Light Absorption Enhancement of Black Carbon in Urban Beijing in Summer

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ABSTRACT

The light absorption enhancement (E_{abs}) of black carbon (BC) caused by non-BC materials is an important source of uncertainty in radiative forcing estimate, yet remains poorly understood in relatively polluted environment such as the megacity Beijing. Here BC absorption enhancement at 630 nm was *in-situ* measured using a thermodenuder coupled with a soot particle aerosol mass spectrometer and a single scattering albedo monitor in Beijing in summer. The project average (± 1σ) E_{abs} was 1.59 (± 0.26), suggesting a significant amplification of BC absorption due to coating materials. E_{abs} presented a clear daytime increase due to enhanced photochemical processing, and a strong dependence on the mass ratios of non-BC coatings to BC (R_{BC}). Our results showed that the increase in E_{abs} as a function of R_{BC} was mainly caused by the increased contributions of secondary aerosol. Further analysis showed that the BC absorption enhancement in summer in Beijing was mainly associated with secondary formation of nitrate, sulfate and highly oxidized secondary organic aerosol (SOA), while the formation of freshly and less oxidized SOA appeared not to play an important role.

Key Words:

Black carbon; Absorption enhancement; Secondary aerosol; Beijing

1 Introduction

Black carbon aerosol (BC), a by-product of incomplete combustion carbonaceous matter (e.g. biomass and fossil fuel) is recognized as the third most important global warming agent after CO_2 and CH_4 (Stocker et al., 2013). BC exerts a great impact on climate change by absorbing direct solar radiation, reducing cloud albedo, and accelerating the melt of snow (Bond et al., 2013). Accurate estimate of light absorption of BC is thus important to improve our understanding on the impacts of these processes on climate radiative forcing.

The BC absorption is enhanced by its coating materials (Lack and Cappa, 2010), and the enhancement can be significant by a factor of ~2 when BC is internally mixed with other components (Bond and Bergstrom, 2006; Chandra, 2004; Shiraiwa et al., 2010). In contrast, the freshly emitted BC tend to be fractal-like and externally mixed with other components (Peng et al., 2016), and has no absorption enhancement (Liu et al., 2017). The freshly emitted BC can be aged rapidly in the atmosphere (Glen, 2010; Moteki et al., 2007), which changes the mixing state, morphology, coating thickness of BC and thereby its absorbing properties. Current climate models usually use a constant enhancement factor (~1.5) to estimate the radiative forcing of BC (Chung and Seinfeld, 2008; Wang et al., 2014b). However, a recent study showed that the BC absorption enhancements (E_{abs}) should be treated as a function of particle mixing state (Liu et al., 2017). Previous studies also showed significant differences in BC absorption enhancement in different regions. For example, the field measurements during CALNex and CARES in California showed small BC enhancements (~ 6%) and the enhancements were weakly dependent on photochemical aging (Cappa et al., 2012). Small absorption enhancement were also observed at Nagoya (Japan)

(Nakayama et al., 2015) and Shenzhen in China(Lan et al., 2013), due to the fact that a large fraction of aerosol species was externally mixed with BC. Liu et al (2015) found that the magnitude of BC absorption enhancement depends strongly on coating amount, which varies largely for different sources and regions. In fact, light absorption enhancement of ~1.8 – 2.2 were observed in heavily polluted areas such as Indo-Gangetic Plain (Thamban et al., 2017), Xi'an (Wang et al., 2014a), and Yucheng(Cui et al., 2016). Peng et al. (2016) found that BC in polluted urban environment (Beijing, China) aged much faster than that in a relatively clean area (Houston, USA), and the absorption enhancement can be up to a factor of 2.4 in a few hours' ageing. Despite previous efforts in characterization of BC absorption enhancements in different regions, *in situ* measurements of E_{abs} is still limited, particularly in relatively polluted region in China.

In this work, the E_{abs} of BC was measured in urban Beijing in summer using a thermodenuder coupled with a soot particle aerosol mass spectrometer (SP-AMS) and a cavity attenuated phase shift single scattering albedo monitor (CAPS PM_{ssa}). The variation of E_{abs} in Beijing in summer and its relationship with BC coating materials are elucidated, and the major factors affecting E_{abs} are investigated.

2 Experimental methods

All measurements were conducted from 4 June to 13 June, 2017 at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (39°58′28″N, 116°22′16″E) (Sun et al., 2012), which is located between north 3rd and 4th ring roads in Beijing. The instruments were deployed on the roof of a two-story building (~8 m). Ambient air was first drawn into the sampling room through a 1/2 inch

stainless steel tubing with a flow rate of 3 L min^{-1}. After passing through a diffusion silica-gel dryer, aerosol particles (~1.5 L min^{-1}) were sub-sampled into a thermodenuder (TD), and then measured by a SP-AMS and a CAPS PM_{ssa}. The SP-AMS removed the tungsten vaporizer and measured refractory BC (rBC) and rBC-containing species only. The CAPS PM_{ssa} measured particle extinction (b_{ext}) and scattering coefficients (b_{sca}) at 630 nm, and the difference between b_{ext} and b_{sca} was absorption coefficient (b_{abs}). Although the b_{sca} measurements had uncertainties due to truncation effects, our previous studies showed that such an effect was small, and b_{abs} derived from the CAPS PM_{ssa} was highly correlated with that measured by photoacoustic extinctiometer and aethalometer (Han et al., 2015; Xie et al., 2019). In this study, the measurements were alternated between TD and bypass line every 10 min (Fig. S1), and the TD cycled through four temperature gradients (50, 100, 150, and 260 °C). The TD loss was corrected with rBC measured by the SP-AMS considering that rBC does not evaporate at 260 °C. The meteorological data including temperature, relative humidity, wind speed and wind direction (Fig. S2) were obtained from the measurements on the Beijing 325 m meteorological tower.

In addition, a single-particle soot photometer (SP2, Droplet Measurement Technologies) was used to measure the spherical equivalent core diameter (D_c) and the particle diameter (D_p) at the same site (Liu et al., 2018). The D_p/D_c in this study is calculated as the bulk relative coating thickness which reflects the integrated coated BC volume and uncoated BC core volume for a given time window. The bulk D_p/D_c is largely independent of the uncertainties arising from smaller particles because of their less important contribution to the integrated volume, therefore, the retrieval rate of successful coating thickness decreases at smaller and larger D_c, because of the reduced

signal-to-noise level for the scattering signal of smaller particle and the detector saturation for larger particle. The uncertainty associated with the missing single particle coating information is examined at each D_c range by extrapolating the coating thickness at the most populated BC in mass with coating retrieval rate > 80%. The resulting uncertainties are by 7-11% for the BC with bulk D_p/D_c > 2, 3-8% at D_p/D_c 1.5-2 and 0.5-3% with D_p/D_c 1-1.5. Recent study indicates this bulk D_p/D_c metric is able to produce the total coating mass associated with BC particles within 25% (Ting et al., 2018).

The E_{abs} was calculated as the ratio of ambient particle absorption ($b_{abs,\ ambient}$) to that passing through the TD at 260 °C ($b_{abs,\ TD}$). As shown in Fig. S3, 76% of non-BC aerosol species evaporated at 260 °C, and the remaining fraction was dominated by rBC and hydrocarbon-like OA(HOA)-rich primary aerosol and more oxidized oxygenated OA (MO-OOA) that were resolved from positive matrix factorization of high-resolution mass spectra of OA of the SP-AMS (Wang et al., 2019b). Therefore, E_{abs} might have a slight underestimation due to the lensing effect of residual materials on BC. $E_{abs,\ MAC}$ can also be estimated as the ratio of measured mass absorption coefficient (MAC_{obs} = $b_{abs,\ ambient}$/rBC) to the reference MAC (MAC_{ref} = 6.55 $m^2\ g^{-1}$) for uncoated BC at 630 nm. The MAC_{ref} was derived from the power law dependence of absorption on wavelength with a MAC of 7.5 $m^2\ g^{-1}$ at 550 nm (Bond and Bergstrom, 2006). E_{abs} was well correlated with $E_{abs,\ MAC}$ (r^2 = 0.66), and the average values were also close (1.59 ±0.26 and 1.63 ± 0.41, respectively), suggesting that these two methods were overall consistent. Therefore, E_{abs} discussed below referred to the TD-CAPS method unless otherwise stated.

3 Results and discussion

The average (±1σ) E_{abs} was 1.59 (± 0.26) for the entire study suggesting approximately 60% light absorption enhancement by BC coatings. Such an enhancement was overall consistent with ~1.5 that is often used in current climate models (Flanner et al., 2007), and agreed with the recent observations at the SIRTA facility (Zhang et al., 2018a) and UK winter (Liu et al., 2015). However, it was much higher than that previously reported in California regions with limited BC absorption enhancement due to coatings (Cappa et al., 2019).

E_{abs} depends strongly on the mass ratios of coating materials on BC to rBC (R_{BC}) that were from the SP-AMS measurements in Beijing in summer. As shown in Fig. 1a, E_{abs} increased substantially as a function of R_{BC}. As R_{BC} increased from 2 to 6, E_{abs} increased by 45% from 1.34 to 1.94. Such an R_{BC} dependence of E_{abs} was remarkably similar to that observed in UK winter although aerosol composition was substantially different (Liu et al., 2015). However, we did not observe further increases in E_{abs} as R_{BC} was larger than 6. One explanation was the few data points increasing the uncertainties for E_{abs} estimates. Another possibility is that E_{abs} was stabilized as BC was fully aged with a high R_{BC} (Wu et al., 2018). Fig. 1b shows that the aerosol composition of rBC coatings varied significantly as a function of R_{BC}. As R_{BC} increased from 2 to 6, the mass fraction of non-BC POA (rBC-rich+HOA-rich) decreased from 54% to 14%, while the contributions of secondary aerosol species (= SOA+SIA) increased from 45% to 85%. These results indicate that the increases in E_{abs} of BC were mainly caused by the enhanced contributions from secondary formation in Beijing in summer. Comparatively, the fractions of primary and secondary aerosol species were relatively stable during periods with R_{BC} > 6, which might also explain the negligible increases of E_{abs}. Compared

with summer, our previous winter studies in 2016 showed that non-BC aerosol composition was dominated by POA (> ~60%) at R_{BC} < 4.5, and the contribution of secondary aerosol species increased rapidly to ~80% as R_{BC} increased up to 7. As a result, the MAC of BC at 630 nm in winter was relatively stable below R_{BC} < 4.5, and then increased by approximately 40% during periods with high R_{BC} (Xie et al., 2019). This is consistent with the conclusion in summer that BC absorption enhancement was mainly associated with secondary coatings, while the influences of non-BC POA on E_{abs} were generally small.

We also compared the measured E_{abs} with that derived from the Mie core-shell model by assuming refractive index of rBC core and coatings at 550 nm as 1.95+0.79i and 1.50+0i, respectively (Liu et al., 2018). The R_{BC} from SP2 measurements was calculated using Eq. 1. The density of rBC is 1.8 g cm^{-3} and that (1.3 ± 0.05 g cm^{-3}) of coatings was estimated based on the chemical composition of BC-containing aerosol particles (Zhao et al., 2017).

$$R_{BC} = \left(\left(\frac{D_p}{D_c}\right)^3 - 1\right) \times \frac{\rho_{coating}}{\rho_{rBC}} \quad (1)$$

As shown in Fig. 1a, the R_{BC} dependence of simulated E_{abs} was similar, while the simulated E_{abs} were slightly lower than those from the ambient TD measurements (Fig. 1a).

Fig. 2a shows that E_{abs} increased as a function of particulate matter (PM) loadings suggesting stronger significant BC absorption enhancements during periods with higher pollution levels. For instance, E_{abs} increased from ~1.4 to 1.8 as PM_1 mass loading increased from ~10 to 50 μg m^{-3}. We found that such enhancements were mainly associated with the increases in rBC coatings (R_{BC}), which is consistent with previously simulations (Zhang et al., 2018b) and chamber experiments in Beijing (Peng et al., 2016). However, we did not observe a clear rBC dependence of E_{abs} in summer,

consistent with the small variations in R_{BC}, and even slight decreases at high rBC loadings (> 2 μg m^{-3}). This is different from winter when R_{BC} showed a considerable increase as a function of rBC (Liu et al., 2018). Such differences can be explained by the differences in rBC sources and coating materials between summer and winter. In winter, high rBC concentration was associated with high POA from coal combustion and biomass burning emissions (Wang et al., 2019a), while in summer it was dominantly from traffic emissions (Hu et al., 2016). The coating materials were also substantially different between summer and winter. For example, SIA and SOA on average accounted for 21% and 34% of the total BC-containing particle mass in summer (Xu et al., 2019), while they were 20.1% and 20.8%, respectively in winter (Wang et al., 2019a). Previous studies showed that rBC from traffic emissions has smaller R_{BC} compared with those from other combustion sources, such as biomass burning and coal combustion (Liu et al., 2018). In fact, R_{BC} was anticorreleated with rBC mass loading near vehicular emissions (Lee et al., 2017) while it was positively correlated with rBC under high pollution with multiple sources of rBC (Lee et al., 2017; Zhang et al., 2018b).

We further evaluated the influence of chemical composition of rBC coatings on E_{abs}. As shown in Fig. 3, the changes in E_{abs} as a function of R_{BC} depended strongly on non-BC composition. The periods with higher contributions of nitrate and sulfate showed correspondingly higher E_{abs} throughout different R_{BC}. For example, E_{abs} was increased by 7 – 21% during periods with higher nitrate contributions (> 10%), while 6 – 17% for periods with higher sulfate contributions (> 10%). These results suggest that secondary nitrate and sulfate coated on BC have the most impacts on absorption enhancement. One explanation is that the increased nitrate and sulfate changed the BC

mixing state to the core-shell structure and thus increased the absorption enhancement (He et al., 2015). For example, recent studies showed that the increases in ammonium nitrate and sulfate can reduce the deliquescence RH substantially and cause phase transitions of aerosol particles (Sun et al., 2018). During periods with high contents of nitrate and sulfate, the BC-containing particles would be more like in concentric core-shell structure due to the changes of particle phase states from solid to aqueous phase, and hence lead to significant light absorption enhancement. Fig. 3 also shows very different impacts of OA factors on BC absorption enhancement. The increased contribution of MO-OOA presented a positive effect on absorption enhancement by approximately 6 – 7%. However, LO-OOA and HOA decreased E_{abs} by 7 – 11% during periods with high contributions (10% and 15%, respectively). Such results indicate that formation of freshly oxidized SOA in summer appears not an important factor driving the increase of BC absorption enhancement. The decrease of E_{abs} as the increase of HOA contribution was due to 1) vehicle emission with low R_{BC} has a very limited influence on light absorption enhancement, and 2) the increase of HOA was associated with the corresponding decreases in rBC coatings of sulfate, nitrate, and MO-OOA (Fig. 3). Considering that E_{abs} calculated from the TD method could be affected by the residual mass at 260 °C, we further checked the composition dependent relationship between $E_{abs,\ MAC}$ and R_{BC} (Fig. S4). As shown in Fig. S4, similar conclusions were obtained that formation of secondary inorganic aerosol can impact BC absorption enhancement significantly while that of SOA has limited influences and even decreases E_{abs}. Our results were different from a recent study in the megacity of Paris, France showing a major contributor of SOA to BC absorption enhancement in summer (Zhang et al., 2018a). One reason was due to the very different aerosol composition between Beijing and Paris. While SOA

contributed more than half (52%) of submicron aerosol in Paris in summer, it was much lower (27%) in Beijing.

The light absorption enhancement of BC presents a strong diurnal variation in Beijing in summer. E_{abs} gradually increased from ~1.5 in the morning to ~1.8 at 12:00 – 13:00, and then decreased slowly to 1.4 at midnight. Such a diurnal trend was overall similar to that of R_{BC}, photochemical age indicated by $-\log(NO_x/NO_y)$, and ratios of secondary nitrate and sulfate to rBC (NO_3/rBC and SO_4/rBC, respectively). These results indicate that photochemical processing played a dominant role in changing rBC coatings and absorption enhancement in summer (Fig. 1c), which is different from the observations in California (Cappa et al., 2012) showing limited dependence of E_{abs} on photochemical aging. However, we also noticed the differences in aerosol composition and BC mixing states before and after noontime. As shown in Fig. 4, NO_3/rBC showed the largest increase from 8:00 to 12:00, while the variations in SO_4/rBC were relatively small, suggesting that the first increase in E_{abs} in daytime was mainly driven by nitrate formation. Although SO_4/rBC, MO-OOA/rBC, and $-\log(NO_x/NO_y)$ continued to increase after noontime between 12:00 and 16:00, E_{abs} decreased slowly instead. We found that R_{BC} and D_p/D_c remained relatively unchanged during this period, while NO_3/rBC showed a clear decrease due to the evaporative loss of nitrate associated with high temperature. Such results are consistent with the conclusion above that E_{abs} is sensitive to the coating fractions of nitrate.

4 Conclusion

The absorption of BC remains a large uncertainty for estimating global warming due to the

controversial lensing effect of absorption enhancement. Here we provide direct evidence for BC absorption enhancement in Beijing in summer using the *in situ* measurements by a thermodenuder coupled with SP-AMS and single scattering albedo monitor. Our results showed that the average E_{abs} at 630 nm was 1.59 (± 0.26) indicating a substantial absorption enhancement due to rBC coatings. E_{abs} showed a strong dependence on rBC coatings (R_{BC}), and the increases in E_{abs} were mainly caused by the production of secondary aerosol species. Further support was from the significant daytime increase in E_{abs} that was associated with enhanced photochemical processing and the formation of secondary organic and inorganic species. By characterizing the composition dependent E_{abs}, we found that the increases in E_{abs} showed different sensitivities to different aerosol species. Formation of secondary nitrate and sulfate in summer has the most impacts on BC absorption enhancements, while freshly oxidized SOA appears not important. Our results highlight an urgent need to characterize the changes of BC mixing states due to the formation of secondary organic and inorganic aerosol species, and the changes of particle phase states.

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Notes

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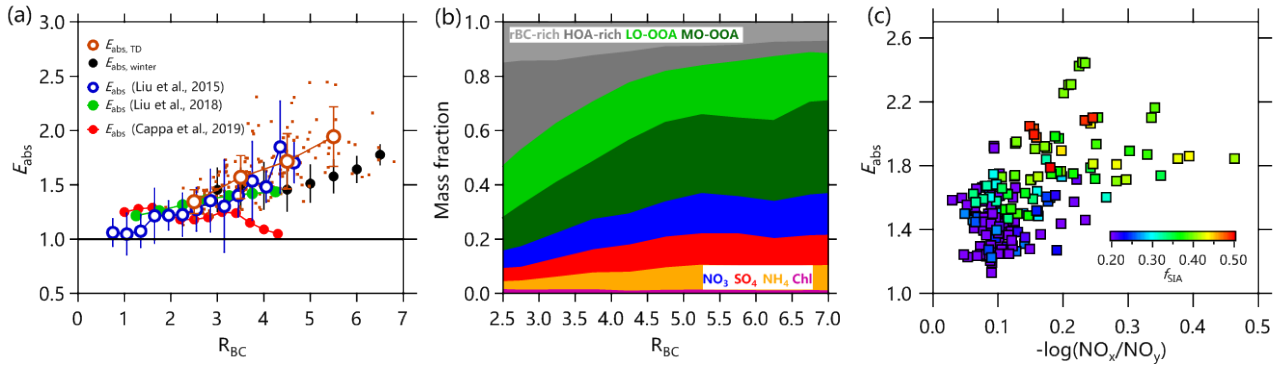

Fig. 1. (a) BC absorption enhancement as a function of R_{BC}. Also shown are the E_{abs} measurements at 532 nm in UK winter (Liu et al., 2015) and Fresno, California (Cappa et al., 2019). The E_{abs} in winter in Beijing was calculated as the MAC divided by 7.4 m^2 g^{-1} (Xie et al., 2019). In addition, E_{abs} in Beijing summer was also modeled with the SP2 measurements (Liu et al., 2018). The error bars in the figure are one standard deviations. (b) Chemical composition of rBC coatings as a function of R_{BC}, and (c) scatter plot of E_{abs} versus -log(NO_x/NO_y) color coded by the fraction of secondary inorganic aerosol (f_{SIA}).

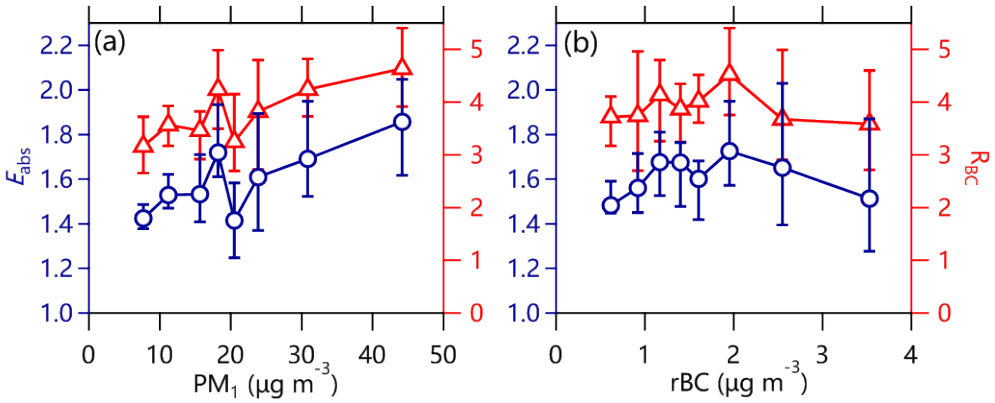

Fig. 2. Variations of E_{abs} and R_{BC} as a function of (a) PM_1 mass loadings and (b) rBC concentrations. The bottom and top error bars represent 25th and 75th percentiles.

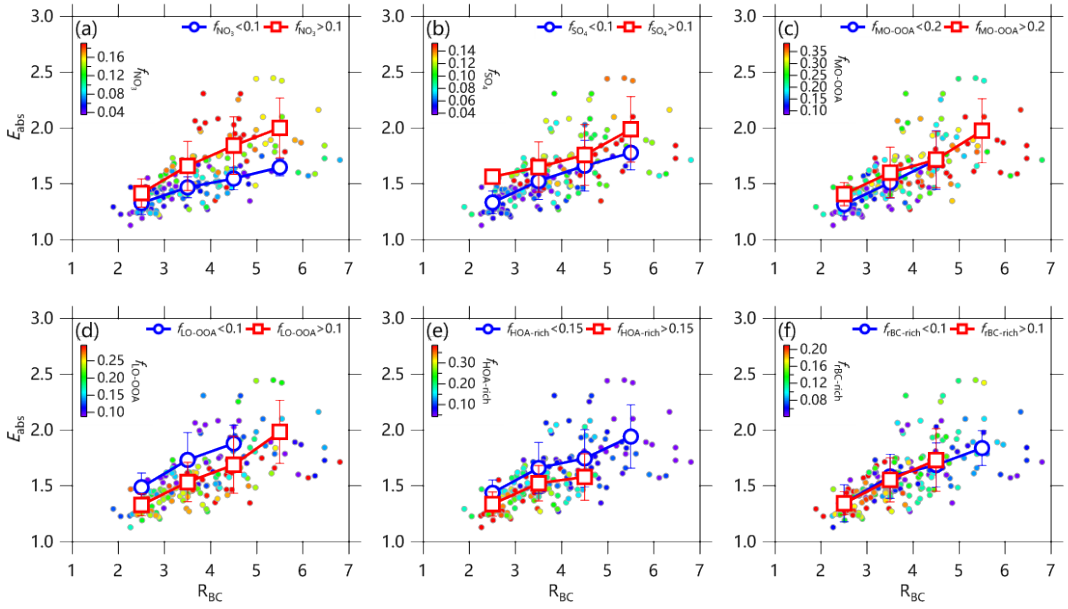

Fig. 3. Variations of BC absorption enhancement as a function of R_{BC}, color coded by mass fractions of (a) NO_3, (b) SO_4, (c) MO-OOA, (d) LO-OOA, (e) HOA-rich, (f) rBC-rich in rBC coatings. The data were binned with low (red squares) and high (blue circles) mass fraction of each aerosol species, and the error bars are one standard deviations.

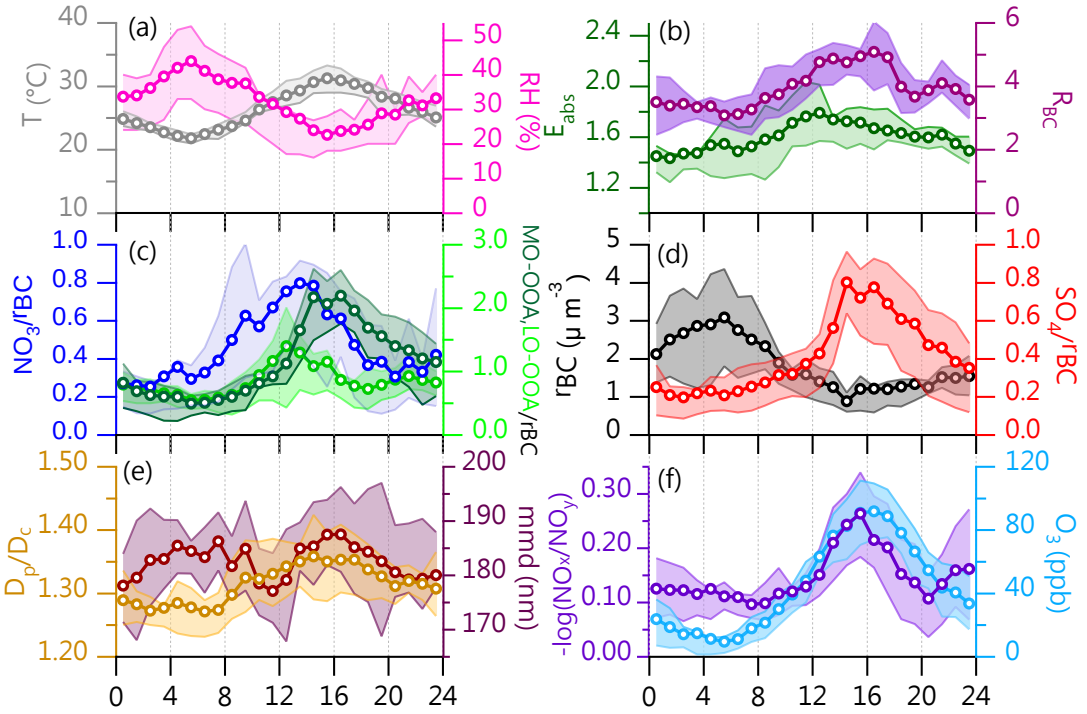

Fig. 4. Diurnal variations of (a) temperature (T) and relative humidity (RH), (b) E_{abs} and R_{BC}, (c) mass ratios of NO_3, MO-OOA, and LO-OOA to rBC, (d) rBC and mass ratio of SO_4 to rBC, (e) D_p/D_c and mass median dimeter of rBC, and (f) –log(NO_x/NO_y) and O_3. The circles are mean values, and the shaded areas represent 25th and 75th percentiles.