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Evolution of mixing state of black carbon in polluted air from Tokyo

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[1] The evolution of the mixing state of black carbon aerosol (BC) was investigated using a single-particle soot photometer (SP2) in polluted air transported from Tokyo. Ground-based measurements of aerosols and trace gases were conducted at a suburban site (Kisai) 50 km north of Tokyo during July–August 2004. The ratio of 2-pentyl nitrate (2-PeONO$_2$) to n-pentane (n-C$_5$H$_{12}$) was used to derive the photochemical age. According to the SP2 measurement, the number fraction of thickly coated BC (Shell/Corel Ratio > ca. 2) with a core diameter of 180 nm increased at the rate of 1.9% h^{-1}, as the photochemical clock proceeded under land-sea breeze circulation. Positive matrix factorization was applied to investigate the time-dependent contributions of different coating materials using the mass concentrations of sulfate, nitrate, and organics measured using an aerosol mass spectrometer. The main coating materials found in this study were sulfate and organics. **Citation:** Shiraiwa, M., Y. Kondo, N. Moteki, N. Takegawa, Y. Miyazaki, and D. R. Blake (2007), Evolution of mixing state of black carbon in polluted air from Tokyo, *Geophys. Res. Lett.*, *34*, L16803, doi:10.1029/2007GL029819.

1. Introduction

[2] Black carbon aerosol (BC), a by-product of incomplete combustion of fossil fuels and biomass, is an important constituent among atmospheric particles. It is considered to make important contributions to the radiative heating of the atmosphere because it absorbs light very efficiently [*Chung and Seinfeld*, 2005]. Freshly emitted soot is initially hydrophobic and mostly externally mixed with non-refractory compounds such as sulfate and organics; with time, it becomes hydrophilic and further internally mixed by condensation. The light-absorbing property of BC can be enhanced by a factor of about 1.5 if BC is thickly coated with non-refractory compounds [*Bond et al.*, 2006].

[3] In addition, depending on the amount of coating [*Kuwata et al.*, 2007], coated BC particles act as cloud condensation nuclei (CCN), thereby leading to more efficient removal of BC by wet deposition. For that reason, coating of BC may also alter spatial distributions of BC particles. For improved evaluations of its radiative forcing, it is extremely important to understand how quickly mixing occurs, in addition to the chemical properties of the mixing state of BC. However, observations of the BC aging process based on measurements of individual particles remain very limited [*Moteki et al.*, 2007]. Herein, we report observations of the evolution of BC mixing state with photochemical age in an urban region in addition to statistical estimations of the time-dependent contributions of major coating materials onto BC particles.

2. Measurements

[4] Ground-based measurements of aerosols and trace gases were performed from July 25 through August 14, 2004 in a Tokyo suburb (Kisai, 36°05′N, 139°33′E) located about 50 km north of Tokyo. Polluted air was transported there from Tokyo under southerly wind conditions [*Takegawa et al.*, 2006]. A dominant source of BC in Tokyo is diesel vehicle emissions [*Kondo et al.*, 2006]. The BC emissions were estimated to be greatest near the center of Tokyo (20 × 20 km^2), rapidly decreasing toward suburban areas [*Kannari et al.*, 2004]. Consequently, Kisai is an appropriate site to investigate the chemical evolution of aerosols transported from Tokyo. These measurements were made as a part of the series of Integrated Measurement Program for Aerosol and Oxidant Chemistry in Tokyo (IMPACT) campaigns. The scientific objectives of this campaign were to quantify anthropogenic aerosol formation processes and to characterize their physical and chemical properties.

[5] The sample air was aspirated from the roof of the observatory (6.5 m AGL) through a 1/2-inch outer diameter stainless steel tube. Aerosol particles with diameters less than about 2.5 μm were selected using a PM$_{2.5}$ cyclone with a sample flow rate of 16.7 l min^{-1}. A single-particle soot photometer (SP2; Droplet Measurement Technologies, Boulder, CO) used laser-induced incandescence (LII) to measure the size distribution and mixing state of individual BC particles. The basic principle of the SP2, including its calibration technique, has been described previously [*Stephens et al.*, 2003; *Schwarz et al.*, 2006; *Moteki and Kondo*, 2007]. The sample air was introduced into the SP2 instruments at a flow rate of 60 ml min^{-1}. The aerosol sample stream passed through an intra-cavity beam of Nd:YAG laser (λ = 1.06 μm). The particle diameter depends on relative humidity (RH) by absorbing water vapor. For that reason, aerosol particles were dried to remove water contents from particles before their optical detection by dried sheath flow with the sheath/sample flow ratio set to 10. The BC particles elastically scatter laser light (scattering signal) and simultaneously absorb energy; thereby heated to their vaporization temperature, and incandesce (LII signal). The scattering and incandescent light are detected by two separate avalanche photo-diodes (APD). The light is digitized at a rate of 5 MHz (i.e., time resolution of 0.2 μs). The relationship between the LII signal and the BC mass was measured using ambient BC particles to estimate the BC mass. The peak intensity of the LII signal does not depend on coating [*Moteki and Kondo*, 2007]. Based on the

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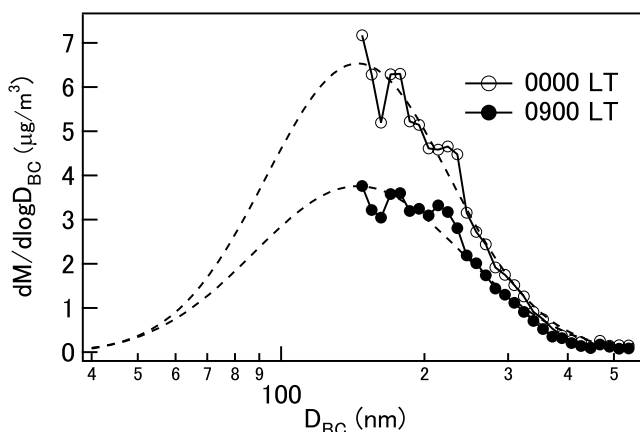
Figure 1. Mass size distributions of BC particles measured using SP2 at 0000 LT and 0900 LT on August 13, 2004. Lognormal functions were fitted to the data for the sizes of 150 nm < D_{BC} < 500 nm (dashed lines).

work of *Slowik et al.* [2007], we assumed that it is also independent of the particle shape. The BC particles were first selected using a heated inlet (400°C) to remove non-refractory compounds (e.g., sulfate, organics, and nitrate); the particles were then introduced to a differential mobility analyzer (DMA) - aerosol particle mass analyzer (APM) system upstream of the SP2 [*Moteki et al.*, 2007]. Multiple charged particles did not influence the calibration because those that had passed through the DMA were rejected by the APM. We defined the mass equivalent diameter (D_{BC}) of a BC particle with mass (M) as $M/\rho = \pi D_{BC}^3/6$ [*Kondo et al.*, 2006], in which ρ is a density for BC particles of 1.77 (±0.07) g cm^{-3} [*Park et al.*, 2004]. The error in the D_{BC} (150 nm < D_{BC} < 800 nm) estimated by the SP2 was 13%. The BC particles coated by non-absorbing materials first scatter laser light, and incandesce several microseconds later. Previous studies showed that the delay time (Δt) between the occurrence of the peaks of the scattering signal and the incandescence signal is an indicator of the coating thickness [*Moteki and Kondo*, 2007].

[6] Measurements of the size-resolved chemical composition of the submicron aerosol were made using a quadrupole aerosol mass spectrometer (Q-AMS; Aerodyne) [*Jayne et al.*, 2000]. Hydrocarbons and alkyl nitrates were measured using a whole-air sampling technique [*Simpson et al.*, 2003] with a 2–6 hour sampling interval, whereas the actual integration time was 5–10 s for each sample. The samples were collected on the roof of the observatory. They were analyzed using gas chromatography (HP-6890) with flame ionization detection for hydrocarbons and electron capture detection for alkyl nitrates.

3. Results and Discussion

3.1. Meteorology and Photochemical Age

[7] Meteorological conditions from July 31 through August 14, 2004 are classified into two phases [*Takegawa et al.*, 2006]. Phase 1 is from July 31 through August 9, when persistent and strong southerly winds (ca. 5 m s^{-1}) were dominant. Clean maritime air passed from Tokyo to Kisai in a short time; most of the BC particles observed by SP2 were thinly coated. Phase 2 is during August 10–14,

when land-sea breeze circulation developed and pollutants were stagnant over the region. Thickly coated BC particles were frequently observed during phase 2. Therefore, a more intense data analysis was made during this phase to investigate the evolution of the mixing state of BC particles.

[8] The photochemical age of polluted air masses was estimated using the ratio of 2-pentyl nitrate (2-PeONO$_2$) to n-pentane (n-C$_5$H$_{12}$) [*Takegawa et al.*, 2006]. In photochemical alkyl nitrate evolution, the ratio of a daughter alkyl nitrate (e.g. 2-PeONO$_2$) to its parent hydrocarbon (e.g. n-pentane) increases as an air mass ages because the daughter alkyl nitrate is produced at the expense of its parent hydrocarbon [*Simpson et al.*, 2003, and references therein]. These ratios can be measured and compared to modeled evolution curves, which are based on OH concentration. The validity of this technique for this dataset was examined by *Takegawa et al.* [2006], estimating the uncertainty of the photochemical age of 30% during phase 2.

3.2. Evolution of BC Mixing State With Photochemical Age

[9] The size distributions of BC measured using the SP2 at 0000 LT and 0900 LT on August 13 are shown in Figure 1, as fit by monomodal lognormal functions with mass median diameters of 145 (±9) and 150 (±10) nm, respectively. These peaks in the mass size distribution are in a similar range (100–200 nm) to those obtained previously in polluted urban areas of Tokyo [*Kondo et al.*, 2006]. Our analysis emphasized particles with a core diameter D_{BC} = 180 (±5) nm. Figure 2 shows histograms of the fraction of Δt, which is the delay time between the occurrence of the peaks of scattering and LII signals, for August 13. Two peaks of approximately 1 μs and 4 μs appear at Δt. As shown by laboratory experiments [*Moteki and Kondo*, 2007], Δt shows a discontinuous increase as the particle diameter (D_p) increases. The transition of Δt occurs when the ratio of particle diameter (D_p) to the core diameter (D_{BC}) becomes greater than 2.0 (±0.5) for D_{BC} = 150–250 nm based on laboratory experiments. The BC particles were
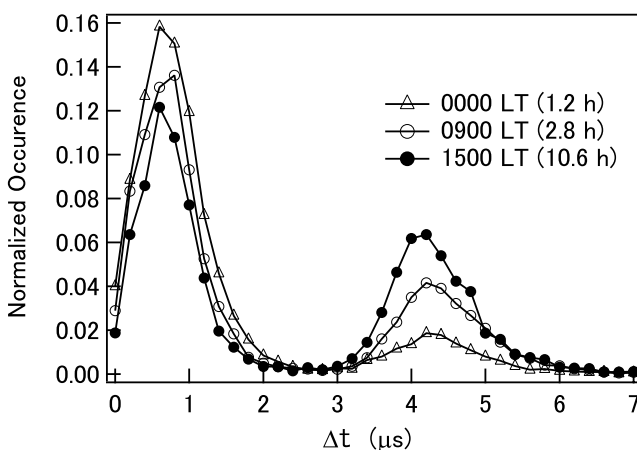

Figure 2. The histograms of the fraction of the time delay (Δt) for BC particles with D_{BC} = 180 nm on August 13, 2004. Particles are divided into two types separated by the 3 μs threshold: thinly coated BC (Δt < 3 μs) and thickly coated BC (Δt > 3 μs). Photochemical age (hours) at each time is also shown in parentheses.
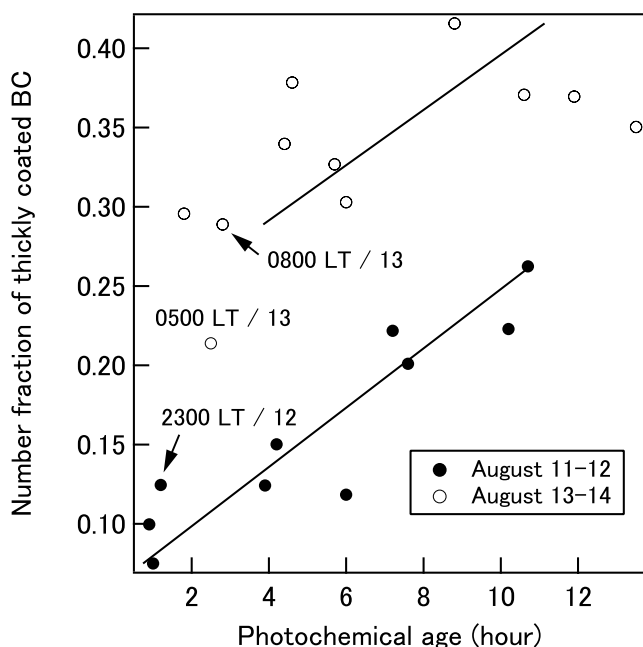
Figure 3. Number fraction of thickly coated BC (D_{BC} = 180 nm) versus photochemical age (hours) on August 11–12 and 13–14, 2004. The solid lines show the least-squares fits of data for each period.

classified into two types using a threshold Δt of 3 μs: thinly coated BC (Δt < 3 μs: Shell/Core Ratio < ca. 2) and thickly coated BC (Δt > 3 μs: Shell/Core Ratio > ca. 2). On the morning of August 13, the photochemical age was short (2–3 h) and only a small fraction of all BC particles were thickly coated. As time progressed, the relative fraction of thickly coated BC increased; the photochemical age increased from ca. 3 hours to 10–14 hours. According to O_3 concentrations measured by Atmospheric Environmental Regional Observation System (AEROS), highly polluted air masses transported from Tokyo reached Kisai during 1500–1700 LT. These observations suggest that the coating on the BC particles was a result of the condensation of photochemically produced secondary inorganic and organic gases in the polluted air masses.

[10] Figure 3 shows the relationship between the number fraction of the thickly coated BC with D_{BC} = 180 (±5) nm - relative to total number of BC with the same D_{BC} - and photochemical age during August 11–12 and 13–14. The slopes of the least-squares fit were determined by regarding the photochemical age as the y-axis because its uncertainty (ca. 30%) is much greater than that of the number fraction of thickly coated BC (ca. 2%). As the photochemical age proceeded, the number fraction of thickly coated BC increased steadily because of formation of condensable gases by photochemical processes followed by condensation on BC. During August 11–12, the thickly coated BC and photochemical age were highly correlated (r^2 = 0.84). The increase rate (R_{coat}) of the fraction of thickly coated BC for D_{BC} = 180 nm was 1.9 (±0.3) % h^{-1}. During the night of August 13, the number fraction of the thickly coated BC increased considerably from 0.12 (2300 LT, August 12) to 0.28 (0900 LT, August 13), although the photochemical age remained almost the same. A large increase also occurred

during the evening of August 14 (Figure 4b). These events are likely to be attributable to the condensation of sulfate, nitrate, and organics on BC, as discussed in section 3.3. The R_{coat} value for August 13–14 is summarized in Table 1.

[11] The R_{coat} was also derived for D_{BC} = 160 (±5), 200 (±5), and 265 (±15) nm to investigate the dependence of R_{coat} on D_{BC}, as shown in Table 1 together with the r^2 values. All of the correlations presented in Table 1 are statistically significant at the 5% level in t-tests. The R_{coat} values were clearly larger at smaller D_{BC} during August 11–12 with high r^2 value. This dependence is considered to be determined by the difference in the amount of materials required to increase the Shell/Core ratio for different D_{BC}. These rates can be compared with that reported by *Moteki et al.* [2007], who reported that the increase rate of thickly coated particles was 2.3% h^{-1} for D_{BC} = 180 nm and 1.0% h^{-1} for D_{BC} = 250 nm in urban plumes over the ocean near the coast of Japan. During August 11–12, the intercepts of the fitted lines were approximately 0.07(±0.02), irrespective of D_{BC}, which indicates that about 7 (±2)% of BC were thickly coated initially.

3.3. Coating Materials on BC Particles

[12] We applied Positive Matrix Factorization (PMF) [*Paatero and Tapper*, 1993; *Paterson et al.*, 1999] to investigate the contribution to the coating on BC particles by sulfate, nitrate, and organics. PMF is a factor analysis that imposes a non-negativity constraint on the resulting factors. The ratio of the mass concentrations of sulfate, nitrate, and organics to those of BC with D_{BC} = 180 (±5) nm, and the number fraction of thickly coated BC (D_{BC} = 180 (±5) nm) were applied to PMF. The parameters (sulfate/BC, nitrate/BC, organics/BC, and number fraction of thickly coated BC) predicted by the PMF model agree quite well with those observed, with r^2 values for the correlations between the observed and predicted values of 0.78, 0.91, 0.88, and 0.98, respectively.

[13] The PMF analysis resulted in three physically interpretable factors (Figure 4a). On the y-axis is the explained variation (EV), which is a dimensionless number that shows a quantitative statement of how important each factor is in explaining each parameter [*Paterson et al.*, 1999]. The EV varies from 0 (no explanation) to 1 (complete explanation). Factor 1, which explains 62 (±10)% of sulfate/BC and 34 (±6)% of thickly coated BC, means that sulfate is the principal contributor to the coating in this factor. Factor 2 explains 89 (±4)% of organics/BC and 49 (±6)% of thickly coated BC, which means that organics is the main contributor in this factor. On the other hand, nitrate is the main contributor in Factor 3. The cumulative variance shows that the use of the three factors explains almost the entire variance (>96%) in every parameter. Figure 4b is the time series of the number fraction of thickly coated BC (D_{BC} =

Table 1. R_{coat} During August 11–12 and 13–14

D_{BC}, nm	August 11–12		August 13–14	
	R_{coat}, % h^{-1}	r^2	R_{coat}, % h^{-1}	r^2
160	2.3 (±0.4)	0.78	1.5 (±0.5)	0.51
180	1.9 (±0.3)	0.84	2.2 (±0.9)	0.40
200	1.5 (±0.2)	0.82	-	-
265	1.4 (±0.3)	0.69	-	-

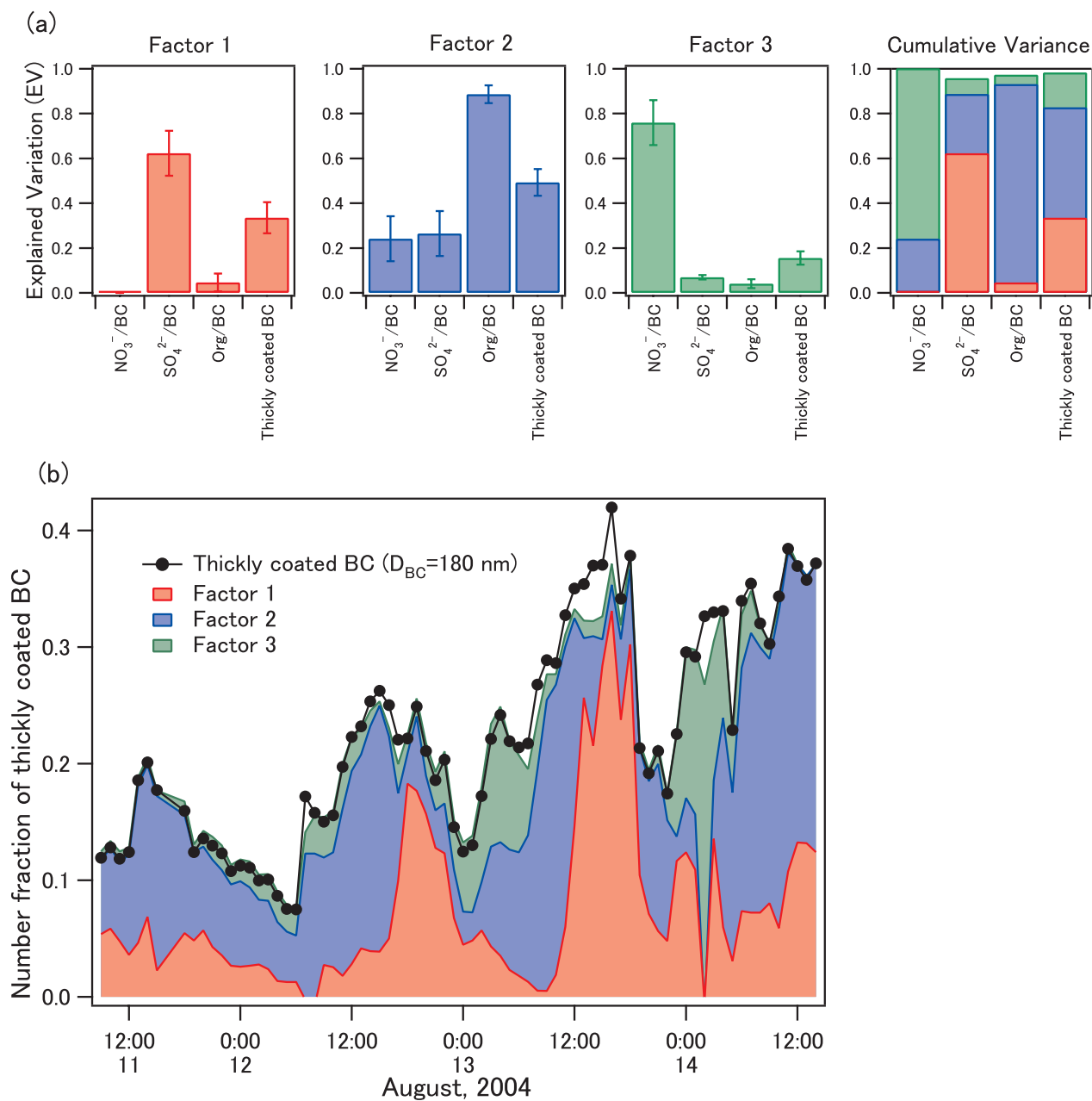**Figure 4.** (a) Explained variance of nitrate/BC, sulfate/BC, organics/BC, and thickly coated BC (D_{BC} = 180 nm) in the three-factor PMF model. In addition to Factors 1, 2, and 3, the cumulative variance explained by the PMF analysis is also shown. (b) Time series of factor contributions for the number fraction of thickly coated BC (D_{BC} = 180 nm).

180 ± 5 nm, solid line) and the factor contribution for this BC particle type. Factors 1 and 2 mainly contribute over the entire period, especially in the daytime (90 ± 7%), indicating that sulfate and organics were the major coating materials.

[14] An evaluation of the diurnal variation shows an enhancement by 40% of Factor 3 from midnight to morning (2300 LT−0600 LT), when the RH was around 80%. Given that this RH was higher than the deliquescence RH of ammonium nitrate (DRH: 62% at 298 K), this inorganic compound would be found in the aqueous state [*Morino et al.*, 2006]. The equilibrium of the nitric acid (HNO$_3$) reaction with ammonia (NH$_3$) to form ammonium (NH$_4^+$) and nitrate (NO$_3^-$) shifts toward the aerosol phase at high ambient RH. Therefore, nitrate likely contributed to the BC coating by dissolving in the liquid aerosol particles during periods of elevated RH around midnight. When the temperature rose in the morning, the equilibrium shifted to the gas phase, and the condensed nitrate on the BC evaporated.

4. Conclusions

[15] Ground-based measurements of BC particles (mass size distribution and mixing state) were made during July–August 2004 using the SP2 instrument at a suburban site about 50 km north of Tokyo. The air mass ages were estimated from the 2-PeONO$_2$/n-C$_5$H$_{12}$ ratios. The BC particles were classified into two types: thinly and thickly coated BC. The fraction of thickly coated BC with

a core diameter (D_{BC}) of 180 nm increased at a rate of 1.9% h^{-1}. The increase rates were lower at larger D_{BC}. In addition, PMF analysis was applied to investigate the relative contributions of different materials to the BC coating. Results show that, at D_{BC} = 180 nm, factors in which sulfate and organics dominated accounted for 90 ($\pm$7)% to the coating on BC during the daytime, while nitrate also contributed substantially to coating during the nighttime (2300 LT-0600 LT) under high-RH conditions.

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