Alteration of the 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 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 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 ($\Delta$BC/$\Delta$CO) ratios, which was used as an indicator of
the transport efficiency of BC. It was found that $\Delta$BC/$\Delta$CO 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 China (20°-35°N) in the spring of 2015. Selective removal of large and
thickly-coated BC-containing particles was detected 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 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 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 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 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 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. 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 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 (MED) 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 maximum value of $D_S/D_{core}$ ratios analyzed is 4 in this study. Retrieved 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 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 outsides 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 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.
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 ($\Delta$BC/$\Delta$CO) against the East Asian background air concentrations as follows:

$$\frac{\Delta BC}{\Delta CO} = \frac{[BC] - [BC]_{bg}}{[CO] - [CO]_{bg}},$$  \hspace{1cm} (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. 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 converging 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 (LatORIG) (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 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 ($\Lambda_{\text{accum}}$) was estimated to be $\sim 1 \times 10^{-3}$ 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 ($0.78 \pm 0.6$ mm h$^{-1}$) as an input to the parameterization. The possible uncertainties in this estimation are derived from the discrepancies in $\Lambda_{\text{accum}}$ the removal rates between the parameterization and some experimental results (Wang et al., 2014). The values of $\Lambda_{\text{accum}}$ 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 $\Lambda_{\text{accum}}$, 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 aerosols and CO

Temporal variations in the concentrations of BC (measured using COSMOS and SP2), $\text{SO}_4^{2-}$ (measured using ACSM and IC), $\text{NO}_3^-$, OM, and CO are shown in Figure 5. ACSM-$\text{SO}_4^{2-}$ generally agreed well with IC-$\text{SO}_4$, thus indicating that the assumed CE (0.5) was valid for the observation period. As $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ were almost fully neutralized by $\text{NH}_4^+$, 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 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 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$^{-1}$, slightly depending on the origin of the air masses (this range is overlaid on Fig. 6a). ∆BC/∆CO 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 ∆BC/∆CO in these ranges show low APT values (less than or ~1 mm). Wet removal (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 ∆BC/∆CO 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 $\text{RH}_{\text{max}}$ (Figure 6b), and these varied from 30.7 to 44.1 ng m$^{-3}$ ppb$^{-1}$ under the conditions without ($\text{RH}_{\text{max}} < 50\%$) and with ($\text{RH}_{\text{max}} > 80\%$) cloud impacts, respectively. The $\text{SO}_4^{2-}/\text{CO}$ slope increased with $\text{RH}_{\text{max}}$ when the APT was zero, thus suggesting that aqueous phase formation and subsequent droplet evaporation partly contributed to the mass concentrations of $\text{SO}_4^{2-}$ observed at Fukue Island. Therefore, the changes in the $\text{SO}_4^{2-}/\text{CO}$ correlation were controlled largely by the 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 $\text{RH}_{\text{max}}$. Four cases are selected here, namely (1) APT of zero (no precipitation), (2) APT of zero with $\text{RH}_{\text{max}} < 50\%$ (no precipitation without cloud impacts), (3) APT of zero with $\text{RH}_{\text{max}} > 80\%$ (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 changes in 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 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 $D_{S}/D_{\text{core}}$ ratio for the BC size of 0.2
(±0.02) µm for source and outflow air masses. The modal values of the $D_{S}/D_{\text{core}}$ 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 $D_{S}/D_{\text{core}}$ 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 $D_{S}/D_{\text{core}}$
ratio. In outflow air masses with BC loss, modal values of the $D_{S}/D_{\text{core}}$ 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 $D_{S}/D_{\text{core}}$ 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 $D_s/D_{\text{core}}$ 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.

Note that the magnitude of the change in 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 $D_s/D_{\text{core}}$ 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. 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. $\Delta$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. $\text{SO}_4^{2-}$ 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 $\mu$m) and modal $D_s/D_{\text{core}}$ ratios (~0.4 for BC of 0.2 $\mu$m) 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 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 in East Asia can be expected to be significant in the PBL as well as in the FT in East Asia.

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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%.
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 $\theta$e (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).
Mar. 22, 2015
00:00 - 12:00 (Ep. 1)

Apr. 5 - 6, 2015
18:00 - 06:00 (Ep. 2)
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 \text{Lat}_{\text{ORIG}} (see text for details) colored by the maximum RH along the backward trajectories.
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), \( \text{SO}_4^{2-} \) (red closed and open markers for ACSM and IC, respectively), ACSM-\( \text{NO}_3^- \) (blue markers), 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.
3.2–8.1 ng m\(^{-3}\) ppb\(^{-1}\) (Kanaya et al., 2016)

**BC (µg m\(^{-3}\) at STP)**

**CO (ppbv)**

**Accumulated precipitation (mm)**

APT > 15 mm
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).
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 $D_{\text{core}}$ 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 are the lognormal fitting results. The shaded band in 7(b) corresponds to the size range analyzed to estimate $D_s/D_{\text{core}}$ ratios. Vertical lines in 7(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 2).
Figure 8. Probability density function of the estimated $D_p/D_{core}$ ratios for BC-containing particles with the size $0.2 \pm 0.02$ µm at Yokosuka (black line) and in the air masses of continental outflow with (gray dashed line) and without (gray solid line) BC loss.
### Table 1. Mean chemical composition of fine aerosols during the observation period

<table>
<thead>
<tr>
<th>Components</th>
<th>Period average</th>
<th>0 mm RH&lt;sub&gt;max&lt;/sub&gt; &lt;50%</th>
<th>0 mm RH&lt;sub&gt;max&lt;/sub&gt; &gt;80%</th>
<th>&gt;15 mm</th>
<th>APT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium sulfate</td>
<td>44.9%</td>
<td>41.8%</td>
<td>34.0%</td>
<td>48.9%</td>
<td>50.4%</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>11.7%</td>
<td>15.7%</td>
<td>10.7%</td>
<td>8.0%</td>
<td>5.0%</td>
</tr>
<tr>
<td>OM</td>
<td>40.9%</td>
<td>40.1%</td>
<td>52.0%</td>
<td>40.4%</td>
<td>42.0%</td>
</tr>
<tr>
<td>BC</td>
<td>2.5%</td>
<td>2.4%</td>
<td>3.2%</td>
<td>2.6%</td>
<td>2.5%</td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>Site</th>
<th>Air mass type</th>
<th>Averaging time* (hrs)</th>
<th>MMD (μm)</th>
<th>1-hr Median D&lt;sub&gt;s&lt;/sub&gt;/D&lt;sub&gt;core&lt;/sub&gt; for selected D&lt;sub&gt;core&lt;/sub&gt; Avg. (1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yokosuka Source</td>
<td>184</td>
<td>-</td>
<td>0.160 (0.019)</td>
<td>1.18 (0.07)</td>
</tr>
<tr>
<td>Yokosuka Outflow</td>
<td>87</td>
<td>&gt;3</td>
<td>0.195 (0.005)</td>
<td>1.37 (0.05)</td>
</tr>
<tr>
<td>Fukue Outflow</td>
<td>51</td>
<td>&lt;1</td>
<td>0.182 (0.011)</td>
<td>1.25 (0.05)</td>
</tr>
</tbody>
</table>

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