Comments by Reviewer #1

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

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

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

Major revision points

1. Terminology

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

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

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

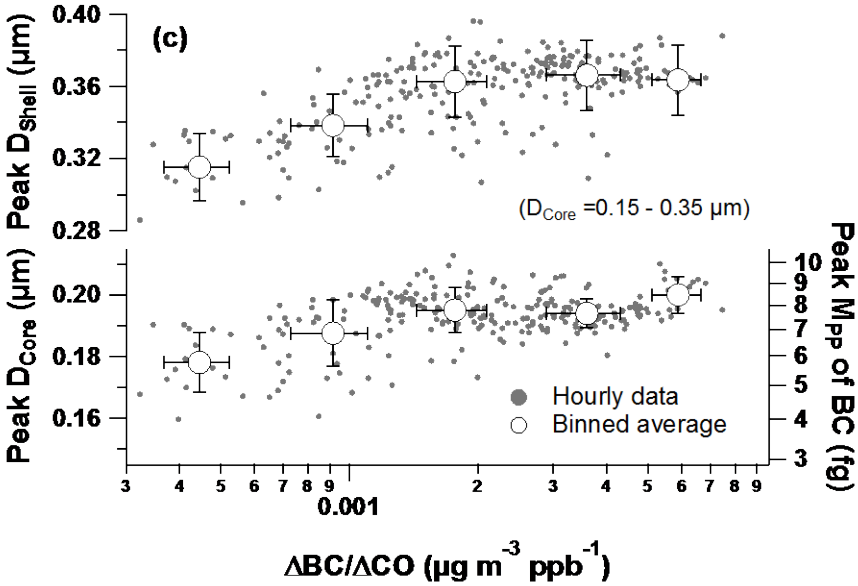

Figure 7c modified

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

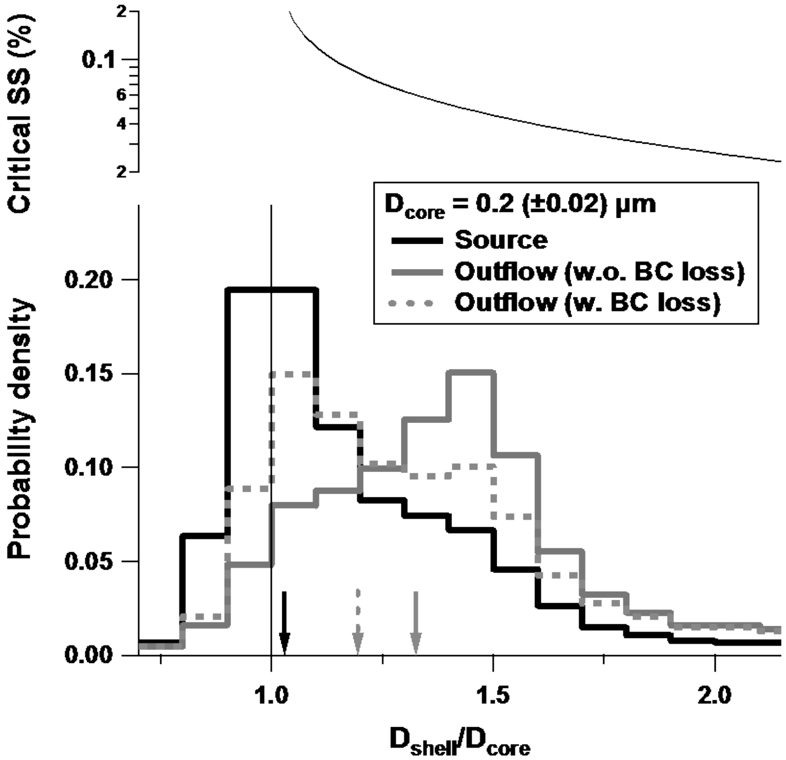

Figure 8 modified

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

3. Chemical composition

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

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

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

Comments.

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

We have corrected as suggested.

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

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

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

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

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

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

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

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

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

We modified the sentences as suggested.

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

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

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

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

We have corrected as suggested.

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

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

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

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

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

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

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

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

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

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

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

We have corrected as suggested.

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

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

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

We have corrected as suggested.

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

We have corrected as suggested.

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

We have corrected as suggested.

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

We have corrected as suggested.

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

We have corrected as suggested.

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

We have corrected as suggested.

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

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

Line 274: sentence reads awkwardly; perhaps omit.

We have removed it as suggested.

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

We have corrected as suggested.

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

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

Comments by Reviewer #2 Dr. Gavin McMeeking

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

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Major revision points

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

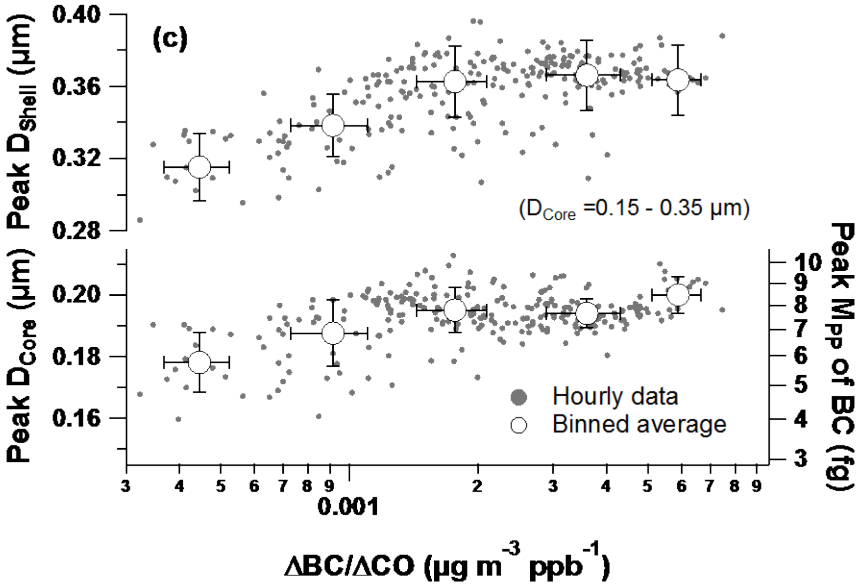
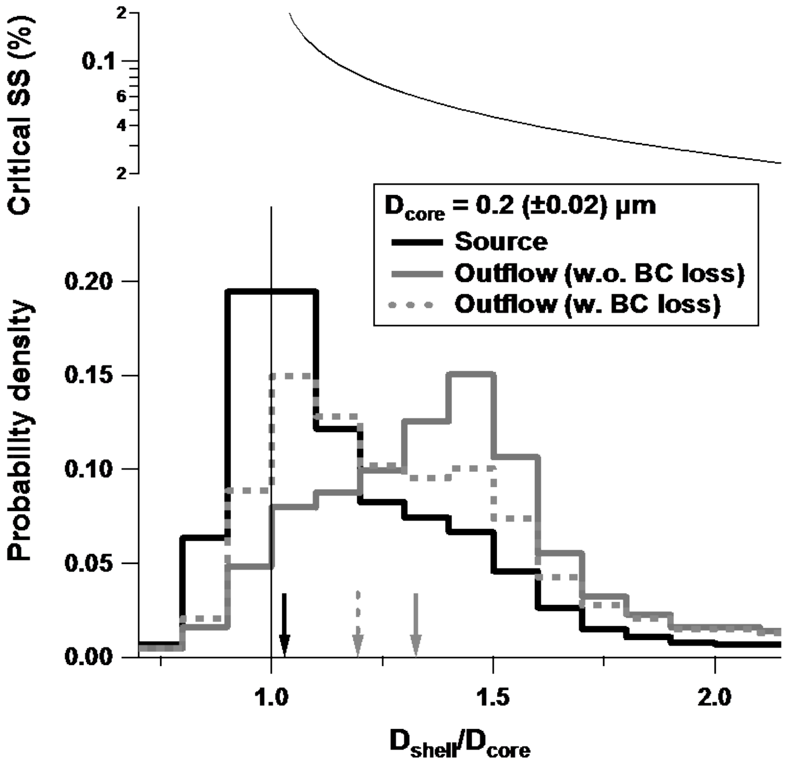


Figure 7c modified

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



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Responses to Reviewer #1

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

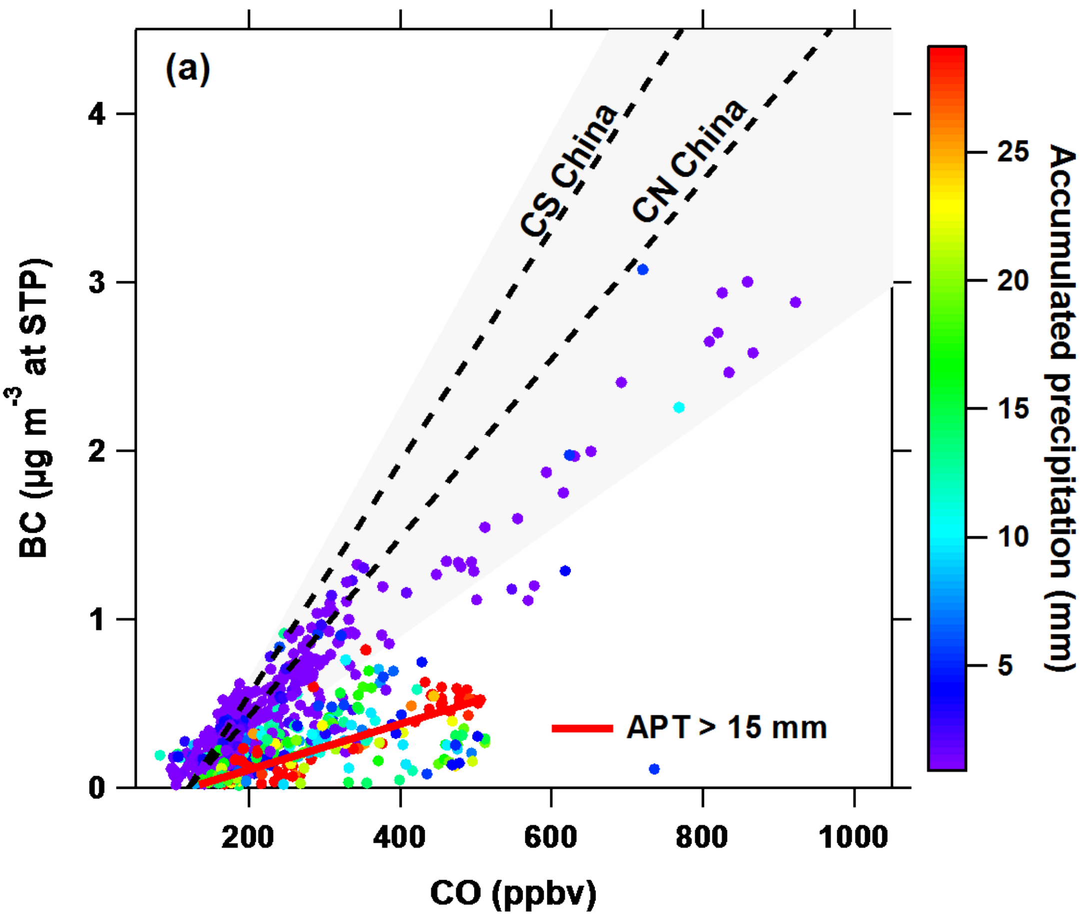
We modified the representations as suggested.

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

We have corrected as suggested.

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

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



Modified figure 6 (a)

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

Response to reviewer comment on line 343:

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

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

Response to reviewer comment on line 345:
The response to the reviewer is weak. It does not address the main point of the comment, that concentrations are too low for coagulation to be an important process in removal of small BC particles. Given the manuscript focuses on changes in BC size distributions it seems such a fundamental topic should be discussed, even briefly, in the manuscript.

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

Response to reviewer comment to line 372:
I'm not clear which uncertainty in section 2.1 is being referred to in the response to this comment, but while I would agree that the SP2 can resolve quite small differences in rBC mass (assuming constant material properties), I think the uncertainty the reviewer is talking about here is the statistical uncertainty associated with the spread in the data, and whether there is a significant difference in fg/particle for the two conditions. Note that the comparisons of log-normal fit MMDs in Table 2 is less reliable because it includes an assumed density, which might not be constant for the two cases.

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

Response to reviewer comment to line 373:

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

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

Responses to my comments:

First general comment (BC removal processes):

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

We have corrected as suggested.

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

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

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

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

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[2]Institute for Arctic Climate Environment Research, Japan Agency for Marine-Earth Science and Technology, 3173-25 Showa-machi, Kanazawa-ku, Yokohama, Kanagawa, 236-0001, Japan.

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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 report the temporal variations in the transport, size distributions, and mixing states of the BC-containing particles. These particles were 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 and organic 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 wet removal on 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~~wet removal 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~~ wet removal originated mainly from a region in South China (20º-35ºN) in the spring of 2015. ~~Selective r~~Removal of large and thickly-coated BC-containing particles was detected in the air masses that were substantially affected by the ~~rainout~~ wet removal 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~~wet removal 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 on increased 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 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 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. 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 BC aging processes (condensational growth and coagulation) in box and regional-scale models, and parameterized timescales for the conversion of BC-containing particles from water-insoluble to -soluble in global models (Oshima et al., 2009; Liu et al., 2011; Oshima and Koike, 2013). However, 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 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 ~~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, as the part of the Aerosol Radiative Forcing in East Asia (A-FORCE) aircraft campaigns (Oshima et al., 2012). 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 processing, 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~~ have a large impact on the global- and regional-scale spatial distributions of BC through their upward transport from the PBL to the FT associated with ~~rainout~~ cloud processes. Despite the importance of the size distributions and mixing states of BC-containing particles in the PBL, the 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.~~This study determined that the transport efficiency of BC aerosol particles through the PBL was substantially reduced by wet removal. 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 describe the meteorological characteristics of the East Asian region in the spring of 2015. Then, we discuss the relative importance of the below-cloud (i.e., washout) and in-cloud scavenging (i.e., rainout) processes for the removal of BC as well as the transport patterns of the East Asian outflow air masses in spring. The 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

Continuous measurements of $PM_{2.5}$ and BC aerosols 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 portion of Fukue Island, approximately 20 km from the main residential area in the southeast. The fine mode $PM_{2.5}$ aerosols sampled at the site are mostly transported from areas beyond the island. The enhanced concentrations of BC aerosols in Fukue Island can be mainly attributed to long-range transport from the Asian continent, according to a previous study (Shiraiwa et al., 2008) and an emission inventory work (**Fig. 1**, REAS ver. 2.1, Kurokawa et al., 2013).

We deployed an SP2 (Droplet Measurement Technologies, Inc., USA) for the analysis of microphysical parameters of refractory BC (rBC, Petzold et al., 2013) from March 26, 2015 to April 14, 2015. The SP2 was calibrated before starting the ambient measurements. The calibration protocol for our SP2 is described in Miyakawa et al. (2016). 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. The analysis of the calibration results suggests that the full width of half maxima (FWHM) was typically 30% of the modal incandescence signal intensity (S_{LII}) for the diameter range studied. Note that the FWHM can be regarded as an upper limit to describe the resolving power of rBC mass per particle using our SP2, because the combination of polydisperse size distribution of FS particles and the transfer function of the DMA can broaden the distributions of S_{LII} for the prepared FS particles. 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 rBC size using the SP2. Mass equivalent diameter (D_{core}~~MED~~) of an rBC particle was derived from the rBC mass per particle (m_{pp}) with an assumed particle density 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 upper limit~~maximum value~~ of the estimation 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,~~ Maximum levels of D_S/D_{core} ratios retrieved ~~of~~ were ~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 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 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~~ outside~~s~~

of the measurable D_{core} range (0.08-0.5 µm). 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 may 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 indicated that SP2-rBC mass concentrations agreed well with COSMOS-EBC within the uncertainty of COSMOS. Therefore we simply use "BC", instead of the EBC and rBC defined depending upon the measurement techniques. We analyzed the COSMOS data for the BC mass concentrations, and the SP2 data for the BC microphysics.

The chemical composition of non-refractory submicron aerosols was measured using an Aerodyne Aerosol Chemical Speciation Monitor (ACSM, Aerodyne, Inc., USA.) placed in an observatory container at Fukue Island during the observation period. The details of the ACSM at Fukue Island have been described in Irei et al. (2014). The collection efficiency (CE) of the ACSM was assumed to be 0.5 for this period (Yoshino et al., 2016). We considered sulfate (SO_4^{2-}) ions as a major non-BC material and one of the most important secondary aerosols in East Asia (Takami et al., 2007) for the data interpretation. The fact that SO_4^{2-} is produced in the cloud phase as well as in the gas phase is beneficial for interpreting temporal changes in SO_4^{2-} concentration associated with the wet removal processes. We also analyzed other non-refractory components such as nitrate (NO_3^-), ammonium (NH_4^+), and organic matter (OM). During the period April 1 -7, 2015, the critical orifice of the inlet assembly of the ACSM became clogged. ACSM-derived SO_4^{2-}, NO_3^-, NH_4^+, and OM (ACSM- SO_4^{2-}, -NO_3^-, -NH_4^+, and -OM) for this period was not used in the analysis.

Two high volume air samplers (HV500F, Sibata Scientific Technology, Ltd., Japan) were deployed on the rooftop of the observatory container. The sampling flow rate for both samplers was 500 liters per minute (lpm). Air sampling was carried out for 21 h (from 10:00 AM to 7:00 AM) on a 110-mm pre-combusted (900°C for 3 h) quartz filter (QR-100, Advantec Toyo Kaisha Ltd., Japan). Both have a $PM_{2.5}$ impactor for 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 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 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~~ spatial 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. 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~~have passed alternately over East Asia 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 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 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 humidity (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 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

In this study, the removal processes including dry deposition and washout below-cloud scavenging were considered to be minor. The dry deposition in this region has already been evaluated by Kanaya et al. (2016), who found minimal decrease in ΔBC/ΔCO for air masses not affected by wet removal but with different transport times. The washout below-cloud scavenging 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 (Wang et al., 2014), 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 below-cloud scavengingwashout process did not play a major role in the removal of BC in East Asian outflow.

3.3. Temporal variations in 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, SO_4^{2-}, and OM were positively correlated with CO at Fukue Island, and these results illustrate the impact of continental outflow affected by incomplete combustion sources 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. 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. 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 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 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, 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

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 (±0.06) and 9.8 (±2.7) 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 relative enhancements of BC and SO_4^{2-} to CO were mainly affected by the APT. 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}~~varied~~,~~ slightly depending on the origin of the air masses (this range is overlaid on **Fig. 6a**). In their study, the ΔBC/ΔCO ratios for Central North and South

China regions were estimated to be 5.3 (±2.1) and 6.9 (±1.2) ng m^{-3} ppb^{-1}, respectively. 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 (in-cloud scavenging~~rainout~~) was one of the most important controlling factors on the transport efficiency of BC in this region during the observation period.~~ The use of the ΔBC/ΔCO ratios is feasible for examining the wet removal of BC during the observation period.~~

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 slopes against RH_{max} when APT was zero was found during the observation period (data not shown). The SO_4^{2-}/CO slopes with the APT values of zero were analyzed as a function RH_{max} (**Figure 6b**), and these varied from 30.7 (±1.8) to 44.1 (±13.4) ng m^{-3} ppb^{-1} under the conditions without (RH_{max} <50%) and with (RH_{max} >80%) cloud impacts, respectively. The difference in the slope between without and with cloud impacts is small, however significant (based on the analysis of covariance to these data sets). The fact that the SO_4^{2-}/CO slope increased with RH_{max} when the APT was zero~~,~~ ~~thus~~ suggests~~sing~~ that aqueous phase formation and subsequent droplet evaporation partly contributed to the mass concentrations of SO_4^{2-} observed at Fukue Island. Therefore, the changes in the SO_4^{2-}/CO correlation were controlled largely by the in-cloud scavenging~~rainout process~~ and weakly by aqueous-phase formation during transport.

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 comparison between cases (3) or (4) and (2) is useful to elucidate the effect of the cloud processing. The results are summarized in **Table 1**. Ammonium sulfate and OM were dominant in all cases. The relative changes in chemical compositions of fine aerosol particles were within around 10%. As all components of fine aerosols were removed through the in-cloud scavenging (Fig. 10 of Kanaya et al., 2016), it is expected that the relative abundance does not largely vary with the in-cloud scavenging. The relative contributions of ~~ammonium sulfate~~fine aerosols in the cases (3) and (4) increased from the ~~average~~case (2), indicating that cloud processes affected their relative abundances~~ of ammonium sulfate~~. Ammonium sulfate contribution slightly increased with the in-cloud scavenging (based on the comparison between cases (2) and (3) or (4)), while the relative contributions of ammonium nitrate, OM, and BC slightly decreased. 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, secondary formation of OM, and cloud-phase formation of OM in East Asia are beyond the scope of this study, and they are not discussed in this study. The former two issues ha~~s~~ve 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 (D_{core}) 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, **(Table 2)** 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 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~~ would be scavenged by larger particles in the coagulation process during transport. The ~~washout process~~ below-cloud scavenging can also affect the BC-containing particles in the smaller size range (<0.1 μm) when the air masses were affected by the precipitation. The peak D_{core} ~~diameter~~ of mass (number) size distributions of BC became larger, from 0.16 (0.06, which is estimated by the mass size distribution) 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 D_{core}~~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 of the core and total (i.e., core and shell) size distributions of BC-containing particles as a function of ΔBC/ΔCO ratios are shown in **Figure 7c**. The peak values of D_{core} and D_S (with the D_{core} range of 0.15 - 0.35 μm) were determined by fitting the log-normal function to the hourly BC mass-D_{core} and BC number-D_S distributions of BC-containing particles, respectively. The reason why we did not analyze the peak values of D_{core} for BC number size distributions is that they were mostly smaller than 0.08 μm (outside the measurable range). The observed ~~changes~~ decreases in the diameters or BC mass per particle were clear and were beyond the uncertainties of SP2 (see section 2.1). The changes in the peak D_{core} and D_S from the highest to lowest bins of ΔBC/ΔCO ratios were 0.02 μm (2-2.5 fg) and 0.05 μm, respectively, which are statistically significant ($p < 0.01$).

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 (in-cloud scavenging~~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 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 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 diameters, D_S and D_{core}, of the BC number and mass size distributions, respectively, 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 for the observed changes in the BC microphysics. The D_S/D_{core} ratios (with D_{core} of 0.2 μm) in **Figure 8** were converted to the critical super saturation (SS_C) of BC-containing particles, which are estimated using the observed chemical composition of non-BC materials at Fukue Island. Hygroscopicity parameters ("CCN-derived" κ, Petters and Kreidenweis, 2007) and material densities used for the estimation are (0.67, 1.73 g cm^{-3}), (0.61, 1.77 g cm^{-3}), (0, 1.8 g cm^{-3}), and (0.1, 1.2 g cm^{-3}) for ammonium nitrate, ammonium sulfate, BC, and OM, respectively. The estimation includes another assumption that all components are internally mixed with BC. As chemical compositions of non-BC materials did not largely vary during the observation period (section 3.5), the average value of κ was calculated using the averaged chemical compositions (Table 1) to be 0.35, and was used for the calculation of SS_C. The estimated SS_C decreases with the increases in the D_S/D_{core} ratios. The observed changes in the D_S/D_{core} ratios indicated that the BC-containing particles with lower SS_C were removed through the wet removal.

Note that the magnitude of the change in the peak D_{core} of the BC size distributions in the PBL (~0.02 µm (~2-2.5 fg)) shown in **Figure 7c** 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~~ may also lead to the further modification of the shape of the particle size distributions and the mixing state distributions which have been affected by cloud processes. This factor is actually expected to be minor because the particle concentrations are too low to have high coagulation coefficients to accelerate this effect. 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).

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. ΔBC/ΔCO 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-} and organic aerosols ~~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 D_{core} and D_S~~diameter~~ of mass and number size distributions (~0.02 and 0.05~~1~~ μm), respectively, 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 in-cloud scavenging~~rainout~~. The observed evidences for the ~~selective~~ removal of large and water-soluble BC-containing particles was qualitatively consistent with the Köhler theory; however the values 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 through in-cloud scavenging in East Asia can be expected to be significant in the PBL as well as in the FT in East Asia.

Acknowledgments

This study was supported by the Environment Research and Technology Development Fund (S7, S12, and 2-1403) of the Ministry of Environment, Japan, and the Japan Society for the Promotion of Science (JSPS), KAKENHI Grant numbers JP26550021, JP26701004, JP26241003, JP16H01772, and JP16H01770, and was partially carried out in the Arctic Challenge for Sustainability (ArCS) Project. The authors would like to thank N. Moteki at the University of Tokyo for assistance with the SP2 calibrations. M. Kubo, T. Takamura, and H. Irie (Chiba University) are also acknowledged for their support at the Fukue-Island Atmospheric Environment Monitoring Station. The authors appreciate Gavin McMeeking and an anonymous reviewer for constructive comments to improve this paper.

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Figures

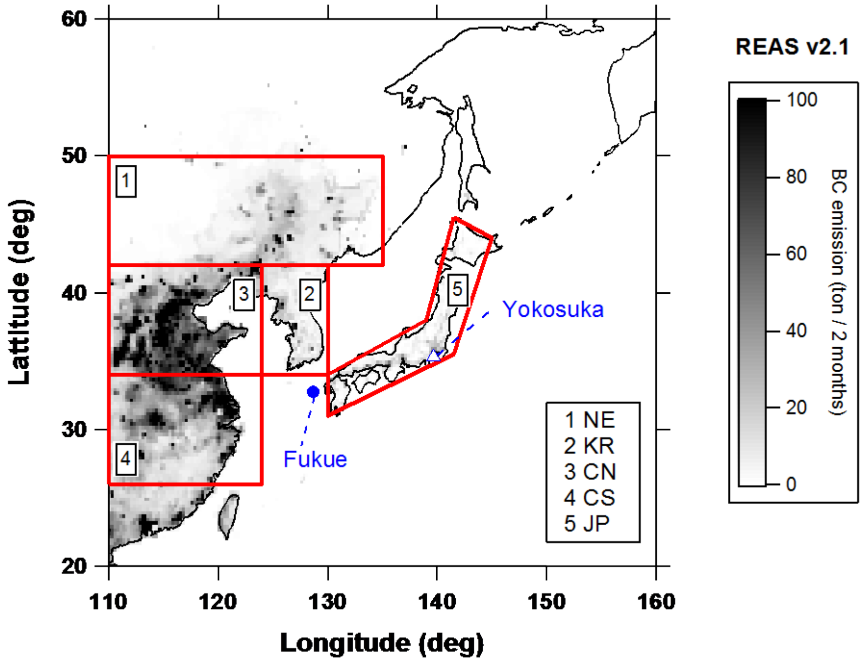


Figure 1. Map of the investigated region with two observation sites (Yokosuka, open triangle; Fukue Island, closed circle) and five defined areas (1 Northeast China; 2 Korea; 3 Central North China; 4 Central South China; 5 Japan). The bimonthly mean BC emission rate (March-April) in 2008 is overlaid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

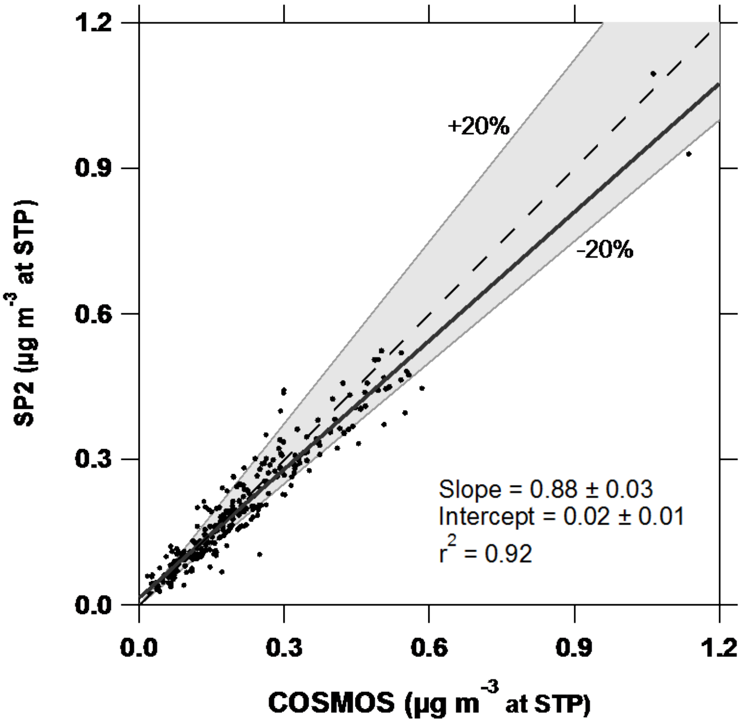
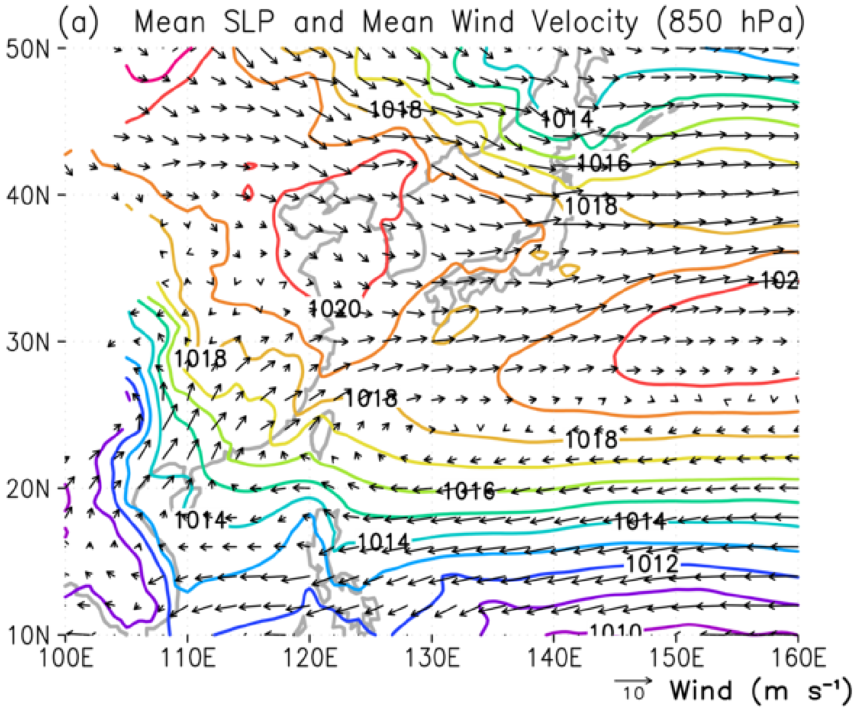


Figure 2. Correlation plot of SP2-rBC and COSMOS-EBC mass concentrations (at standard temperature and pressure). The shaded region corresponds to within ±20% from 1 : 1 line (the dashed line). The bold line depicts the linear regression line.


(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
102
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1018
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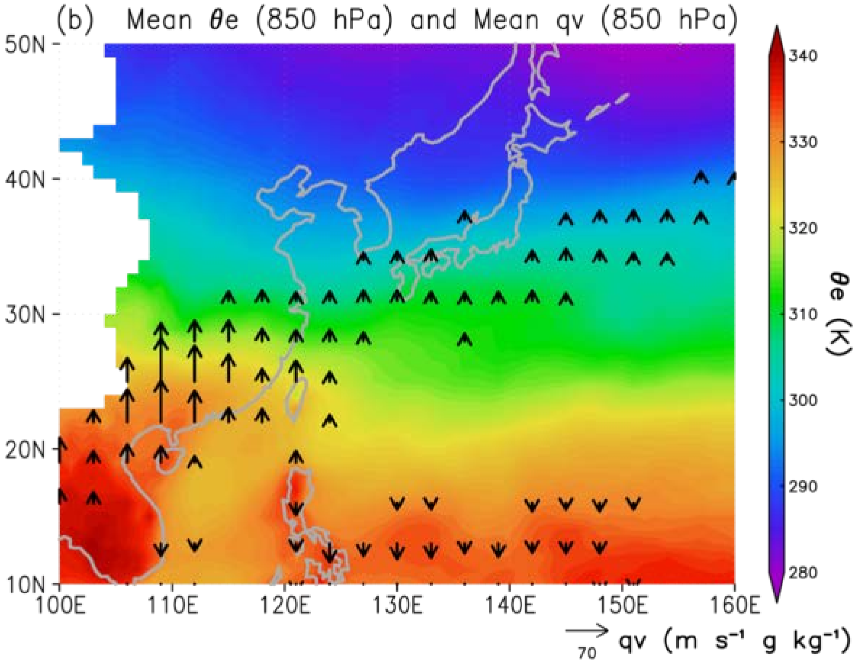
10 Wind (m s⁻¹)

764


(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)

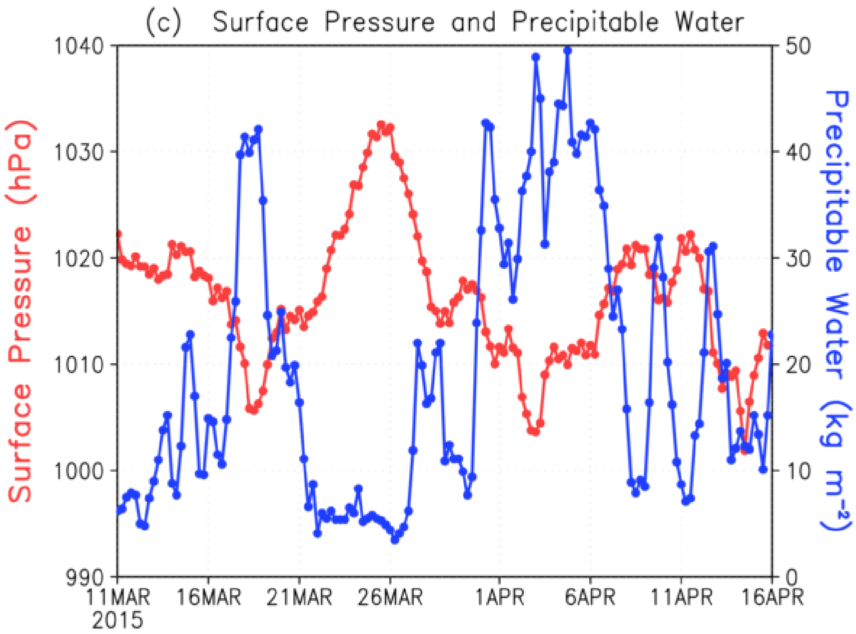
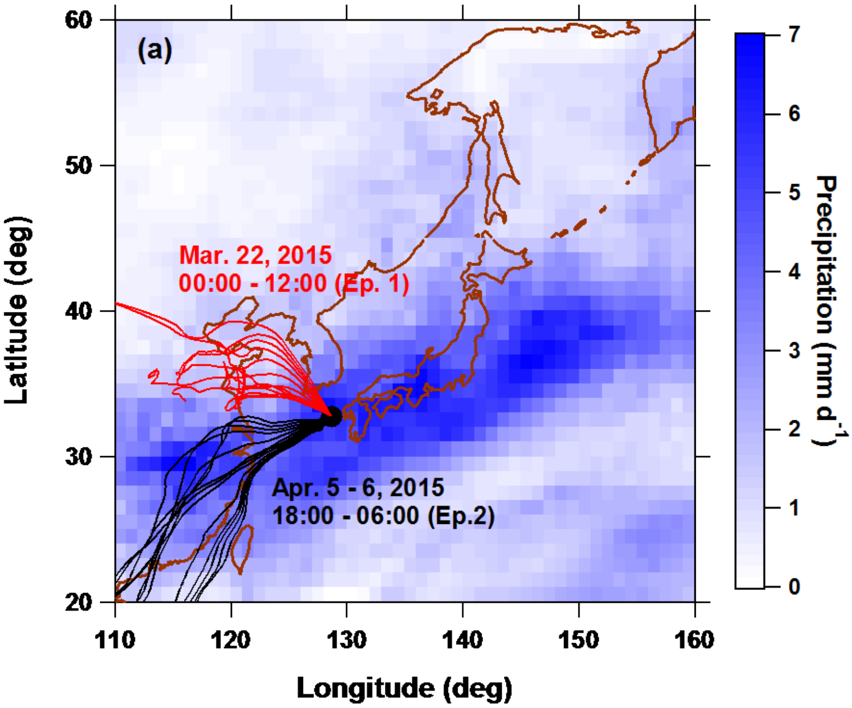


Figure 3. Meteorological fields in East Asia during the observation period (March 11-April 14, 2015) based on NCEP FNL data. (a) Mean SLP (hPa, contours) and mean horizontal wind velocity at the 850-hPa level (m s^{-1}). Regions without data correspond to those of high-altitude mountains. (b) Mean θe (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

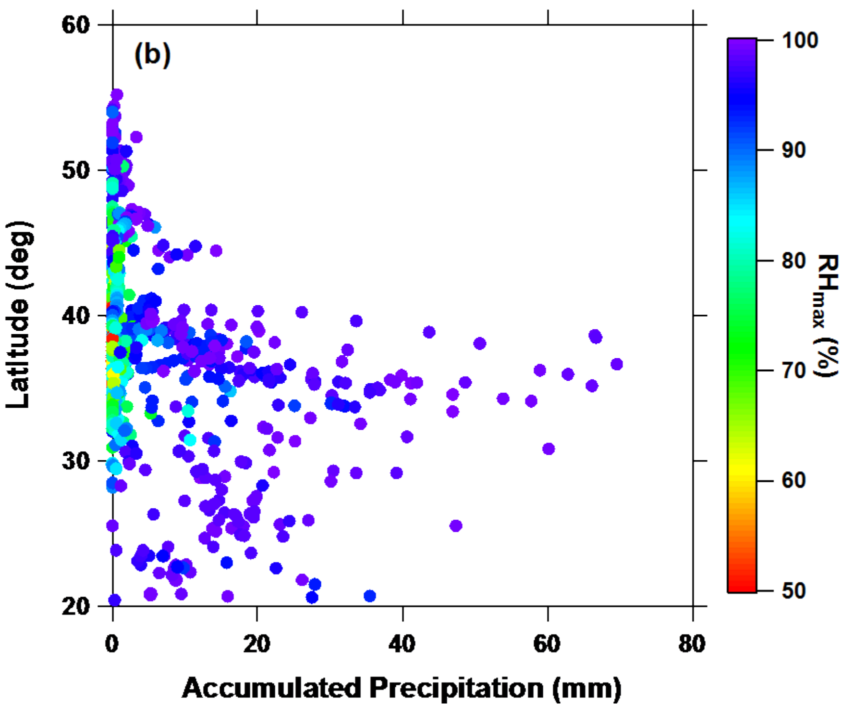


Figure 4. (a) Mean precipitation derived from GPCP during the observation period (March 11-April 14, 2015). Three-day backward trajectories for selected periods are overlaid (red lines, 00:00-12:00LT March 22, 2015 (Ep.1); black lines, 08:00LT April 5-06:00LT April 6, 2015 (Ep.2)). (b) The relationship between APT and Lat_{ORIG} (see text for details) colored by the maximum RH along the backward trajectories.

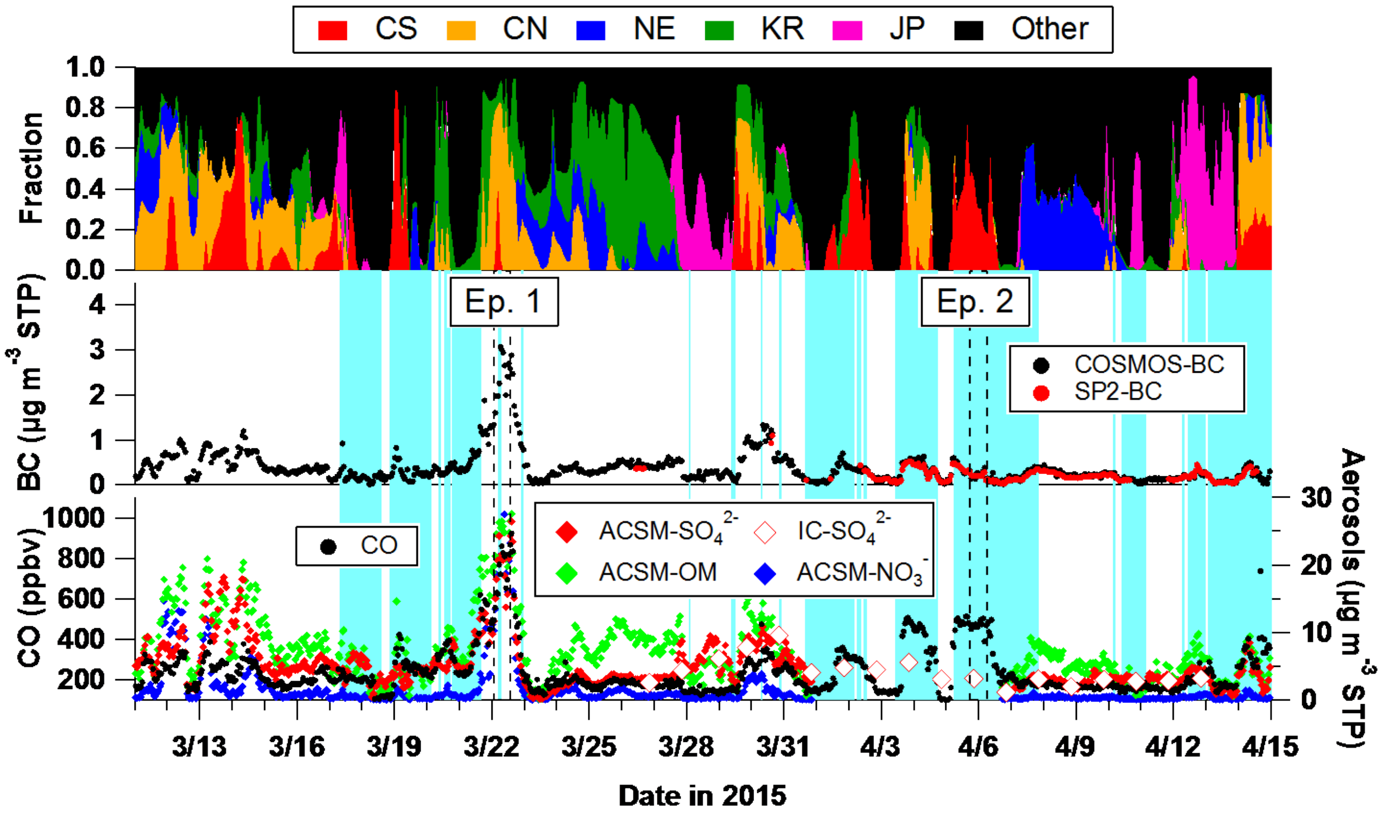
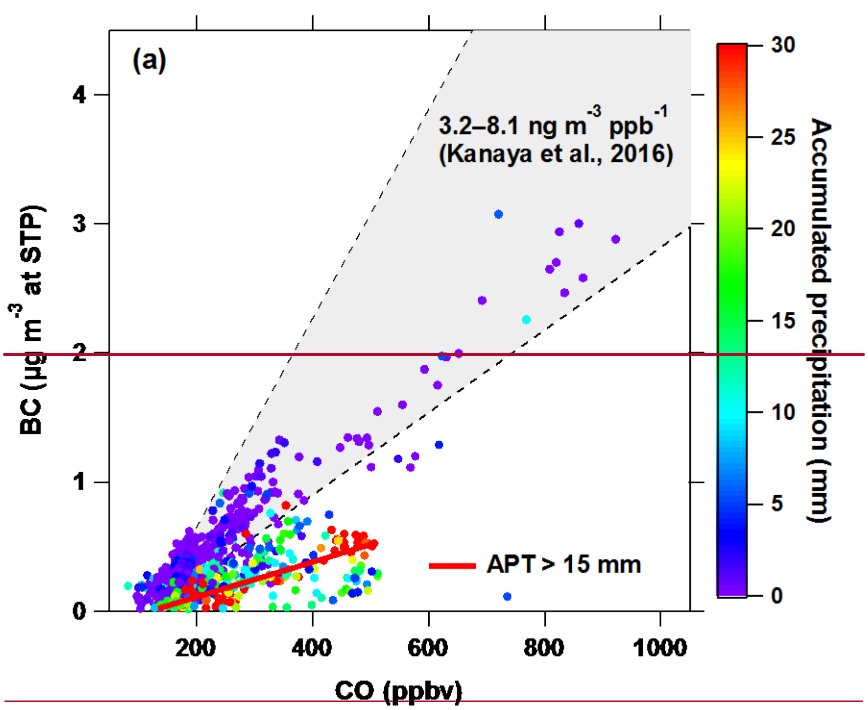
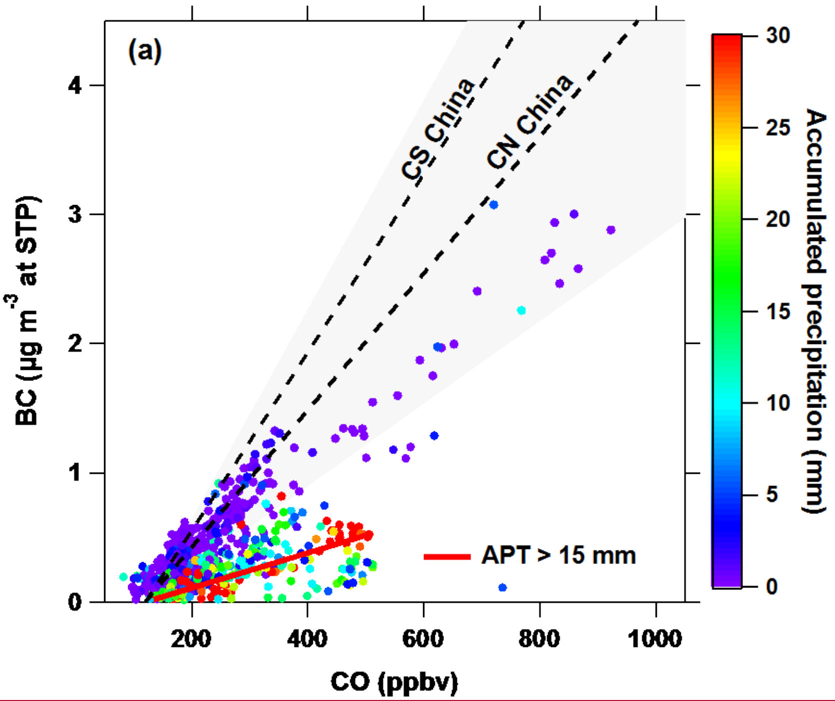

CS
CN
NE
KR
JP
Other
Fraction
1.0
0.8
0.6
0.4
0.2
0.0
Ep. 1
Ep. 2
BC (µg m^{-3} STP)
COSMOS-BC
SP2-BC
CO
ACSM-SO_4^{2-}
IC-SO_4^{2-}
ACSM-OM
ACSM-NO_3^-
CO (ppbv)
Aerosols (µg m^{-3} STP)
3/13
3/16
3/19
3/22
3/25
3/28
3/31
4/3
4/6
4/9
4/12
4/15
Date in 2015

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 (red markers). (Bottom panel) concentrations of CO (black markers), SO_4^{2-} (red closed and open 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


(a)
CS China
CN China
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

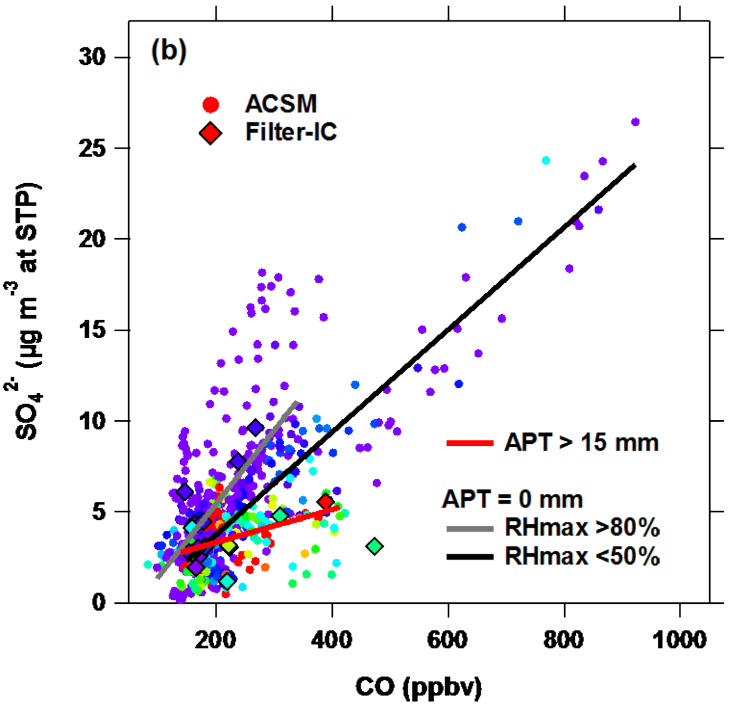
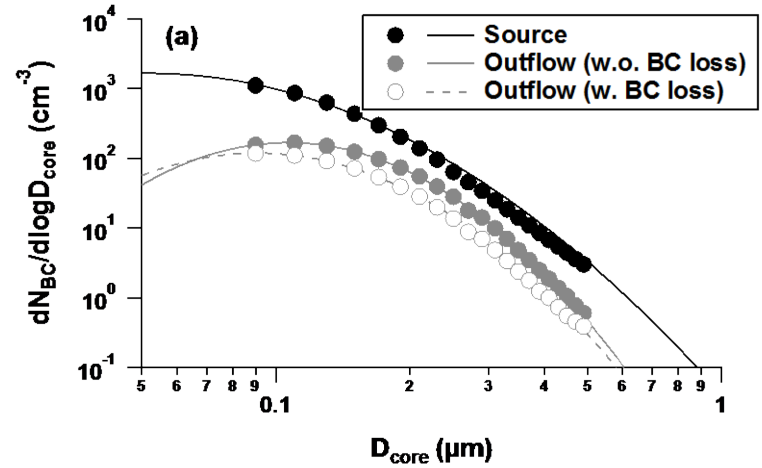
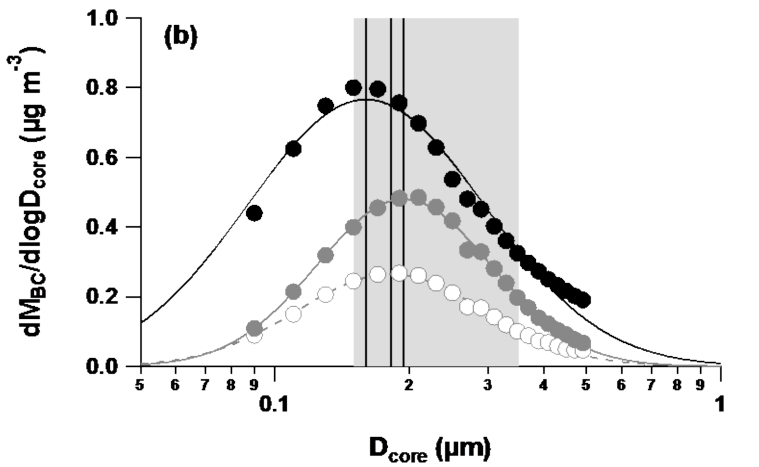
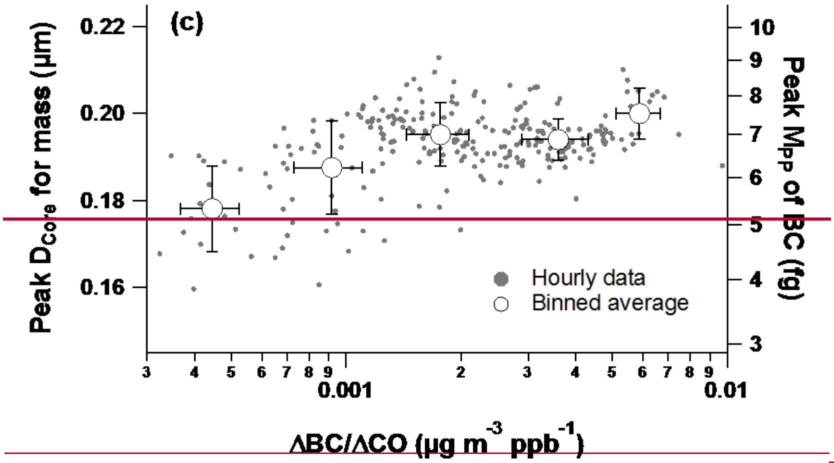


Figure 6. Correlation between aerosol mass concentrations and CO mixing ratio colored according to the APT. (a) BC measured by COSMOS and (b) SO_4^{2-} measured by ACSM and IC (circles and diamond markers, respectively). Dashed lines and shaded area in 6 (a) represent the emission ratios of BC to CO over central North and South (CN and CS) China and their variation ranges, respectively (Kanaya et al., 2016). The bold lines shown in 6 (a) and (b) 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).


(a)
Source
Outflow (w.o. BC loss)
Outflow (w. BC loss)
dN_BC/dlogD_core (cm^-3)
D_core (μm)


(b)
dM_BC/dlogD_core (μg m^-3)
D_core (μm)



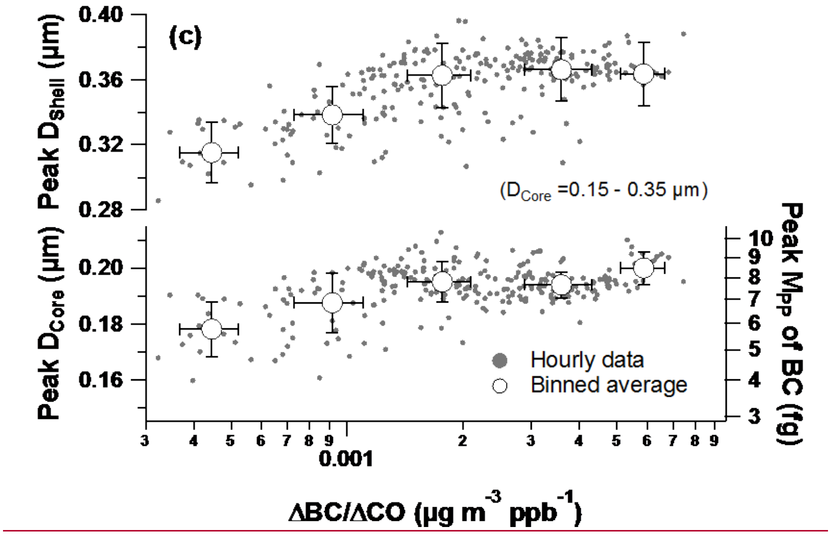


Figure 7. The (a) number and (b) mass size distributions of BC measured at Yokosuka (black markers) and at Fukue Island (gray markers). (c) The evolution of the peak D_s and D_{core} as a function of the degree of removal of BC. The size distributions at Fukue Island include the data for the outflow air masses with (open markers) and without (closed markers) BC loss. Lines in 7(a) and 7(b) are the lognormal fitting results. The shaded band in 7(b) corresponds to the size range analyzed to estimate D_s/D_{core} ratios. Vertical

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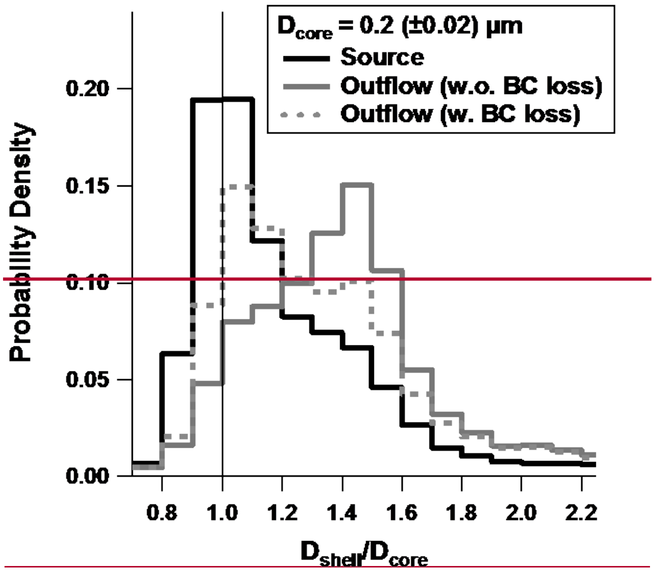
lines in 7(b) represent the peak D_{core}~~diameter~~ of the lognormal fit for each of three mass size distributions. Note that the peak D_{core}~~diameter~~ of log-normal fit for the BC number size distributions at Yokosuka was estimated from the peak D_{core}~~diameter~~ of its mass size distribution (**Table 2**). The peak values of D_s and D_{core} shown in 7(c) were determined by fitting the lognormal function to the hourly number and mass size distributions of BC-containing particles, respectively.


D$_{core}$ = 0.2 (±0.02) µm
Source
Outflow (w.o. BC loss)
Outflow (w. BC loss)
Probability Density
0.20
0.15
0.10
0.05
0.00
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
D$_{shell}$/D$_{core}$

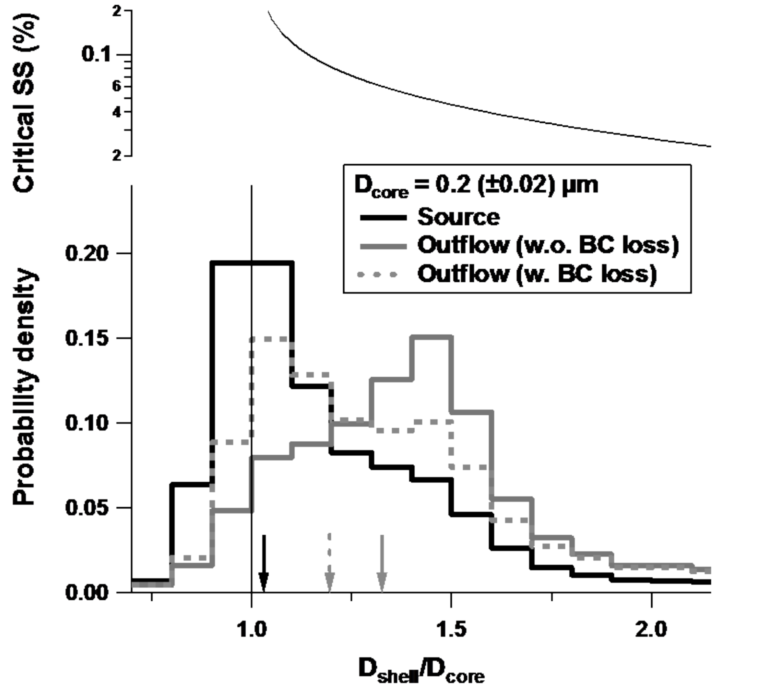

Critical SS (%)
2
0.1
6
4
2
D$_{core}$ = 0.2 (±0.02) µm
Source
Outflow (w.o. BC loss)
Outflow (w. BC loss)
Probability density
0.20
0.15
0.10
0.05
0.00
1.0
1.5
2.0
D$_{shell}$/D$_{core}$

Figure 8. Probability density function of the estimated D_s/D_{core} ratios for BC-containing particles with the size 0.2 (±0.02) μm at Yokosuka (black line) and in the air masses of continental outflow with (gray dashed line) and without (gray solid line) BC loss. Vertical allows indicate the median values of D_s/D_{core} ratios for three different air masses. The estimated critical super saturation of BC-containing particles detected at Fukue Island was also shown as a function of the D_s/D_{core} ratios (see the text for details).

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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. Summaries of BC microphysical parameters measured at Yokosuka and Fukue Island

Site	Air mass type	Averaging time* (hrs)	ΔBC/ΔCO ($ng\ m^{-3}\ ppb^{-1}$)	APT (mm)	Log Normal Fit Parameters Avg. (1σ)		1-hr Median D_S/D_{core} for selected D_{core} Avg. (1σ)			
					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.