# Size dependence of wet removal of black carbon aerosols during transport from the boundary layer to the free troposphere

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[1] Size distributions of black carbon (BC) measured by aircraft over East Asia in spring 2009 were highly correlated with BC transport efficiency in air parcels uplifted from the planetary boundary layer to the free troposphere. The average single-particle BC mass decreased with decreasing transport efficiency, which suggests that aerosols containing larger BC mass were removed more efficiently. This is the first successful observation of the size-dependent wet removal of aerosols, qualitatively consistent with the Köhler theory. The size distribution of BC uplifted to the free troposphere with high efficiency was similar to the size distribution of BC in the planetary boundary layer. Conversely, the size distribution of BC uplifted with low efficiency was similar to that of background air in the free troposphere. We conclude that wet removal during upward transport is important in controlling the size distribution of BC in the free troposphere. **Citation:** Moteki, N., Y. Kondo, N. Oshima, N. Takegawa, M. Koike, K. Kita, H. Matsui, and M. Kajino (2012), Size dependence of wet removal of black carbon aerosols during transport from the boundary layer to the free troposphere, *Geophys. Res. Lett.*, *39*, L13802, doi:10.1029/2012GL052034.

## 1. Introduction

[2] Atmospheric species concentrated in the planetary boundary layer (PBL) are occasionally transported to the free troposphere (FT) in "uplifted plumes" via systematic vertical motions of air in synoptic-scale cyclones or mesoscale convection in cumulus clouds. During the upward transport of plumes, the process of incorporation of aerosols into liquid water (in cloud droplets or raindrops) followed by precipitation removes a large fraction of both the number and the mass of aerosols in the plume (this constitutes *wet removal* of aerosols). The incorporation of aerosol mass into cloud water is due mainly to nucleation scavenging. The effect of impaction scavenging in a cloud is negligibly small compared to that of nucleation scavenging when mass is considered, whereas impaction scavenging can also be important when the number of aerosols is considered [*Flossmann et al.*, 1985]. The critical super saturation ($SS_c$) is a parameter characterizing the activity of aerosol particles as cloud condensation nuclei. This parameter is determined both by the curvature of a particle surface (curvature effects) and by the mass of hygroscopic compounds (solute effect). The $SS_c$ of an aerosol particle decreases as its size increases and as the amount of internally mixed hygroscopic compounds increases. Therefore, larger aerosol particles consisting of more internally mixed hygroscopic compounds will more likely be removed via nucleation scavenging. Another possible contributor to wet removal is collection of aerosols by falling raindrops below precipitating clouds (below-cloud scavenging). For submicron aerosols, the below-cloud scavenging is more efficient for smaller particles [*Seinfeld and Pandis*, 2006]. Observational evidence of these size dependences would support the incorporation of the microphysical properties of aerosols into wet removal schemes in atmospheric modeling. We desire an improved modeling scheme of wet removal for quantitative simulations of the upward transport of aerosols from the PBL to the FT, which is still challenging [*Textor et al.*, 2006]. To our knowledge, no observational evidence of the size dependence of wet removal of aerosols has been reported, because it is quite difficult to observe this phenomenon, as explained below. One strategy to investigate the changes of size distribution of aerosols by wet removal is to observe aerosols in air parcels before and after they pass through cloud-precipitation processes. Some major components of aerosols are produced in cloud droplets and then released as aerosols into the air as clouds evaporate [*Flossmann et al.*, 1987]. Also, new particles frequently form in the troposphere, especially near clouds [*Perry and Hobbs*, 1994]. Production of new aerosols occurs at the same time and places as wet removal of aerosols. Therefore, it is difficult to unambiguously observe the change of size distribution due solely to wet removal in air undergoing cloud-precipitation processes. Refractory black carbon, or simply black carbon (BC), generated from incomplete combustion of fossil fuel or biomass, is an aerosol component that strongly absorbs light and is insoluble in water, refractory, chemically inert, and ubiquitous in the atmosphere. BC particles are generally coated by nonrefractory compounds (sulfates, nitrates, or organics). Currently, BC is the only compound in atmospheric aerosols whose absolute mass in single particles can be quantified independent of their mixing state, with time resolutions high enough for aircraft measurements. The BC mass and coating thickness of single particles can be

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**Table 1.** List of Data Sets in the A-FORCE Campaign Used in This Study

| Type of Air | General Description | Criteria for Data Selection | Number of 1-min Data Samples (n) |
|---|---|---|---|
| PBL-outflow | Polluted outflow from China close to the sea surface without any history of wet deposition | 1. "dry PBL" air parcels defined by *Oshima et al.* [2012].<br>2. Altitude < 1 km, longitude < 128°E, and exclude data in the vicinity of airports.<br>3. [CO] > 220 ppbv, [BC] > 494 ng $m^{-3}$ at STP. | n = 45 |
| FT-outflow | Polluted outflow in the free troposphere uplifted from the boundary layer over China | 1. "uplifted air parcels" defined by *Oshima et al.* [2012].<br>2. [CO] > 180 ppbv. | n = 227, with 3 subsets: n = 65, where $TE > 0.8$ n = 96, where $0.3 < TE < 0.8$ : n = 66, where $TE < 0.3$. |
| FT-clean | Clean free tropospheric air which is probably close to regional background conditions. | 1. Altitude > 2 km<br>2. [BC] < 60 ng $m^{-3}$ at STP. | n = 963 |

measured by means of a single-particle soot photometer (SP2) [*Gao et al.*, 2007, and references therein]. Because it is chemically inert and because its absolute mass (i.e., mass equivalent diameter) can be detected in single particles, BC is a useful parameter for investigating changes in the size distribution of aerosols in the atmosphere due solely to physical processes. In this paper, we use the BC data obtained by aircraft observations to explore relationships between the size of aerosols and their removal by wet processes. Specifically, we discuss the relationships between the size distribution of BC and the degree of wet removal in air parcels during transport from the PBL to the FT over Asia.

## 2. Aircraft Measurements

[3] We used the data collected during the Aerosol Radiative Forcing in East Asia (A-FORCE) aircraft campaign, conducted over the Yellow and East China Seas from 18 March to 25 April 2009. *Oshima et al.* [2012] described the campaign, including flight tracks and instrumentation in detail. For individual BC-containing particles, the mass of BC ($m$) within a mass-equivalent diameter ($D$) range from 75 to 850 nm and the thickness of coatings on BC were measured by the SP2 on the aircraft. We assumed the void-free material density of BC to be 2 g $cm^{-3}$ in converting $m$ to $D$. From this point forward, the mass $m$, and the diameter $D$, refer only to properties of BC. The thickness of a coating on BC was estimated using a position-sensitive detector [*Gao et al.*, 2007] for detection of scattering, and then applying the concentric coated-sphere model to convert the raw data into a coating thickness. For this purpose, we assumed the refractive indices of the core and coatings of BC to be $1.76 + 0.44i$ and $1.52 + 0.015i$, respectively, which are refractive indices for "soot" and "water soluble" aerosols at a wavelength of 1 $\mu$m (i.e., the approximate wavelength of the SP2 laser) according to a data base of OPAC (Optical Properties of Aerosols and Clouds) [*Hess et al.*, 1998]. The CO mixing ratio was measured with a vacuum ultraviolet resonance fluorescence instrument (AL5002, Aero-Laser GmbH). We used 1-minute averages of BC and CO data, and also calculated backward trajectories every 1 minute for the present analysis. *Oshima et al.* [2012] described the details of the backward trajectory calculations. We excluded data within clouds to eliminate possible artifacts on aerosol measurements.

## 3. Method of Data Analysis

[4] *Oshima et al.* [2012] defined the transport efficiency ($TE$) of BC in air parcels arriving from the Asian continent and measured during A-FORCE as the ratio of the mass concentration of observed BC to that anticipated if there had been no wet removal of BC. The $TE$ of plumes was calculated as $TE = (\Delta[BC]/\Delta[CO])/R_{BC\text{-}CO}$, using a comparison of CO mixing ratios ($\Delta$[CO]) and BC mass concentrations ($\Delta$[BC]) to their background levels. The $\Delta$[BC] values were estimated by assuming a background level of zero (0 ng $m^{-3}$) at standard temperature (273 K) and pressure (1013 hPa) (STP). The $\Delta$[CO] values were estimated by assuming a background level of 118 parts per billion by volume (ppbv). The $R_{BC\text{-}CO}$ represents the ratio of the emission of BC to the emission of CO over the source region, for air parcels sampled during A-FORCE. This ratio was estimated to be 4.84 ng $m^{-3}$/ppbv (at STP). The detailed reasoning for obtaining the values of $R_{BC\text{-}CO}$, $\Delta$[BC], and $\Delta$[CO] was described in *Oshima et al.* [2012]. We defined three major groups of air parcel data (Table 1) to analyze the effects of wet removal on the size distribution of BC. First, the air parcels in "PBL-outflow" air were defined as those arriving directly from China in the PBL and sampled at altitudes below 1 km over the Yellow Sea. These air parcels were sampled a relatively short distance (200–400 km) from China. The 45 PBL-outflow air parcels form a subset of the 231 "dry PBL" air parcels as defined by *Oshima et al.* [2012], which were sampled at altitudes below 2 km at distances up to ~1000 km from China. We use the PBL-outflow samples to represent boundary layer air before its transport upward. After analyzing backward trajectories, *Oshima et al.* [2012] defined "uplifted air parcels" as those parcels sampled in the FT above an altitude of 2 km and which had been lifted from the PBL over China, then transported by the subtropical westerlies to the sampling locations. Some of the uplifted air parcels which had high values of [CO] were clearly influenced by pollution in the PBL over China. For this second group in Table 1, we defined 227 parcels having [CO] higher than 180 ppbv as "FT-outflow" air parcels, a subset of the 361 "uplifted" air parcels. For all "uplifted" air

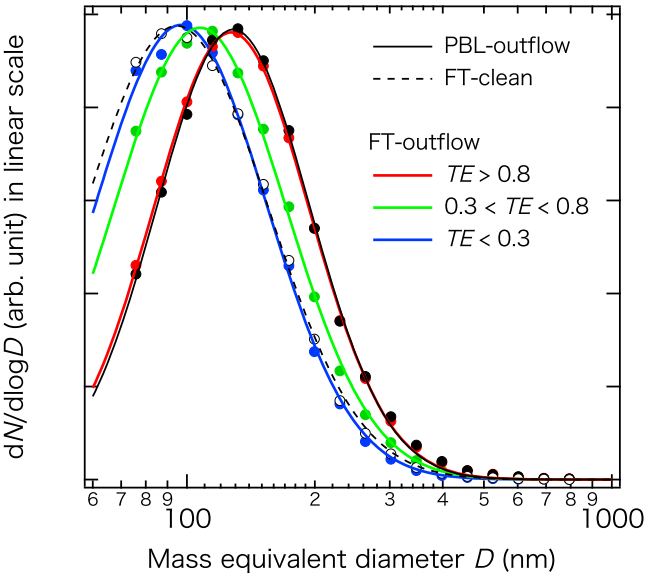


**Figure 1.** The number size distribution of BC particles in five different types of air. Each distribution is scaled differently in the vertical so as to adjust the peak of its curve to a fixed value.

parcels, the *TE* was negatively correlated with accumulated precipitation (APT) along backward trajectories [see *Oshima et al.*, 2012, Figure 14]. For "uplifted" air parcels, the *TE* tended to be lower for higher sampling altitudes where greater APT values were estimated. At similar altitudes, the typical *TE* values were lower for air parcels uplifted over southern China (SC; latitude < 33°N) compared to those over northern China (NC; latitude > 33°N), consistent with the spatial trend of greater APT in air parcels uplifted over the southern regions of China [*Oshima et al.*, 2012]. These systematic relationships between APT and *TE* support the validity of using the *TE* as a parameter measuring the wet removal of BC in FT-outflow air parcels. The FT-outflow air parcels were divided into three subgroups by the *TE* value: $TE < 0.3$, $0.3 < TE < 0.8$, and $TE > 0.8$, as in Table 1. Finally, for the third group we defined 963 "FT-clean" air parcels as those parcels sampled in the FT (above 2 km) with [BC] < 60 ng m$^{-3}$ (at STP), at any latitude and longitude on the flight tracks. These parcels are assumed to represent clean free-tropospheric air. For the present analysis, we also introduce a useful parameter $\langle m \rangle$, the average of single-particle mass ($m$) of BC as

$$\langle m \rangle = \frac{1}{n}\sum_{i=1}^{n} m_i.$$

[5] The $m_i$ is the mass of BC in the $i$-th BC-containing particle, and $n$ is the total number of BC-containing particles detected by the SP2 during a given time interval. We used the parameter $\langle m \rangle$ to quantify systematic changes in the size distribution of BC. The averaging time interval was fixed at 1 minute, and the corresponding $n$ ranged from approximately $10^2$ to $10^4$ depending on the number concentration of BC.

## 4. Results and Discussion

[6] The average number size distribution (d$N$/dlog$D$) of BC in five different types of air masses are shown in Figure 1, with fitted lognormal functions. Each distribution is scaled differently in the vertical so as to adjust the peak of its curve at a fixed value. The geometric standard deviations ($\sigma_g$) of the lognormal functions were within a narrow range from 1.51 (for PBL-outflow air) to 1.64 (for FT-clean air). The count median diameters (CMDs) of the lognormal functions are markedly different in different types of air parcels: 128 nm (in PBL-outflow air), 127 nm (in FT-outflow air with $TE > 0.8$), 107 nm (in FT-outflow air with $0.3 < TE < 0.8$), 96.8 nm (in FT-outflow air with $TE < 0.3$), and 94.5 nm (in FT-clean air). The CMD decreased as *TE* decreased (Figure 1). The size distribution of FT-outflow air with $TE > 0.8$ was very similar to that of PBL-outflow air. Note also that the size distribution of FT-outflow air with $TE < 0.3$ was very similar to that of FT-clean air. *Schwarz et al.* [2010] also measured size distributions of BC over pristine remote Pacific sites with the SP2, which was calibrated using the same BC standard (fullerene soot), enabling direct comparison with our data. The lognormal parameters of the size distributions of BC were stable for CMD values from 78 to 97 nm, with $\sigma_g = 1.64 \pm 0.06$. (These CMD values were calculated from the mass median diameter values given in *Schwarz et al.* [2010].) The CMD and $\sigma_g$ values observed for the FT-clean air parcels in our study are within the reported ranges for pristine air over the remote Pacific. On a correlation plot of $\langle m \rangle$ versus *TE* in FT-outflow air (Figure 2), the $\langle m \rangle$ values decreased as *TE* decreased. As shown in Figure 2, the general trend of the correlation was surprisingly similar for air parcels uplifted over NC and over SC. For the FT-outflow air parcels, the correlation coefficient ($r^2 = 0.79$) between $\langle m \rangle$ and *TE* (Figure 2) was greater than that between $\langle m \rangle$ and [BC] ($r^2 = 0.57$). Therefore, the observed correlation between $\langle m \rangle$ and *TE* in FT-outflow air is very likely a

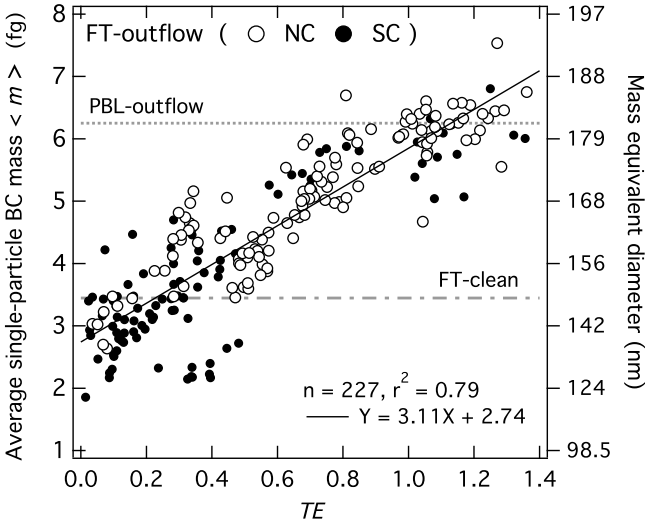


**Figure 2.** Correlation between $\langle m \rangle$ and *TE* for 227 FT-outflow air parcels. Among these parcels, the 126 parcels uplifted over northern China (NC) and the 101 uplifted over southern China (SC) are shown by open and filled circles, respectively. The solid line gives the fitted linear correlation for all data points. The median values of $\langle m \rangle$ in PBL-outflow air and FT-clean air are also indicated by the dotted and dash–dotted lines, respectively. The right-side axis shows the mass equivalent diameters of BC that correspond to $\langle m \rangle$ values shown on the left-side axis.

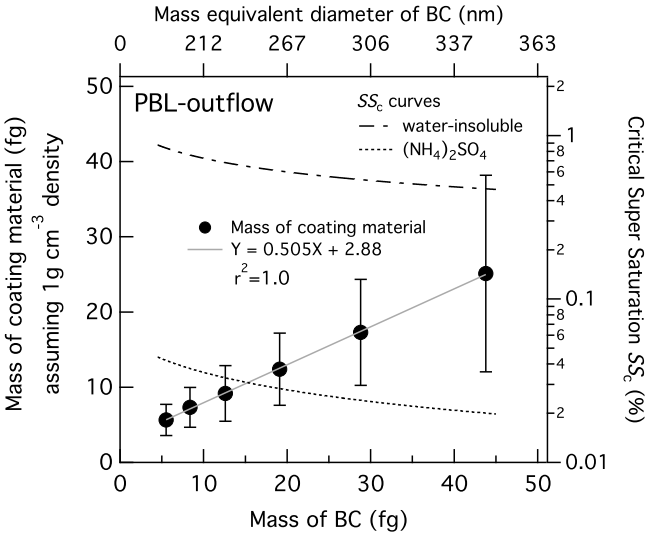


**Figure 3.** Mass of coating material on BC as a function of the mass of BC itself, observed in PBL-outflow air. Mass equivalent diameter of BC is also shown on the upper horizontal axis. Averages (black circles) and standard deviations (error bars) of observed 1-min data are plotted. Critical super saturation $SS_c$ values were calculated as a function of BC mass, after assuming that the mean observed mass of coating materials shown on this plot was added. For the $SS_c$ calculations, we assumed that the coating material was either ammonium sulfate ($(NH_4)_2SO_4$, lower dotted curve) or water-insoluble material (therefore no solute effects, upper dashed curve).

consequence of an atmospheric process that strongly controls both $\langle m \rangle$ and *TE*. The median values for the $\langle m \rangle$ in PBL-outflow air and FT-clean air were 6.25 and 3.45 fg, which were close to the upper and lower limits of $\langle m \rangle$ in FT-outflow air. These results indicate that BC size distributions in air parcels tend to shift to lower sizes by wet removal processes during upward transport from the PBL to the FT. The BC size distribution underwent little change in less-processed air parcels (where $TE > 0.8$), even after vertical transport into the FT. In contrast, the size of BC in well-processed air parcels (where $TE < 0.3$) decreased to sizes typical of FT-clean air. The mass of coating material monotonically increased with the mass of BC in the range from 5.5 to 45 fg, for BC-containing particles observed in PBL-outflow air (Figure 3). Coating mass was calculated from the coating thickness measured by the SP2, assuming 1 g cm$^{-3}$ density. *Wang et al.* [2002] measured size-resolved mass fractions associated with the chemical composition of aerosols in Asian outflow air over the East China Sea in spring (in a similar location and season as in this study) and observed that the mass fractions of $NH_4^+$, $SO_4^{2-}$, $NO_3^-$, organic carbon, and BC changed little with the particle size. If these aerosol chemical compositions are internally mixed, the results of Wang et al. are consistent with our finding that the mass of coating materials is linearly proportional to the mass of BC. The $SS_c$ of a BC-containing particle was calculated using Köhler theory as a function of the mass of BC, assuming two coatings materials on BC: one is $NH_4(SO_4)_2$ (representing the upper limit of the solute effect) and the other is a water-insoluble material (neglecting the solute effect). The assumption that the chemical composition of a coating material is size-independent in the $SS_c$ calculation may be reasonable, according to observations by *Wang et al.* [2002]. The calculated $SS_c$ curves depict a systematic decrease of $SS_c$ with increasing BC mass (Figure 3). The correlation of $\langle m \rangle$ with *TE* is observed to be a tight one (Figure 2), and may be due to wet removal of BC-containing particles via nucleation scavenging becoming more efficient as BC mass increases. Our calculated dependence of $SS_c$ on BC mass for BC-containing particles in PBL-outflow air supports this hypothesis. In our dataset, the contribution of below-cloud scavenging would be minor because the expected size dependence of removal efficiency is opposite to the observed size dependence.

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