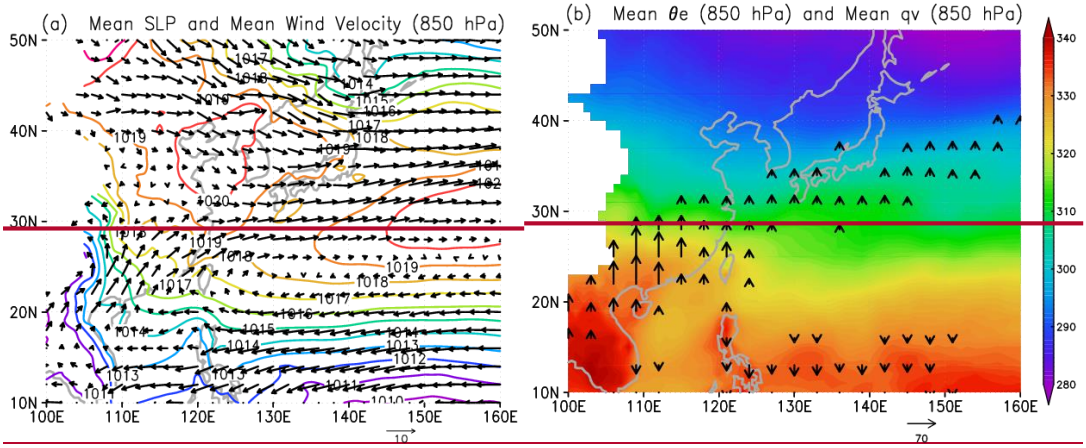
758


(b) Mean θe (850 hPa) and Mean qv (850 hPa)
50N
40N
30N
20N
10N
100E
110E
120E
130E
140E
150E
160E
340
330
320
310
300
290
280
θe (K)
70
qv (m s⁻¹ g kg⁻¹)

759


(c) Surface Pressure and Precipitable Water
Surface Pressure (hPa)
Precipitable Water (kg m⁻²)
1040
1030
1020
1010
1000
990
50
40
30
20
10
0
11MAR 2015
16MAR
21MAR
26MAR
1APR
6APR
11APR
16APR

760


(a) Mean SLP and Mean Wind Velocity (850 hPa)
(b) Mean θe (850 hPa) and Mean qv (850 hPa)
50N
40N
30N
20N
10N
100E
110E
120E
130E
140E
150E
160E
340
330
320
310
300
290
280

761

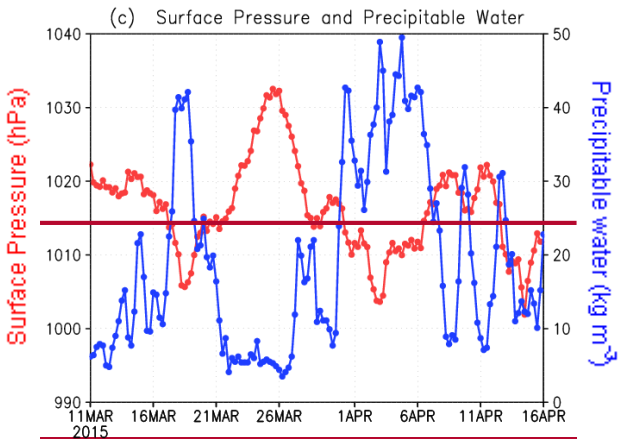
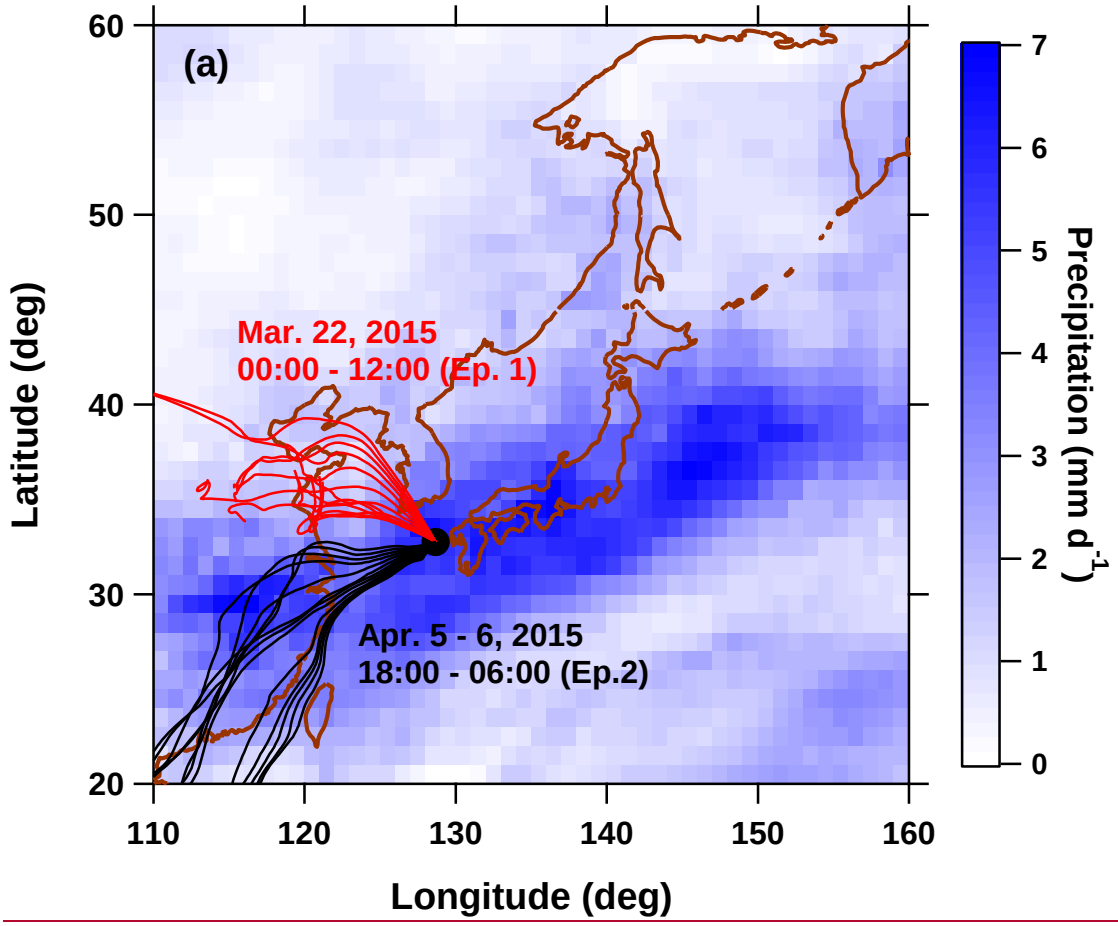
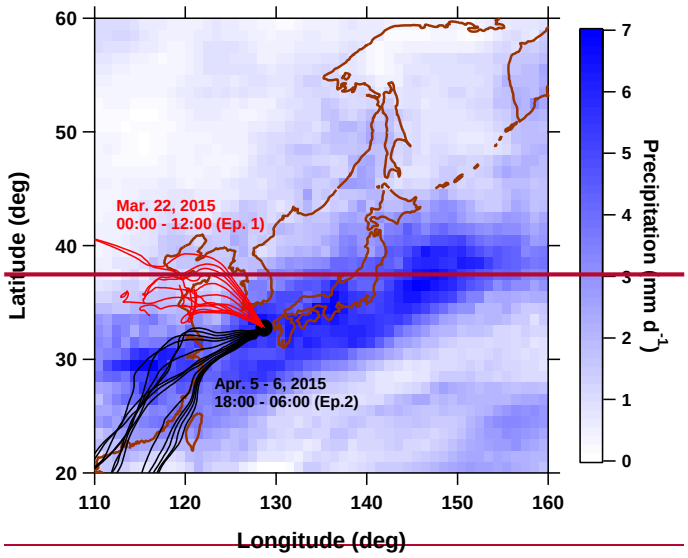


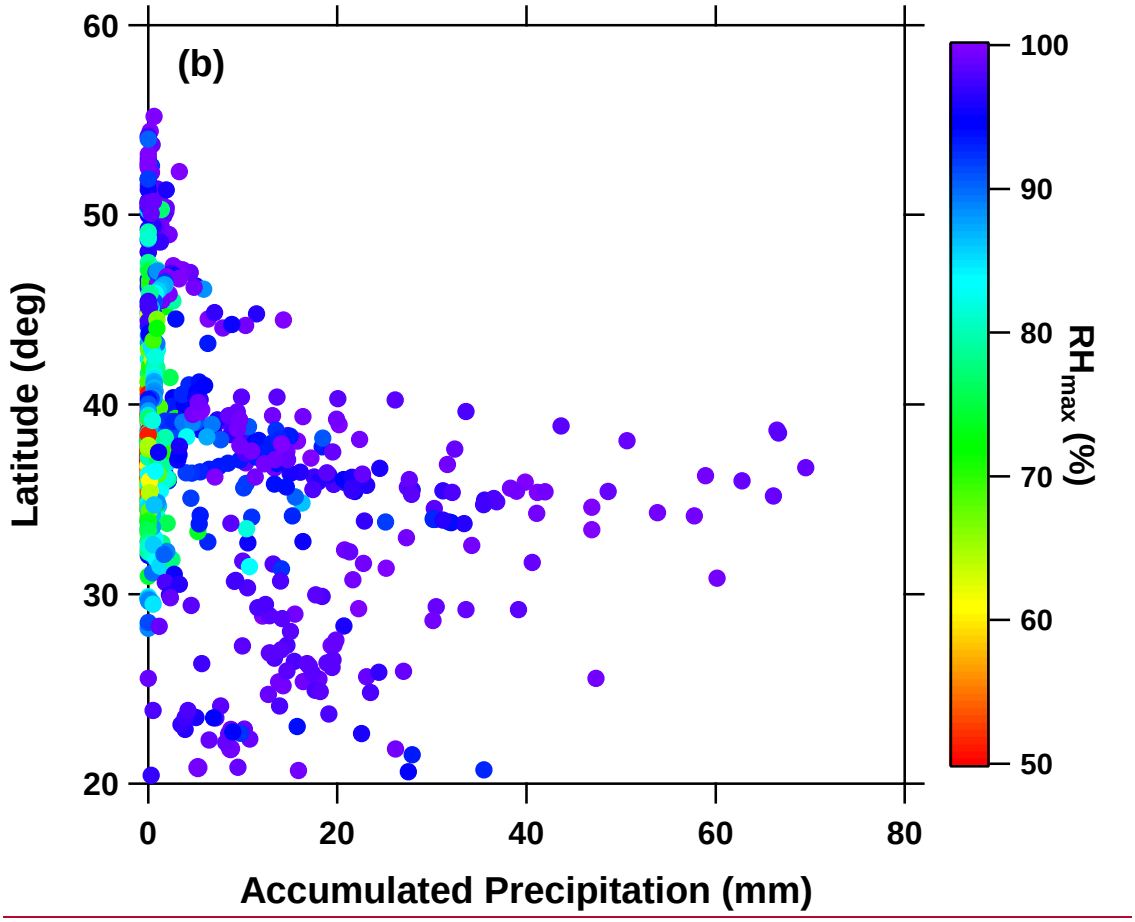
Figure 3. Meteorological fields in East Asia during the observation period (March 11-April 14, 2015) based on NCEP FNL data. (a) Mean SLP (hPa, contours) and mean horizontal wind velocity at the 850-hPa level (m s^{-1}). Regions without data correspond to those of high-altitude mountains. (b) Mean θe (K) and total meridional moisture transport (qv values) at the 850-hPa level (m s^{-1} g kg^{-1}). Only qv vectors with magnitudes greater than 10 m s^{-1} g kg^{-1} were plotted. (c) Temporal variations in the surface pressure (hPa, red line and markers with left axis) and precipitable water (kg m^{-2}, blue line and markers with right axis) at the Fukue observation site (32.75°N, 128.68°E).


(a)
Mar. 22, 2015
00:00 - 12:00 (Ep. 1)
Apr. 5 - 6, 2015
18:00 - 06:00 (Ep.2)
Latitude (deg)
Longitude (deg)
Precipitation (mm d-1)
60
50
40
30
20
110
120
130
140
150
160
0
1
2
3
4
5
6
7

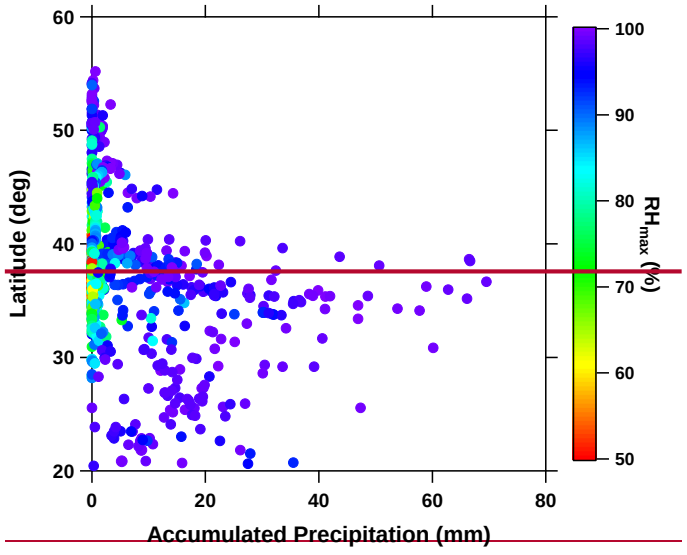
774


Mar. 22, 2015
00:00 - 12:00 (Ep. 1)
Apr. 5 - 6, 2015
18:00 - 06:00 (Ep.2)
Latitude (deg)
Longitude (deg)
Precipitation (mm d-1)
60
50
40
30
20
110
120
130
140
150
160
0
1
2
3
4
5
6
7

775



776



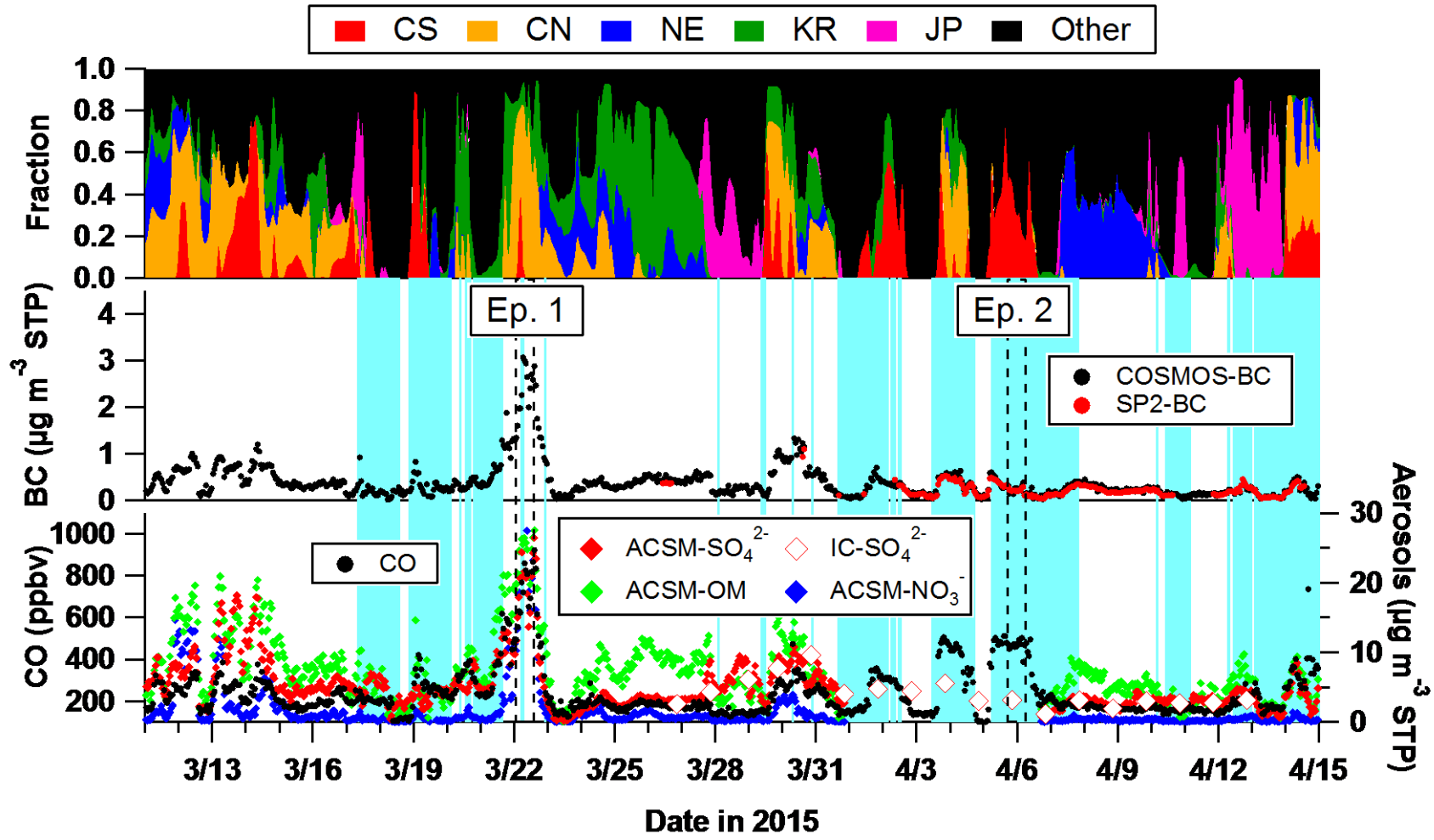
777

778

779 **Figure 4.** (a) Mean precipitation derived from GPCP during the observation period

780 (March 11-April 14, 2015). Three-day backward trajectories for selected periods are

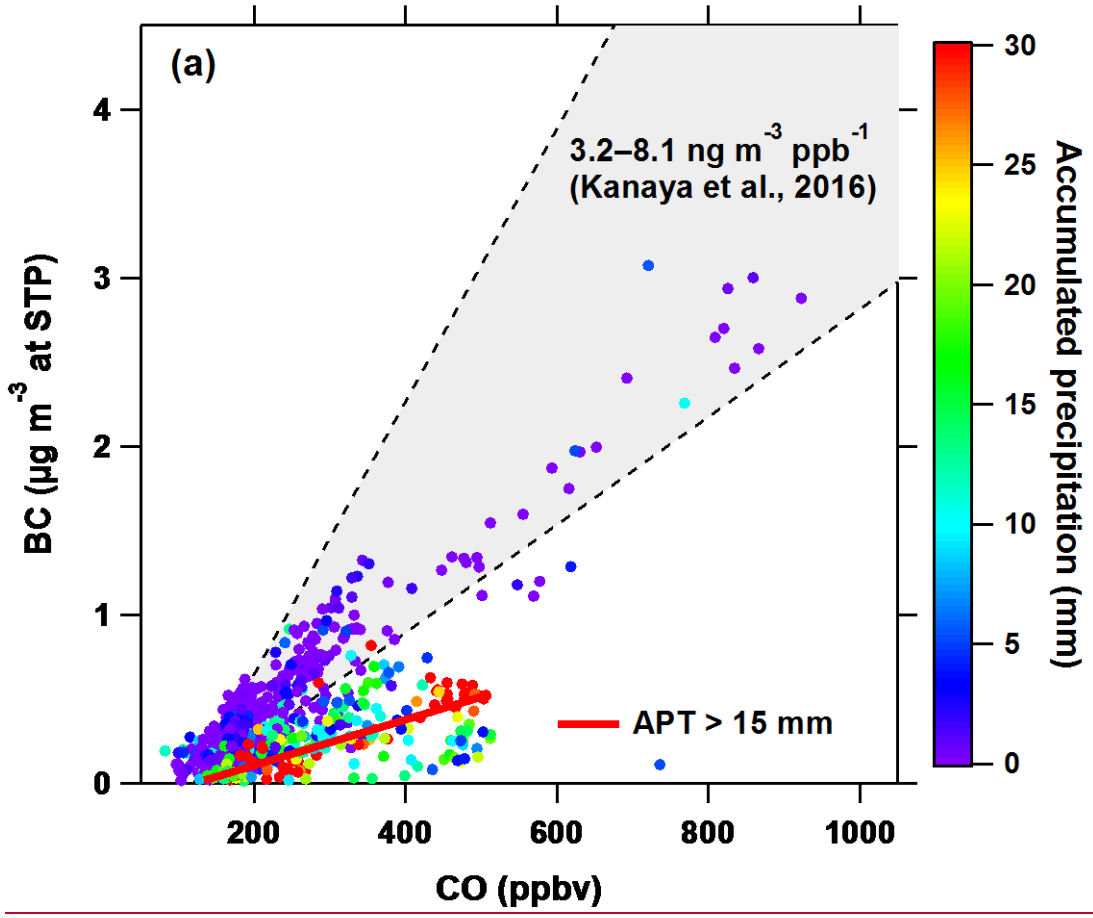
781 overlaid (red lines, 00:00-12:00LT March 22, 2015 (Ep.1); black lines, 08:00LT April
782 5-06:00LT April 6, 2015 (Ep.2)). (b) The relationship between APT and Lat_{ORIG} (see
783 text for details) colored by the maximum RH along the backward trajectories.
784


CS
CN
NE
KR
JP
Other
Fraction
1.0
0.8
0.6
0.4
0.2
0.0
Ep. 1
Ep. 2
BC (μg m-3 STP)
4
3
2
1
0
COSMOS-BC
SP2-BC
CO (ppbv)
1000
800
600
400
200
CO
ACSM-SO4 2-
IC-SO4 2-
ACSM-OM
ACSM-NO3 -
Aerosols (μg m-3 STP)
30
20
10
0
3/13
3/16
3/19
3/22
3/25
3/28
3/31
4/3
4/6
4/9
4/12
4/15
Date in 2015

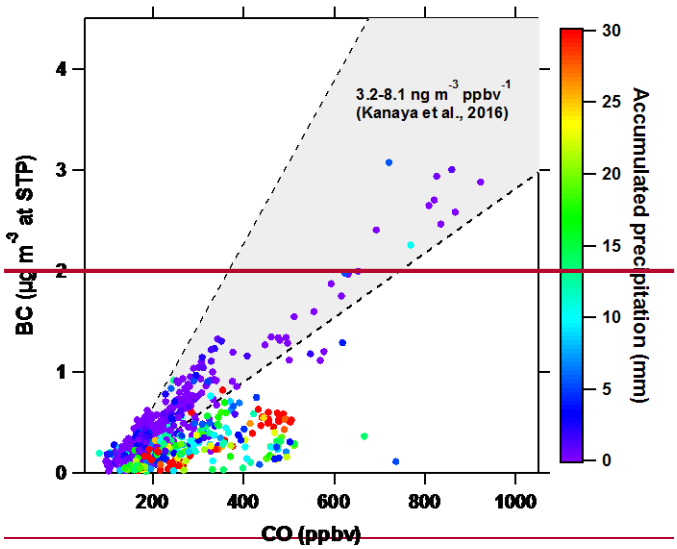
785

786

Figure 5. Temporal variations in air mass origin and concentration of trace species. (Top panel) Fractional residence time of air masses passed over selected area (Red, Central South China; Orange, Central North China; Blue, Northeast China; Green, Korea; Pink, Japan; Black, other regions such as Ocean). (Middle panel) mass concentrations of BC measured using the COSMOS (black markers) and SP2 (~~blue~~ red markers). (Bottom panel) concentrations of CO (black markers)~~,~~ ~~and~~ SO_4^{2-} (red ~~circles~~ closed and open ~~diamond~~ makers for ACSM and IC, respectively), ACSM-NO_3^- (blue makers), and ACSM-OM (light green markers). The periods with the APT > 3 mm are highlighted in light blue in the middle and bottom panels. The periods denoted as Ep.1 and Ep.2 (see the text for details) were enclosed by dashed lines.


(a)
3.2–8.1 ng m-3 ppb-1
(Kanaya et al., 2016)
APT > 15 mm
BC (μg m-3 at STP)
CO (ppbv)
Accumulated precipitation (mm)
0
1
2
3
4
200
400
600
800
1000
0
5
10
15
20
25
30

794


3.2-8.1 ng m-3 ppbv-1
(Kanaya et al., 2016)
BC (μg m-3 at STP)
CO (ppbv)
Accumulated precipitation (mm)
0
1
2
3
4
200
400
600
800
1000
0
5
10
15
20
25
30

795

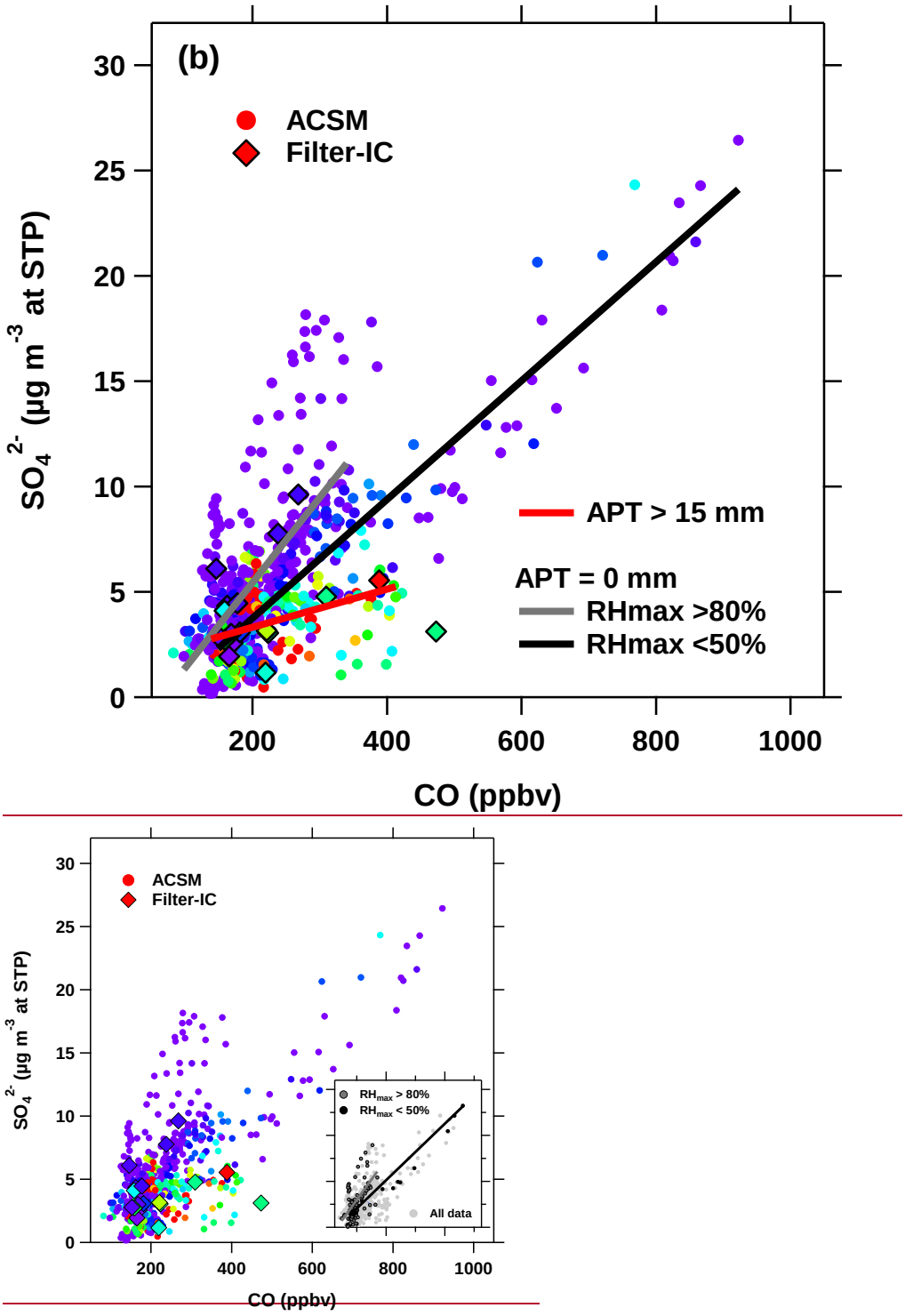
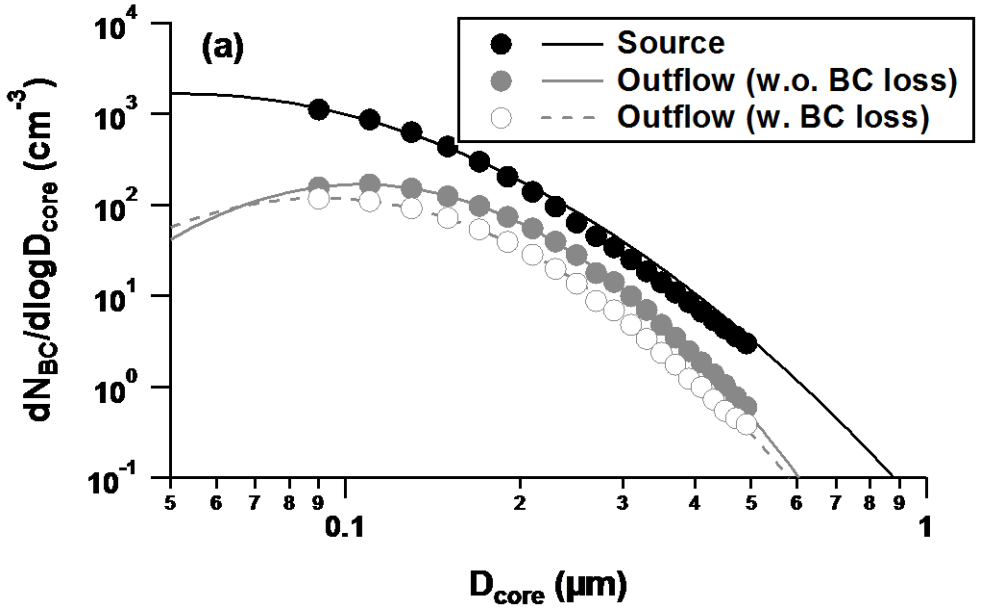
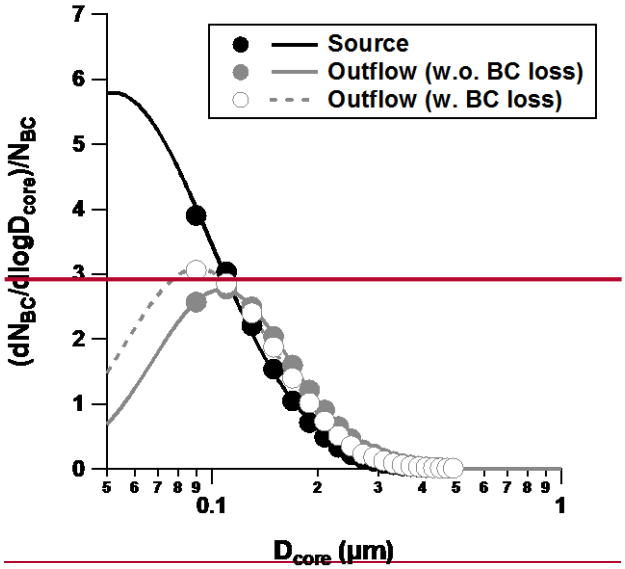


Figure 6. Correlation between aerosol mass concentrations and CO mixing ratio colored according to the APT. (a) BC measured by COSMOS and (b) SO_4^{2-} measured by ACSM and IC (circles and diamond markers, respectively). The bold lines are the linear fitting to the BC/CO and ACSM-SO_4^{2-}/CO correlations for the selected data

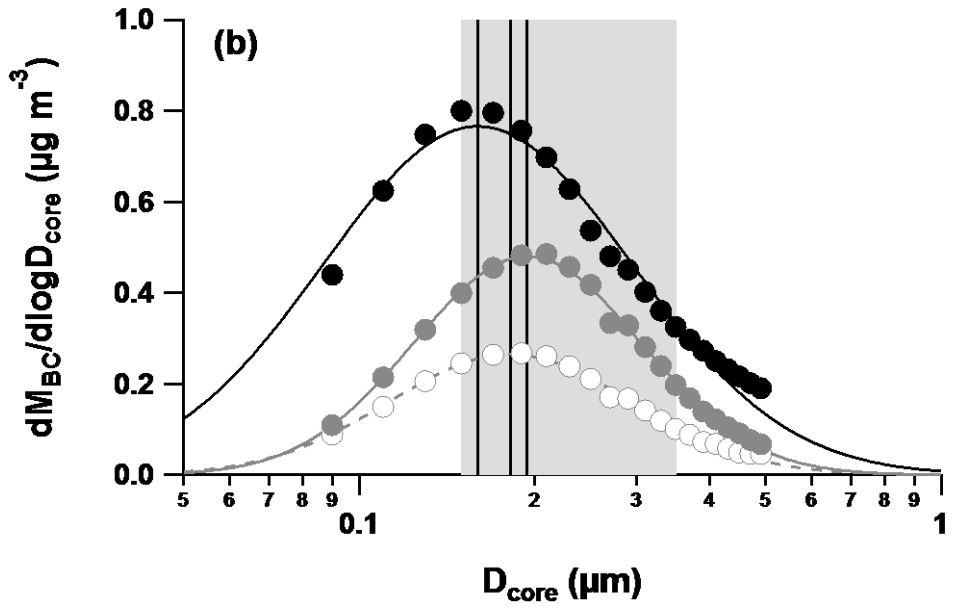
points, i.e., those with the APT >15 mm for BC and SO_4^{2-} (red lines), those with the APT of zero and the RH_{max} <50% for SO_4^{2-} (black line), and those with the APT of zero and the RH_{max} >80% (shaded line). ~~ACSM-SO_4^{2-}/CO correlations for the zero-APT air masses (no precipitation during transport) with RH greater than 80% (dark shaded markers) or less than 50% (black) are in the subset of 6b.~~


(a)
Source
Outflow (w.o. BC loss)
Outflow (w. BC loss)
$dN_{BC}/dlogD_{core}$ (cm^{-3})
D_{core} (μm)

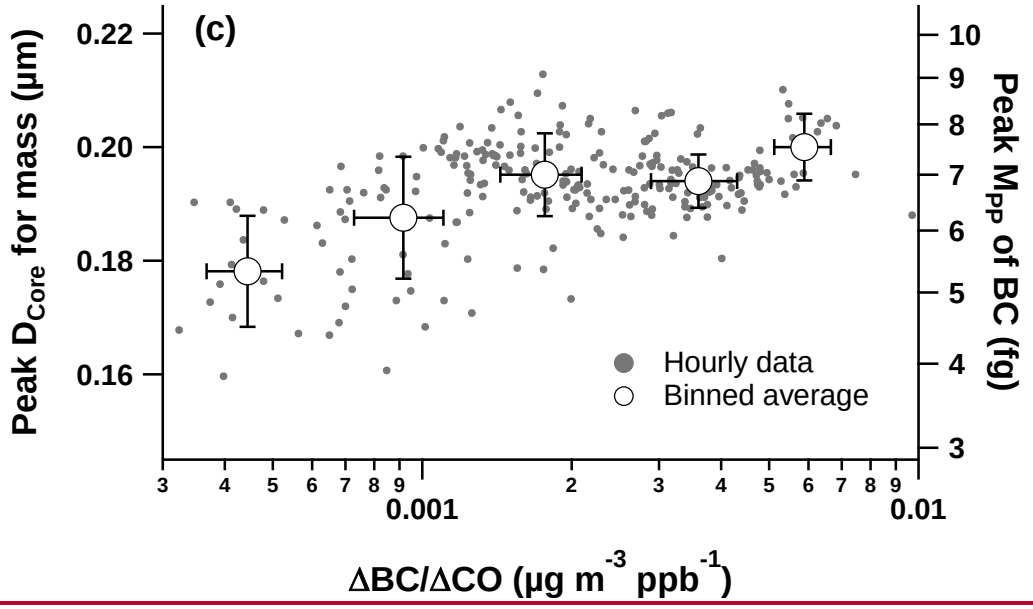
809


Source
Outflow (w.o. BC loss)
Outflow (w. BC loss)
$(dN_{BC}/dlogD_{core})/N_{BC}$
D_{core} (μm)

810


(b)
1.0
0.8
0.6
0.4
0.2
0.0
dM_BC/dlogD_core (µg m^-3)
5 6 7 8 9
0.1
2 3 4 5 6 7 8 9
1
D_core (µm)

811


(c)
0.22
0.20
0.18
0.16
Peak D_Core for mass (µm)
10
9
8
7
6
5
4
3
Peak M_PP of BC (fg)
Hourly data
Binned average
3 4 5 6 7 8 9
0.001
2 3 4 5 6 7 8 9
0.01
ΔBC/ΔCO (µg m^-3 ppb^-1)

812

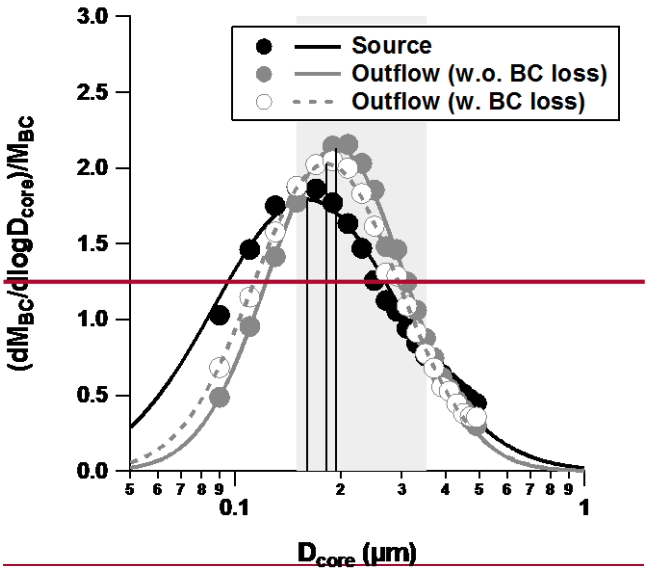
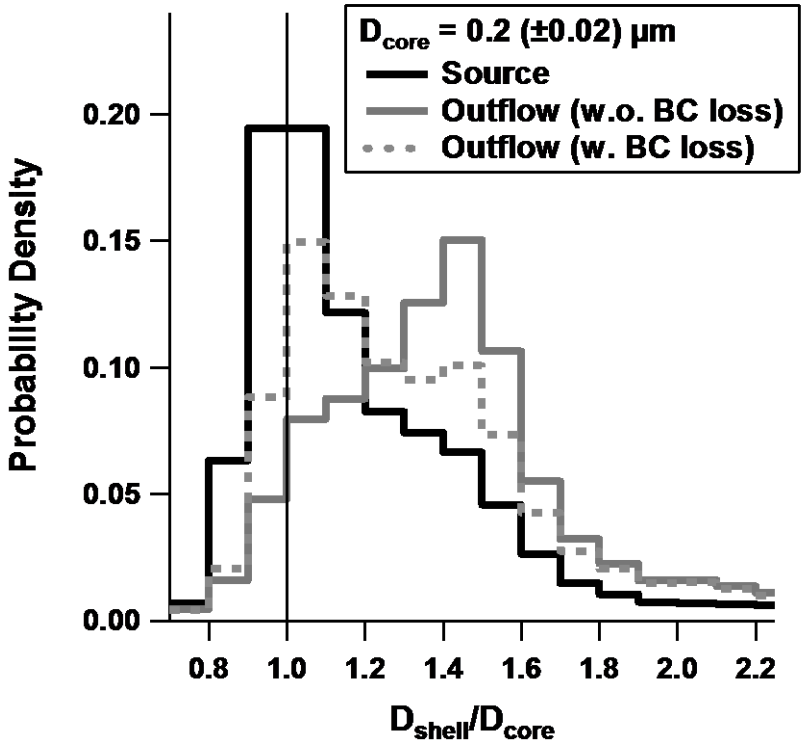


Figure 7. The (a) number and (b) mass size distributions of BC measured at Yokosuka (black markers) and at Fukue Island (gray markers). (c) The evolution of the peak D_{core} as a function of the degree of removal of BC. ~~All the size distributions are normalized by the number or mass concentrations of BC integrated for the diameter range of 0.08-0.5 μm.~~ The size distributions at Fukue Island include the data for the outflow air masses with (open markers) and without (closed markers) BC loss. Lines are the lognormal fitting results. The shaded band in ~~6~~7(b) corresponds to the size range analyzed to estimate D_s/D_{core} ratios. Vertical lines in 7~~6~~(b) represent the peak diameter of the lognormal fit for each of three mass size distributions. Note that the peak diameter of log-normal fit for the BC number size distributions at Yokosuka was estimated from the peak diameter of its mass size distribution (**Table ~~1~~2**).



826

827

828 **Figure 8.** Probability density function of the estimated D_s/D_{core} ratios for BC-containing
829 particles with the size 0.2 (±0.02) µm at Yokosuka (black line) and in the air masses of
830 continental outflow with (gray dashed line) and without (gray solid line) BC loss.

831

Tables

Table 1. Mean chemical composition of fine aerosols during the observation period

Componnents	Period average	APT			
		0 mm	0 mm RH_{max} <50%	0 mm RH_{max} >80%	>15 mm
Ammonium sulfate	44.9%	41.8%	34.0%	48.9%	50.4%
Ammonium nitrate	11.7%	15.7%	10.7%	8.0%	5.0%
OM	40.9%	40.1%	52.0%	40.4%	42.0%
BC	2.5%	2.4%	3.2%	2.6%	2.5%

Table 2~~1~~. Summaries of BC microphysical parameters measured at Yokosuka and Fukue Island

Site	Air mass type	Averaging time*	ΔBC/ΔCO	APT	Log Normal Fit Parameters Avg. (1σ)		1-hr Median D_S/D_{core} for selected D_{core} Avg. (1σ)			
		(hrs)	(ng m^{-3} ppb^{-1})	(mm)	MMD (μm)	σ_g	0.15 - 0.2	0.2 - 0.25	0.25 - 0.3	0.3 - 0.35 (μm)
Yokosuka	Source	184	-	-	0.160 (0.019)	1.84 (0.08)	1.18 (0.07)	1.15 (0.06)	1.10 (0.04)	1.07 (0.04)
Fukue	Outflow	87	>3	1.2	0.195 (0.005)	1.57 (0.05)	1.37 (0.05)	1.32 (0.03)	1.21 (0.03)	1.17 (0.03)
Fukue	Outflow	51	<1	19.9	0.182 (0.011)	1.62 (0.09)	1.25 (0.05)	1.24 (0.04)	1.16 (0.02)	1.12 (0.03)

*Time used for calculating averaged statistics of the microphysical properties of BC-containing particles.