Mixing state of refractory black carbon in fog and haze at rural sites in winter on the North China Plain

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Abstract. The variability of the mixing state of refractory black carbon aerosol (rBC)
and the corresponding complicated light absorption capacity impose great uncertainty
for its climate forcing assessment. In this study, field observations using a single particle
soot photometer (SP2) were conducted to investigate the mixing state of rBC under
different meteorological conditions at a rural site on the North China Plain. The results
showed that the hourly mass concentration of rBC during the observation periods was
2.6 ± 1.5 µg m^{-3} on average with a moderate increase (3.1 ± 0.9) during fog episodes.
The mass–equivalent size distribution of rBC exhibited an approximately lognormal
distribution with a mass median diameter (MMD) of 213 nm. We found that the count
median diameter (CMD) of rBC particles during snowfall episodes was obviously larger
than that before–snowfall, indicating that smaller rBC–containing particles were much
more effectively removed by snowfall. The droplet collision and Wegener–Bergeron–
Findeisen (WBF) processes are possible explanations. Based on the Mie–scattering
theory simulation, the relative and absolute coating thicknesses of rBC–containing
particles were estimated to be 1.6 and ~52 nm for the rBC core with a mass–equivalent
diameter (Dc) of 170 – 190 nm, respectively, indicating that the most of rBC–containing
particles were thinly coated. Furthermore, moderate light absorption enhancement (E_{abs}
= 1.3) and relatively low absorption cross–section (MAC = 5.5 m^2/g) at 880 nm were
observed at the GC site in winter compared with other typical rural sites.

The relationships between the microphysical properties of rBC and meteorological
conditions were also studied. We found that the coatings of rBC–containing particles
increase only when both ambient RH and secondary components increase at the same
time, with the thickest coating during fog events and the thinnest on clean days. And –4
~ 0 ℃ may be the most suitable temperature range for coating formation of rBC in this
study. The sulfate formation from aqueous–phases reactions may have a limited
contribution to E_{abs} under high RH conditions (RH > 80%). The enhancement of E_{abs} of
rBC–containing particles was strongly related to an increase in the mass fraction of
nitrate instead of organics at appropriate temperature conditions.

Keywords: Refractory black carbon; Mixing state; Aging process; Snowfall

1 Introduction

As an absorbing aerosol produced by incomplete combustion, black carbon plays a leading role in the absorption of shortwave solar radiation, and changes atmospheric thermodynamics through the heating effect. Black carbon is an important factor leading to highly uncertain climate warming (Bond et al., 2013; Moffet and Prather, 2009). Black carbon aerosols enhance haze pollution by absorbing solar radiation to change the meteorological characteristics of the planetary boundary layer (PBL) (Ding et al., 2016). Freshly discharged black carbon is hydrophobic and becomes hydrophilic when mixed with hydrophilic material during aging, acting as cloud condensation nuclei (Sarangi et al., 2019; Twomey, 1974) and increasing the cloud drop number concentration (Cherian et al., 2017). Wet removal is a key factor in determining the lifetime of black carbon (BC) aerosols in the atmosphere, which determines their vertical and horizontal distribution, local and regional diffusion, and direct, semidirect and indirect radiative forcing effects (Liu et al., 2013).

The burning of fossil fuels such as coal and oil and the burning of biomass in agricultural production caused by human activities are the main factors leading to the increasing black carbon emissions. Using a transmission electron microscope fitted with an environmental cell (ETEM), we observed that fresh black carbon presents a loose and porous chain structure, and then in the atmosphere through condensation, coagulation, heterogeneous oxidation condensation or heterogeneous chemical reaction, rBC is coated by soluble material, and the coating gradually becomes thicker with increasing RH (He et al., 2015; Freney et al., 2010). The mixing state determines the morphology and optical properties of black carbon, affects its wet removal efficiency, and thus affects the atmospheric lifetime (Yu et al., 2020). The extent of rBC coating has been considered to be an important factor in evaluating aerosol radiative capacity (Oshima et al., 2009). It has been shown that the mixing of BC and other non–BC materials can enhance radiation absorption, which is interpreted as exhibiting a "lensing effect," with the magnitude strongly dependent on the rBC coating amount (Cappa et al., 2012; Liu et al., 2015; Moffet and Prather, 2009). Generally, a thicker coating of rBC–containing particles with increased hygroscopic properties and the ability to act as CCN under severe pollution conditions (Ding et al., 2019a; Schwarz et al., 2008). Under high pollution and RH conditions, the adsorption efficiency of black carbon was significantly increased. Reducing the emission of

80   BC and related secondary coating precursors is an effective way to alleviate the thermal effect

of BC in urban environments. However, the change in the mixing state of black carbon aerosols

and their driving factors are not clear under high pollution and RH conditions.

The North China Plain is one of the BC hotspots with intensive anthropogenic emissions (Cao

et al., 2006). Recently, the spatiotemporal distribution and optical properties of rBC and its

85   influence on climate and the environment have been reported (Zhao et al., 2020; Ding et al.,

2019a; Liu et al., 2020b). However, observations of the mixing state of black carbon under

different meteorological conditions are still insufficient. SP2 with high resolution and high

precision has significant advantages in estimating the mixing state of black carbon. In recent

years, an increasing number of observations have used SP2 to observe the mixing state of black

90   carbon in China (Wang et al., 2014; Gong et al., 2016; Liu et al., 2020b; Pan et al., 2017). Most

studies have focused on the mixing state of BC on severe haze days because of the presence of

large amounts of particulate matter and gaseous precursors in the atmosphere. Studies have

focused on the chemical mechanisms such as condensation, coagulation, and heterogeneous

oxidation for coating formation (He et al., 2015; Bond et al., 2013), while the connection

95   between meteorological factors and coatings is relatively rare. Previous studies have shown that

wind speed and variation in the planetary boundary layer (PBL) can influence the concentration

of BC (Talukdar et al., 2019) and that relative humidity (RH) affects the morphology and

hygroscopic growth of rBC–containing particles (Laborde et al., 2013; Freney et al., 2010).

Meteorological fields may have an impact on the mixing state of rBC.

100   In this study, SP2 was deployed at a moderately polluted rural site on the North China Plain in

winter to characterize the size distribution and mixing state of rBC. This work is unique due to

the largely different meteorological conditions during the campaign. The differences in rBC

particle size under different meteorological conditions are illustrated, and the main factors

influencing the rBC mixing state are discussed. The results of this paper were exhibited in the

105   following sequence: (1) the size distribution of rBC in different campaigns; (2) the relative,

absolute coating thickness and optical properties of rBC–containing particles and its

influencing factors; and (3) the relationship of the aging process of rBC with meteorological

conditions such as RH, temperature and pollution conditions.

2 Observations

2.1. Site description and measurements

The observation of refractory BC (rBC) particles was performed from December 7th, 2019 to January 1st, 2020, in an air–conditioned container located in a farmland of the Gucheng (GC, latitude:39°7.8′N; longitude:115°48′E) site in Dingxing County, Hebei Province, China, which is part of the China Atmosphere Watch Network (CAWNET) operated by the Chinese Meteorological Administration (CMA). As shown in Fig.S1(a), the observation station is located ~120 kilometers southwest of Beijing, adjacent to National Highway 107 (G107) and the Beijing–Hong Kong–Macau Expressway (G4). This result indicates that the sampling site was affected by traffic emissions sources, which is a feature compared to other typical rural sites mainly affected by biomass burning sources at home and abroad. A single particle soot photometer (SP2, Droplet Measurement Technologies Inc. USA) was used to measure rBC and HR–AMS was used to measure the nonrefractory submicron aerosol species (NR–PM1).

2.2 SP2 data analysis

2.2.1 Instrument and calibration

The measurement of the size distribution and mixing state of individual rBC–containing particles in GC was characterized using an SP2. The aerosol sampling inlet was placed on a lift tower 3.5 m above the ground, and ambient air entered the container through a 1/2 in. soft black carbon tube. The SP2 was operated at a sampling flow rate of 100 vcmm. There was a continuous intracavity Nd:YAG laser beam (1064 nm, TEM00 mode) in the SP2 measurement chamber. SP2 used particle identification by laser–induced incandescence technology to observe and identify rBC (Stephens et al., 2003; Schwarz et al., 2006). All particles scatter light, but only when they contain highly absorbent and refractory components, such as rBC, they absorb the laser radiation and are heated to their boiling point temperature before emitting blackbody radiation (Liu et al., 2010; Moteki and Kondo, 2007). When particles cross the laser, particles' composition and size can be determined by detecting the incandescence signal when particles evaporated and the elastic scattering signal of particles. The detection of the incandescence signal can provide information on the boiling point temperature of incandescent particles and determine the particle composition. If only the scattering signal was detected, it was proven that the particles do not contain rBC and are purely scattering particles (non–rBC). If both the scattering signal and the incandescence signal were recorded, it was an rBC–containing particle.

140   In general, rBC–containing particles need more time to evaporate the nonrefractory matter before reaching their boiling point temperature. Therefore, there was a lag time (Δt) for the peak of the incandescence signal and the scattering signal, which can be used to qualitatively study the mixing state of rBC–containing particles. For SP2, the detectable size range of the scattering signal was 200–400 nm diameter. Assuming a black carbon density of 1.8 g/cm^3 and

145   an ideally spherical structure, the mass equivalent diameter of black carbon detected by the incandescence signal is 70 – 500 nm.

Prior to the observation field campaign, the scattering and incandescence signals of SP2 were calibrated in the laboratory. Aquadag aerosols (Lot #9627, Acheson Inc., USA) were used to calibrate the incandescence signal. We used an atomizer (model 3072, TSI Inc, USA) and a

150   diffusion dryer to prepare monodispersed Aquadag aerosols, which were selected by mobility diameter using a differential mobility analyzer (DMA; Model 3081, TSI Inc., 150 USA). The calibration coefficient values for broadband high gain (BBHG) and broadband low gain (BBLG) of incandescence signals are shown in Fig. S2. We corrected the incandescence signal for ambient rBC with a scaling factor of 0.75, because the SP2 is more

155   sensitive to Aquadag than diesel emission rBC in the same mass range (Laborde et al., 2012; Baumgardner et al., 2012). The scattering signal was calibrated using polystyrene latex spheres (PSL, Nanosphere Size Standards, Duke Scientific Corp., USA). In addition to the above instruments, a condensation particle counter (CPC, model 3775, TSI Inc., USA) was adopted to measure the number concentration of particles to compare with SP2.

160   **2.2.2 Shell–core calculation**

A single particle rBC mass was obtained by the incandescence signal. We usually refer to the mass equivalent diameter converted by the rBC mass (ρ = 1.8 g/cm^3 for ambient BC) as the rBC core diameter (Dc), which is the diameter of a void–free, spherical structure, as expressed in Eq. (1):

165   $$Dc = \sqrt[3]{\frac{6*M_{rBC}}{\pi*\rho_{rBC}}},\qquad\qquad\qquad\qquad\qquad\qquad\qquad (1)$$

Information about the scattering signal of rBC–containing particles detected by SP2 is distorted, because when individual rBC particles passed through the laser beam, they absorb laser energy and are heated up to ~4000 K, resulting in mass loss of a single rBC particle directly. Thus, the

methodology of leading edge only (LEO) fitting is adopted to characterize the original
scattering properties and coating thickness of rBC–containing particles. The scattering signal
of purely scattering particles is Gaussian, as detected by SP2. In this method, the Gaussian
fitting of the original scattering signal is reconstructed from the leading edge of the scattering
signal (before the volatilization of particles) of rBC–containing particles (Gao et al., 2007). In
this study, rBC–containing particles are assumed to be shell–core structures. The optical
diameter of rBC–containing particles or coated diameter (Dp) is calculated by Mie table
calculations. Using a core refractive index $n_c = 2.26 + 1.26i$ and a coating refractive index
$n_s = 1.48 + 0i$, we input the LEO fitted scattering signal and rBC core size into Mie calculations
(Taylor et al., 2015). Further, the relative coating thickness (RCT), namely, the shell / core ratio
and absolute coating thickness (ACT) of an rBC–containing particle are calculated as D_p/D_c
and $(D_p - D_c)/2$, respectively.

2.2.3 Calculation of rBC optical properties

The ensemble effect of light absorption by rBC–containing particles is calculated at 880 nm,
because the optical properties of rBC–containing particles at this wavelength are hardly affected
by brown carbon (BrC). Based on the size information of rBC–containing particles (i.e., Dc and
Dp) obtained by SP2 observation, optical parameters such as the mass absorption cross–section
(MAC), absorption enhancement (E_{abs}) and absorption coefficient (σ_{abs}) of rBC–containing
particles can be obtained based on Mie scattering theory. The refractive index of the rBC core
was $2.26 + 1.26i$ (Bond and Bergstrom, 2006), and the refractive index of $1.48 + 0i$, was used
for coatings in the Mie calculation assuming rBC–containing particles is a core–shell model. In
addition to the absorption of light by the rBC core, coating materials on the surface of rBC can
attract more light to the rBC core, which called lensing effect, enhancing the light absorption
of rBC. The E_{abs} can be used to quantify the theoretical light absorption capability of BC–
containing particles. E_{abs} is determined by the ratio of the absorption cross–section of the whole
rBC–containing particle ($C_{abs,s}$) to the absorption cross–section of the bare rBC core ($C_{abs,c}$),
as shown in Eq. (2):

$$E_{abs} = \frac{C_{abs,s}}{C_{abs,c}} \tag{2}$$

MAC reflects the optical absorption characteristics of rBC–containing particles in unit mass

concentration. The larger the value is, the stronger the radiation absorption capacity of rBC–containing

particles is. The mass absorption cross–section (MAC_i) of a single rBC–containing particle is defined

200 as the absorption cross–section of the whole rBC–containing particle ($C_{abs,s}$) per unit rBC mass

($m_{rBC,i}$), as expressed in Eq. (3):

$$MAC_i = \frac{C_{abs,s}}{m_{rBC,i}} \qquad (3)$$

The MAC in bulk for a given period is calculated as:

$$MAC = \frac{\sum_i MAC_i \times m_{rBC,i}}{\sum_i m_{rBC,i}}. \qquad (4)$$

205 The σ_{abs} of rBC–containing particles is calculated based on the MAC and the mass concentration (C_{rBC})

measured by SP2, as shown in Eq. (4):

$$\sigma_{abs,calculated} = MAC \times C_{rBC} \qquad (5)$$

Previous studies have shown that the light absorption of rBC—containing particles is related to their

morphology (Liu et al., 2017; Liu et al., 2020b). A simple core–shell model, used in Mie theory to

210 calculate optical properties, causes uncertainty due to the lack of observation of optical size information

and morphology.

2.3 Dispersion and trajectory analysis

The HYSPLIT (Hybrid Single–Particle Lagrangian Integrated Trajectory) model developed by

NCEP (National Center for Environmental Prediction) and NCAR (National Center for

215 Atmospheric Research) was used to simulate the air footprint area during the observation of the

sampling site, which was based on the Lagrangian transport model

(https://ready.arl.noaa.gov/HYSPLIT_traj.php, last access: February 28th, 2020) (Cohen et al.,

2015). The dataset provided for HYSPLIT is the global reanalysis data in GDAS format

(ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1, last access: February 26th, 2020). It produces

220 meteorological data four times a day, namely, at 00:00, 06:00, 12:00 and 18:00 UTC, and the

horizontal resolution is 2.5°×2.5°. The vertical direction has 17 levels, ranging from the ground

surface to 10 hPa. Meteorological parameters including wind, temperature, humidity, potential

height and ground precipitation are also provided. During the simulation, the trajectory

ensemble option starts multiple trajectories from the first selected starting location. Each

225 member of the trajectory ensemble is calculated by offsetting the meteorological data by a fixed

grid factor (one meteorological grid point in the horizontal direction and 0.01σ units in the

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concentration of rBC in winter 2016 in Beijing was 6.4 µg m^{-3} due to the strict air pollution control on coal combustion and biomass burning (Ji et al., 2017) Xie et al. (2020) found a decrease in mass concentration (3.2 µg m^{-3}) in winter 2018. A similar urban–high and rural–low pattern was also found in Shenzhen, and the average mass loading of rBC in rural areas

260 (2.6 µg m^{-3}) in autumn was much lower than that in urban areas (6 µg m^{-3}) (Huang et al., 2012). One possible explanation was that rural sites have lower traffic emissions than urban sites, open biomass burning has been strictly controlled in recent years, and the project of changing fuel from coal to natural gas has been well implemented at least in NCP (Huang et al., 2006; Ji et al., 2017).

265 Based on the meteorological conditions and concentrations of the total particles, six observation periods were chosen, as denoted in Fig. 1a: EP1 (December 7th 17:40 – December 11th 09:00), EP2 (December 12nd 19:00 – December 14th 00:00), EP3 (December 15th 00:00 – December 17th 00:00), EP4 (December 21st 00:00 – December 26th 00:00), EP5 (December 27th 00:00 – December 29th 20:00) and EP6 (December 30th 00:00 – December 31st 00:00). The periods with

270 RH = 100% during EP1 were defined as the fog period. The average RH was 96% and the average rBC mass concentration was 3.6 (± 1.4) µg m^{-3} during EP1. During EP3, there was snow from December 15th 19:00 to December 16th 13:00. Therefore, during EP3, the discussion is divided into before–snow, snow and after–snow. In the other four periods, EP6 was the clean period with an average rBC mass concentration of 0.5 (± 0.3) µg m^{-3}, while EP2, EP4 and EP5

275 represented polluted periods with average rBC mass concentration of 3.4 (± 1.4), 1.2 (± 1.2) and 3.4 (± 1.3) µg m^{-3}, respectively. The variables related to rBC and the meteorological conditions in the selected different periods are shown in Table S1. The Hysplit model was used to analyze the origin of the air masses during the different periods. As shown in Fig.2a–f, the air masses over GC mainly came from the northwest and northeast directions during the clean

280 period, and the wind speed was relatively high. During the pollution period, the air masses mainly came from the southwest and south directions and local areas. During the period of EP1 and EP3 with high RH, part of the air mass originated from the eastern Bohai Sea direction.

3.2 Size distribution of rBC

The time series of the mass size distribution of rBC during the whole experimental period was stable with a modal size peaking at approximately 200nm (Fig. S3). The rBC–containing particles measured by SP2 at the GC site mainly were distributed in the range of 70–400 nm and the rBC mass was concentrated at 100 – 400 nm. dM / dlogDc showed an apparent diurnal trend. The peak period of diurnal variation was between 20:00 and 09:00 LST, while low diurnal variation occurred in the afternoon. This pattern was determined by the dual effects of diurnal variation in the boundary layer and local rBC emissions. To better study dM / dlogDc, the mass median diameter (MMD) was used to represent the characteristics of dM / dlogDc for detailed discussion.

Field measurements of the size of rBC around the world are summarized in Table 1. The size distribution as a function of rBC core mass equivalent diameter (Dc) measured by SP2 is shown in Fig. 3. During the whole experiment, the mass size distribution followed the lognormal distribution and peaked at 213 nm (MMD) (Fig. 3a). As shown in Table 1, the MMD of rBC at the GC site in winter was slightly smaller than the value (222 nm) observed in rural areas in Shenzhen in November (Huang et al., 2012) and consistent with the biomass burning emission observed in Texas (MMD = 210 nm) (Schwarz et al., 2008). However, the rBC emitted by biomass burning in the laboratory was larger (189 nm) (Pan et al., 2017). In addition, this mode was identical to the rBC mode observed in the aged continental air mass during a Paris study (Laborde et al., 2013). In comparison with most studies in urban areas, we found that the MMD of rBC in urban areas was smaller than that in our study (Huang et al., 2012; Gong et al., 2016; Liu et al., 2019; Lan et al., 2013; Liu et al., 2020b; Schwarz et al., 2008). Laborde et al. (2013) found that MMD was significantly related to the source of rBC–containing particle emissions. Pan et al. (2017) showed that the MMD of rBC was also determined by combustion conditions and burning materials in a laboratory study. Many studies have indicated that the MMD of rBC from traffic emissions was smaller than that from biomass burning, coal combustion and aged air masses (Laborde et al., 2013; Schwarz et al., 2008). According to previous studies, MMD presented a trend of small size in summer large size in winter, small size in urban areas and large size in rural areas (Liu et al., 2019; Liu et al., 2020b; Huang et al., 2012; Kondo et al., 2016; Wu et al., 2021). The dense traffic arteries in urban areas and large amount of traffic

emissions may be the reason that MMD in urban areas is smaller than that in rural areas (Huang et al., 2006; Laborde et al., 2013; Schwarz et al., 2008). The different trends of MMD in seasons

315   and spaces may be because rBC–containing particles came from different emission sources. In addition, the MMD was higher in pollution events (i.e., EP1, EP2, EP3 and EP5). This was similar to the results of previous studies in which under the condition of a higher rBC mass concentration, the rBC core size usually increased (Liu et al., 2019). It could be that coagulation of rBC particles or regional transport causes changes in rBC–containing particle sources at

320   higher concentrations.

The number size distribution followed the lognormal distribution and peaked at 122 nm (CMD) (Fig. 3a). Because most rBC particles (by number) emitted from urban areas were below the SP2 detection limit of 70 nm, the comparison of the number size distribution between urban and rural areas was meaningless (Schwarz et al., 2008). There was snowfall during the

325   observation period, and the mass and number size distributions of the rBC core mass equivalent diameter (Dc) during the snow event are illustrated in Fig. 3b–c. During before–snow, snow and after–snow periods, the MMD was 213 nm, 210 nm and 206 nm, decreasing by 3.3%, and the CMD was 120 nm, 126 nm and 129 nm, an increase of 7.5% respectively. Previous studies found that wet deposition is the main mechanism for removing of rBC–containing particles

330   (Taylor et al., 2014). Wet removal plays an important role in determining the size distribution of rBC during vertical transport in the free troposphere (Moteki et al., 2012), and rainfalls, as a means of wet removal, preferentially removes large rBC–containing particles, resulting in a decrease in MMD after rain events (Liu et al., 2020b; Wang et al., 2018). However, this study found that the CMD of rBC–containing particles increased after–snowfall; that is, snow events

335   would preferentially remove rBC–containing particles with smaller rBC core sizes. This may be because the wet removal mechanism of snow was different from that of rain, which was consistent with the finding that the rBC core size maintained a stable growth trend from 200 to 260 nm during snowfall that lasted for more than 8 hr in an observation (Ding et al., 2019b). Although the CMD increased significantly, the effect of removing a large amount of rBC with

340   a small core size was small on the MMD because the large mass of rBC had a greater weight for the MMD. The slight decrease in MMD may be a result of snowfall, as wet removal is also

similar to rain, and can remove rBC with a large core size. In addition, the droplet collision and Wegener–Bergeron–Findeisen (WBF) processes may be the mechanism for extremely high removal of rBC with a small core size during snowfall, unlike rains (Liu et al., 2020a;

345   Ding et al., 2019b).

3.3 Mixing state of rBC–containing particles under different conditions
3.3.1 Coating thickness of rBC–containing particles

Figure 4 provides the temporal variation of ACT, RCT and CMD of rBC–containing particles during the entire period. The relative coating thickness (RCT) and absolute

350   coating thickness (ACT) of rBC–containing particles were calculated by the LEO fitting method, see Sect. 2.2.2 for details. Herein, rBC cores with Dc = 180±10 nm and Dc = 190±10 nm were selected because the low scattering signal of small rBC is easily influenced by signal noise. The average RCT (±1σ) (Dc@70–500nm) was 2.0 (±0.3), RCT (±1σ) (Dc@170–190nm) was 1.6 (±0.2), RCT (±1σ) (Dc@190–210nm) was 1.5

355   (±0.2), ACT (±1σ) (Dc@70–500nm) was 57.8 (±17.0) nm, ACT (±1σ) (Dc@170–190nm) was 52.4 (±21.8) nm, and ACT (±1σ) (Dc@190–210nm) was 54.2 (±20.4) nm. As shown in Table 1, the RCT (Dc@190–210nm) of GC site was consistent with the RCT (1.2–1.4) with Dc = 200 nm of rBC–containing particles emitted from biomass burning through laboratory research (Pan et al., 2017), but was larger than the value (RCT (@Dc= 180

360   nm) = 1.2) during the summer in Beijing, which was mainly influenced by traffic emissions (Liu et al., 2020b). In the meantime, the RCT (2.0) with an rBC core size of 70–500 nm at the GC site was slightly larger than that in Beijing summer 2017 (~1.4) and smaller than that in Beijing winter 2016 (~2.5) (Liu et al., 2019). The ACT (Dc@190–210nm) at the GC site was smaller than that at Texas (65 nm), which was

365   affected by biomass burning. The different sources and aging processes of rBC–containing particles affect the coatings. Laborde et al. (2013) reported that rBC–containing particles emitted by traffic are essentially uncoated with median coating thickness of 2±10 nm at a core size of 180–220 nm, the median ACT of rBC–containing particles emitted by biomass burning was approximately 20–40 nm, and the median ACT

370   of rBC–containing particles in continental aged air masses reached ~80 nm.

In addition, we compared the coating thickness of rBC–containing particles during 6 different periods. As shown in Table S1, the average RCT and ACT ($\pm 1\sigma$) ($Dc@170$–190nm) were 2.0 (± 0.3) and 92.7 (± 23.8) nm, respectively, during the fog event, which were the highest values during the whole observation period. According to Fig. 7, the ambient mass concentrations

375   of NR–PM1 were almost the same during the fog, after–snow and EP4 periods. The RH during these 3 periods was different, where the RH during the fog event was highest (RH=100%), and the RH during EP2 was lowest (RH~81%). This indicates that a high RH significantly affected on the formation of coatings under the same concentration of pollutants in the atmosphere. Fig. 5a and Fig. S4a show the RCT and ACT as a function of the rBC core diameter during the fog event,

380   respectively. In these 2D images, the results of a smaller Dc (<110 nm) were meaningless due to a failed LEO fitting or the measured particle scattering signal falling outside of the Mie predictable range (Liu et al., 2014). Therefore, we only focused on the part of the Dc > 110 nm. The coating thickness of rBC–containing particles exhibited a bimodal distribution, and rBC–containing particles in the first peak usually had an RCT (ACT) value of 1.0 (0

385   nm), and the second peak had an RCT (ACT) value of ~ 1.8 (~ 70 nm) during fog events. More than 30% of the rBC–containing particles had an RCT of 1.5–2.2 and more than 50% of the rBC–containing particles had an ACT of ~ 50 nm. During the before–snow, snow and after–snow periods, the average RCTs (ACTs) ($\pm 1\sigma$) ($Dc@170$–190nm) were 1.4 (± 0.1) (39.9 (± 43.6) nm), 1.5 (± 0.1) (46.9 (± 4.5) nm) and 1.7 (± 0.1) (61.3 (± 4.7) nm), respectively. Fig. 5b–d and

390   Fig. S4b–d show the RCT and ACT as a function of the rBC core diameter during before–snow, snow and after–snow events. The coating thickness of rBC–containing particles exhibited a unimodal distribution during before–snow, snow and after–snow events, with peak of RCT (ACT) values of 1.1 (15 nm), 1.2 (15 nm) and 1.2 (25 nm). From the before–snow to after–snow period, the coating thickness of rBC–containing particles increased gradually. We

395   observed an increase in the secondary inorganic components and a decrease in the organic compounds in the concentration and fraction in the ambient atmosphere (Fig. 7), indicating that the coating thickness of rBC was intrinsically affected by the types of pollutants.

The RCT and ACT as a function of an uncoated rBC core diameter in pollution and clean

400   periods are shown in Fig. 6 and Fig. S5. During the pollution events (i.e., EP2 and EP5),

the rBC mass concentrations were almost the same, while the ambient RH during EP5

was larger than that during EP2. The coating thickness of rBC during EP5 with ACT ($\pm$

1σ) (Dc@170–190nm)48.9 ($\pm$ 14.1) nm was larger than that during EP2 with ACT ($\pm$ 1σ)

(Dc@170–190nm) 42.3 ($\pm$9.4) nm. The rBC mass concentration during EP4 was lower than

405   that during EP5; however, due to the higher RH and higher mass fraction of nitrate during

EP4 (Fig. 7b), the coating thickness of rBC–containing particles during EP4 was larger

than that during EP5. EP6 was a clean period characterized by a low rBC mass

concentration and low ambient RH and a relatively higher mass fraction of organics in

NR–PM1. The large fraction of uncoated rBC–containing particles indicated that the coating

410   processes of condensation of semi–volatile organics on rBC particles were insignificant.

3.3.2 Absorption enhancement of rBC–containing particles

The E_{abs}, σ_{abs} and MAC of rBC–containing particles during the whole campaign are

shown in Fig.4. The average E_{abs} and MAC at 880 nm were 1.3 and 5.5 m^2/g, respectively, as

calculated by Mie theory. Comparisons of E_{abs} in various field studies are shown in Table 2. The E_{abs} at

415   the GC site we simulated was consistent with the value measured by Sun et al. with TD–PAX (Droplet

Measurement Technologies) at 870 nm (1.32 $\pm$ 0.15) (Sun et al., 2021). The E_{abs} calculated by Mie

theory is only related to the core size of rBC, the refraction index of rBC–containing particles and

the coating thickness. Therefore, it is difficult to determine the relationship between E_{abs} and aerosol

species in the environment by this method. It has been suggested out that the correlation between σ_{abs}

420   calculated by Mie theory and σ_{abs} measured by AE33 is as high as 0.98, indicating that the optical

properties of rBC–containing particles calculated by Mie theory can represent the actual rBC–

containing particles in a specific area (Zhang et al., 2018b). Therefore, we compared the differences

in E_{abs} between the GC site and other regions. A moderate E_{abs} (1.21 $\pm$ 0.09) at 870 nm was found in

California 2013 during winter which was close to the present study (Zhang et al., 2016).

425   The E_{abs} was slightly larger than the value simulated using core–shell in Beijing 2018 during summer at

550 nm (1.15) (Liu et al., 2020b). Slightly high E_{abs} values were observed in Xian (1.8 at 870 nm) (Wang

et al., 2014) and Paris (1.53 $\pm$ 0.93 at 880 nm) (Zhang et al., 2018a) which represent the more polluted

urban areas. Previous studies have found that the E_{abs} is generally higher in rural areas than in urban areas, such as Shouxian (2.3 ± 0.9 at 532 nm) (Xu et al., 2018) and Yuncheng (2.25 ± 0.55 at 678 nm) (Cui et al., 2016). In addition, we studied the absorption enhancement of rBC–containing particles during 6 different periods, and specific information is detailed in Table. S1. From the before–snow to after–snow period, the coating thickness and E_{abs} of rBC–containing particles increased gradually. During the clean period, rBC with a larger core size was mostly emitted from primary sources, and the E_{abs} close to 1. In the fog event, the coating thickness was the highest among the 6 periods, while the E_{abs} was lower. This may be because the core size (Dc) of rBC during fog events was larger, rBC with a large core size (Dc) had a lower MAC, and the addition of coatings to rBC with a large Dc did not significantly affect the final total MAC compared to rBC with a small Dc (Liu et al., 2019). Compared with other rural sites, the E_{abs} and MAC of rBC–containing particles at the GC site were low. Sun et al. (2021) found that the absorption due to the lensing effect at the GC site correlated best with chloride and less well with SIA and SOA. Chloride is mainly from coal combustion and biomass burning emissions, which means that the E_{abs} at the GC site of rBC–containing particles was dominantly affected by primary species and that the coatings formed by secondary reaction products had little effect on E_{abs}. This result was consistent with the findings observed at Fresno with similar emission sources as the GC site, where the average mixing–induced absorption enhancement of BC due to the coatings can be very small (Cappa et al., 2019).

3.4 Diurnal variation of the mixing state of rBC

Figure 8 exhibits the diurnal trend of the mixing state of rBC–containing particles. The temporal variation in rBC exhibited a clear noon–low and morning and evening–high pattern while the diurnal variation in wind speed was the opposite (Fig. S6). The mean rBC mass loading increased during the evening, with a peak (3.5 µg m^{-3}) at 20:00 LST and a minimum (1.4 µg m^{-3}) at 16:00 LST, which was later than that in Beijing (Liu et al., 2020). From the diurnal variation of wind speed (Fig. S6), it can be seen that the wind speed started to increase at approximately 9:00 LST and reached a maximum (2.2 m s^{-1}) at 13:00 LST. These two–time points corresponded to the start of rBC decline and the lowest value of rBC respectively. This diurnal variation in rBC and wind speed can be explained by the diurnal variation in the boundary layer (Simpson and McGee, 2012; Talukdar et al., 2019). In the early morning, calm

inversion conditions predominate in the boundary layer. The temperature rose, the wind speed increased to an average of over 2 m s^{-1} at midday, and the rBC declined rapidly with decreased atmospheric stability and increased turbulence. After sunset, the temperature dropped sharply,

460   due to inversion and increased emissions from heating activities, and the surface pollution of rBC was enhanced. The diurnal cycle of σ_{abs} was similar that of rBC mass concentration, which may be because σ_{abs} of rBC depends on its concentration (Zhang et al., 2018b). The diurnal variation in MAC showed an opposite trend to the MMD, indicating that MAC with a smaller rBC core size was larger. The coating thickness of freshly emitted rBC–containing particles

465   was thin but thicker through a complex aging process, indicating that the RCT (ACT) was controlled by the competing effects of the aging process and emissions. The temporal variation in RCT did not present a clear day–high and night–low pattern like Beijing during summer (Liu et al., 2020b). Three peaks of the mean RCT appeared at 0:00, 8:00 and 18:00, indicating that rBC emissions increased after 0:00, 8:00 and 18:00 at the GC site, and fresh rBC decreased the

470   coating thickness. In addition, there was a significant increase in RCT from the late afternoon. The light absorption enhancement of rBC also did not present a strong diurnal variation trend like Beijing during June (Xie et al., 2019). This trend was consistent with the diurnal variation trend of MAC but different from that of RCT. As shown in Fig. S7, a good correlation was found between MAC (880 nm) and E_{abs} with an R^2 of 0.75 and a weak anticorrelation was found

475   between RCT and E_{abs} with an R^2 of 0.14. This is consistent with the results discussed in Sect 3.3.2, where the E_{abs} at the GC site was more influenced by the MAC of the rBC than the coating thickness. The diurnal variation in the mass fraction of aerosol species is shown in Fig. 8d. The daily cycle of mass fractions in chloride, organics and ammonium began to decrease in the late afternoon, while nitrate increased. The two higher diurnal peak values of the mass fraction of

480   sulfate occurred at 09:00 and 16:00 LST, and the daily variation peak of the mass fraction of nitrate occurred at 16:00 LST. This may explain the increase in RCT in the late afternoon, and an increase in the mass fraction of sulfate and nitrate in the environment may favor an increase in the coating thickness of rBC–containing particles. However, the diurnal cycle of light absorption enhancement of rBC presented limited dependence on the aerosol species in the

485   environment.

3.5 The dependence of the aging degree of *r*BC–containing particles on meteorological and pollution conditions

The factors that affect the aging degree of *r*BC–containing particles include photochemical reactions, aerosol species in the atmosphere and the meteorology of the environment (Laborde et al., 2013;Saathoff et al., 2003;Schnaiter, 2005). In this study, 9 RH levels (0%–20%, 20%–30%, 30%–40%, 40%–50%, 50%–60%, 60%–70%, 70%–80%, 80%–90% and 90%–100%) were selected to investigate the RH dependence of the mixing state of *r*BC. As shown in Fig. 9, we found a strong dependence of coating thickness, E_{abs} and aerosol species on RH. The average RCT increased from ~ 1.6 to 2.3 and ACT increased from ~ 41 nm to 76 nm at the GC site (Fig. S8a) as RH increased from 0% to 100%. The average E_{abs} increased from ~ 1.2 to 1.4 as RH increased from 0% to 80% and remained almost constant after RH exceeded 80%. The RH dependence of E_{abs} was likely caused by the RCT as supported by the gradual increase in the mass concentration of secondary components as a function of RH (Fig. 9c). The growth rate of coating thickness increases after RH exceeds 70%, which may be due to the liquid phase and heterogeneous reactions of secondary coatings (Collier et al., 2018;Wu et al., 2016), as explained by the steep increases in the mass concentration of nitrate and sulfate dependency on RH in the atmosphere (Fig. 9c). In addition, the mass concentration and mass fraction of Chl at the GC site showed a similar increasing trend as E_{abs}, which may imply that primary emissions contribute more to E_{abs} than secondary components. Moreover, only the mass fraction of sulfate in the secondary components increased steeply when the RH was above 80%, which may indicate that the sulfate formed by the aqueous–phase reaction made a limited contribution to the E_{abs}.

The temperature effect on the mixing state of *r*BC–containing particles is examined in Fig. 10. A positive response of RCT, RH and mass concentration of aerosol species to temperature was observed for the temperature range of –14 ~ 0 ℃, suggesting that this temperature range was a favorable condition for coating formation on *r*BC at the GC site. However, a further temperature increment beyond 0 ℃ led to a decline in the coating thickness. This can be explained by the variation trend of aerosol species in the environment with temperature. When the temperature was below 0 ℃, the concentration of secondary components increased as the temperature rose,

515   which may favor the formation of coatings on rBC. Previous studies have found that particles'

growth depends on the competition between particles and water vapor under heavy pollution

conditions, and the temperature has a significant influence on condensation growth (Okuyama

et al., 2007). Therefore, –4 ~ 0 ℃ may be the most conducive temperature range for water vapor

to compete with particles and condense on the surface of rBC. Note that E_{abs} increased with

520   increasing temperature when the temperature range was below 4 ℃ and decreased when the

temperature exceeded 4 ℃, which was different from the temperature dependence on RCT. In

this study, we found that the mass concentration and mass fraction of nitrate decreased after the

temperature exceeded 4 °C (Fig. 10d). The evaporation of volatile components due to increased

temperature could be the explanation (Sun et al., 2020). Higher temperatures facilitate the

525   transition of volatile components such as nitrates and volatile organic compounds from the solid

phase to the gas phase. As shown in Fig. S6, the temperature at the GC site increased in the

afternoon, and the nitrate decreased significantly at the same time, indicating that nitrate

evaporated. A study in Beijing found that nitrate evaporation weakens E_{abs} (Xie et al., 2019).

Another chamber study found that during the chemical aging process of rBC, E_{abs} was reduced

530   due to the evaporation of SOA (Metcalf et al., 2012). Temperature–dependent gas–particle

partitioning also played an important role in E_{abs}.

4 Conclusions

The size distribution, coating thickness and optical properties of individual rBC–containing

particles were measured by a single–particle soot photometer (SP2) during the period December

535   7th to December 31st, 2019 to characterize the mixing state of rBC–containing particles in rural

areas on the North China Plain. We analyzed the mixing state and optical properties of rBC–

containing particles in different episodes and discussed the factors affecting the aging degree

of rBC. The MMD of rBC in the GC site was 213 nm which was smaller than that in other rural

areas. Meteorological conditions can significantly affect the mass size distribution. Snowfall

540   preferred to remove rBC–containing particles with smaller core sizes due to droplet collision

and Wegener–Bergeron–Findeisen processes. The average RCT (ACT) was 1.6 (52 nm)

when the Dc was in the range of 170 nm ~ 190 nm, indicating a moderate coating thickness of

rBC during the winter. The coating thickness of rBC–containing particles in the fog event was

thicker than that in other periods due to the high RH and high concentration of secondary

545 aerosols. The ensemble-average mixing-induced E_{abs} and MAC at the GC site were smaller than those at other rural areas. The RCT (Dc@70–500nm) and E_{abs} did not show clear diurnal cycles with little variations in the range of ~1.9–2, and 1.3–1.4, respectively. A good correlation was found between MAC (880 nm) and E_{abs} with an R^2 of 0.75 and a weak anticorrelation was found between RCT and E_{abs} with an R^2 of 0.14 under diurnal cycle. This may because the optical

550 properties of rBC in the GC site were mainly influenced by primary emissions (such as coal combustion, biomass burning and traffic emission), and the absorption due to lensing effect contributes less to it.

Our results showed that the mixing state of rBC–containing particles depends on the synergistic effects of ambient RH, temperature and aerosol species due to complex chemical reactions.

555 With the increase in the mass fraction of secondary components and the decrease in the mass fraction of organic matter, the coating thickness of rBC–containing particles tended to be thicker. RH > 70%, secondary components (e.g., nitrate and sulfate) generated by the liquid phase and non–homogeneous reactions favored the formation of coatings. RH>80%, the contribution of sulfate formed by the aqueous phase reaction to E_{abs} was limited. The effect of

560 temperature on the aging degree of rBC–containing particles was reflected in the temperature dependence of particle condensation growth and gas–particle partitioning. Volatile components such as nitrate and organics are sensitive to temperature. The temperature range of –14 ~ 0 ℃ was favorable for coating thicknesses formation. Our study found that when the temperature in the rural areas of GC rises to 4 ℃, the coating thickness and E_{abs} of rBC–containing particles

565 decrease; in addition, the mass concentration and mass fraction of nitrate decrease, correspondingly. This suggests that when the temperature in rural areas rises to 4 ℃, volatile components such as nitrate move from the solid phase to the gas phase, resulting in a smaller coating thickness and E_{abs} of rBC–containing particles. Our results highlight that the aging degree of rBC in different chemical environments needs to be considered in regional climate

570 models to better evaluate the radiative forcing of rBC.

Data availability. To request the data given in this study, please contact Xiaole Pan at the Institute of Atmospheric Physics, Chinese Academy of Sciences, via email (panxiaole@mail.iap.ac.cn).

575 *Author contributions.* YZ, SL, HL, and XP designed the research. YZ, SL, HL, XP, WX, YT, WY, XL, QL, JL, CC, YS, PF, JX, JC and ZW performed the experiments. YZ, SL, HL and XP performed the data analysis. YZ, HL, XP and SL wrote the paper.

Competing interests. The authors declare that they have no conflict of interest.

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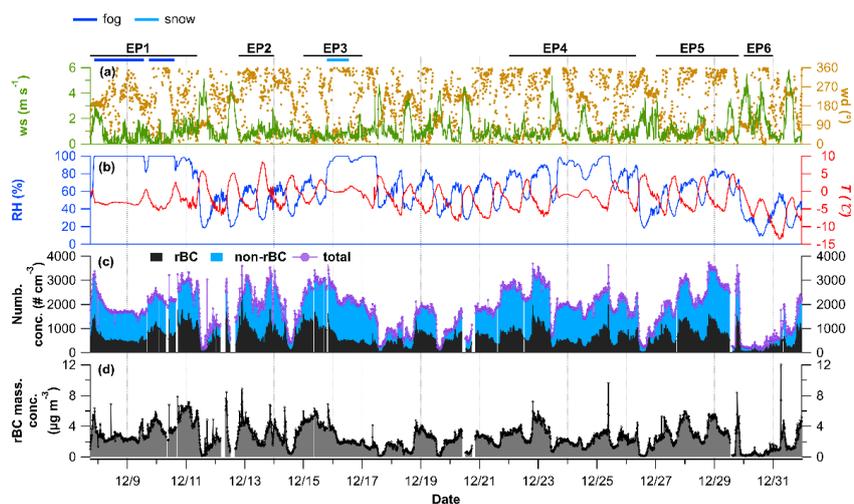


Figure 1: Time series of (a) wind speed (ws) and wind direction (wd), (b) relative humidity (RH) and ambient temperature (T), (c) number concentration of *r*BC–containing particles, purely scattering particles and total particles measured by SP2 in GC and (d) *r*BC mass loading.

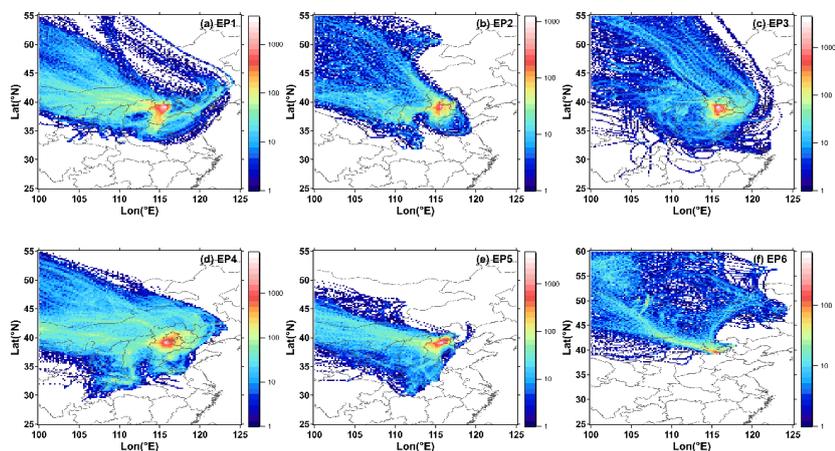



Figure 2: The backward trajectories from which the air mass over GC originated in varying periods.

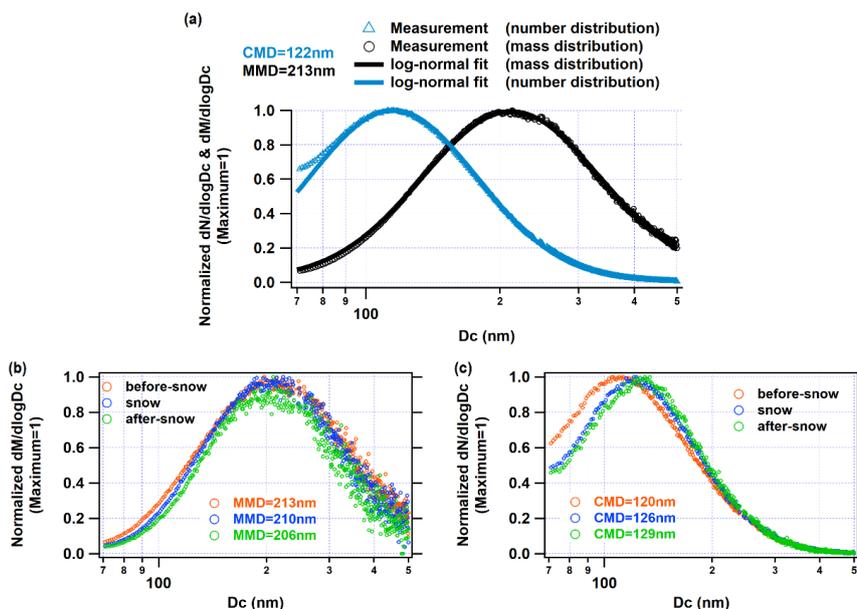



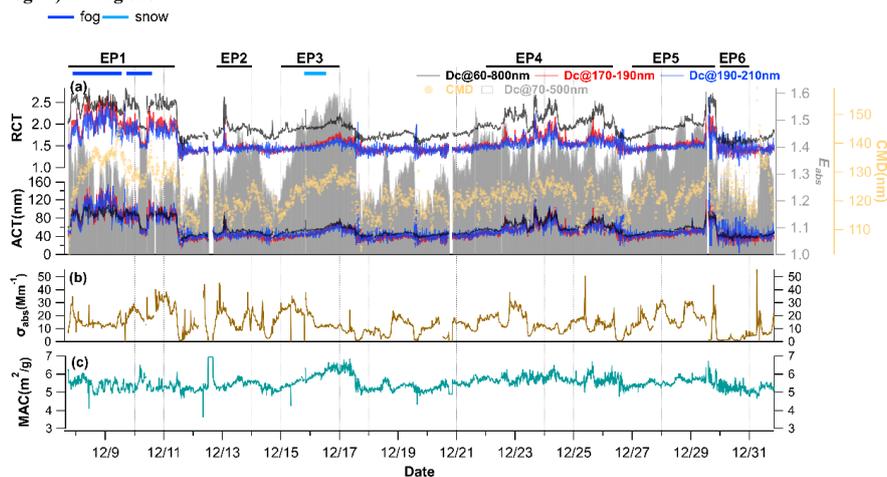
Figure 3: (a) Number and mass size distribution (dN / dlogDc and dM / dlogDc) of rBC core during the whole campaign. (b) Mass size distribution (dM / dlogDc) during snowfall and (c) number size distribution (dN/ dlogDc) during snowfall.

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Figure 4: (a) Time series of the relative and absolute coating thicknesses of rBC–containing particles within the Dc range of 170–190 nm, 190–210 nm and the entire SP2 detectable Dc range (70–500 nm). The gray bars denote the absorption enhancement (E_{abs}) of rBC within the Dc range of the entire SP2 detectable Dc range (70–500 nm). The light yellow circles denote the size of the rBC core. Time series of the (b) absorption
820 **coefficient (σ_{abs}) and (c) mass absorption cross–section (MAC).**

Table 1. Brief summary of some of the experiments on the size and mixing state of *rBC*-containing particles.

rBC source	Location	Time	CMD (nm)	MMD (nm)	RCT	ACT (nm)	Reference
Urban emission (UE)	Beijing, China	Jun (Summer)		171	1.2($@Dc$=180 nm)		Liu et al. (2020)
	Shenzhen, China	Aug-Sep (Fall)		180*			Lan et al. (2013)
	Shenzhen, China	Oct-Nov (Fall)	110	210*			Huang et al. (2012)
	Shanghai, China	Dec (Winter)		200	2-8	50-300	Gong et al. (2016)
	Texas, US	Sep (Fall)		170		20($@Dc$=200 nm)	Schwarz et al. (2008)
	Beijing, China	Nov-Dec (Winter)		195-211	2.5		Liu et al. (2019)
		May-June (Summer)		185	1.4		
	Beijing, China	winter		209			Wu et al. (2021)
		summer		167			
Rural emission (RE)	Shenzhen, China	Nov (Fall)	120	222			Huang et al. (2012)
	This study	Dec (Winter)	122	213	1.6 ($@Dc$=180 nm)	52.4 ($@Dc$=180 nm)	
Biomass burning (BB)	Laboratory			189	1.2-1.4($@Dc$=200 nm)		Pan et al. (2017)
	Texas, US	Sep (Fall)	140	210*		65($@Dc$=200 nm)	Schwarz et al. (2008)
Remote ocean (RO)	Finnish Arctic	Dec-Jan (winter)		194	2.0($@Dc$=150~200 nm)		Raatikainen et al. (2015)
Background Continent (BC)	Paris, FR	Jan (Winter)		200		76($@Dc$=200 nm)	Labrode et al. (2013)
	Texas, US	Sep (Fall)				48($@Dc$=200nm)	Schwarz et al. (2008)

*The density of *rBC* is 2 g cm^{-3}

826 **Table 2. Comparisons of E_{abs} in various field studies.**

Method	Location		Time	E_{abs} (λ nm)	Reference
TD+PAX+HR–AMS+AE33	Gucheng, (rural)	China	Dec 2019–Jan 2020	1.32 ± 0.15 (870)	(Sun et al., 2021)
TD+PAX+SP2+AMS	California, (urban)	USA	Jan–Feb 2013	1.21 ± 0.09 (870)	(Zhang et al., 2016)
SP2+CPMA+DMA	Beijing, (Urban)	China	May–June 2018	1.15 (550)	(Liu et al., 2020)
SP2+PAX+ACSM	Xi'an, (urban)	China	Dec 2012–Jan 2013	1.8 (870)	(Wang et al., 2014)
AE33+ACSM+OC/EC	Paris, (suburban)	France	Mar 2014–Mar 2017	1.53 ± 0.93 (880)	(Zhang et al., 2018a)
TD+BBCES+IS	Shouxian, (rural)	China	Jun–Jul 2016	2.3 ± 0.9 (532)	(Xu et al., 2018)
AFD	Yuncheng, (rural)	China	Jun–Jul 2014	2.25 ± 0.55 (678)	(Cui et al., 2016)
SP2	Gucheng, (rural)	China	Dec 2019	1.33 ± 0.57 (880)	This work

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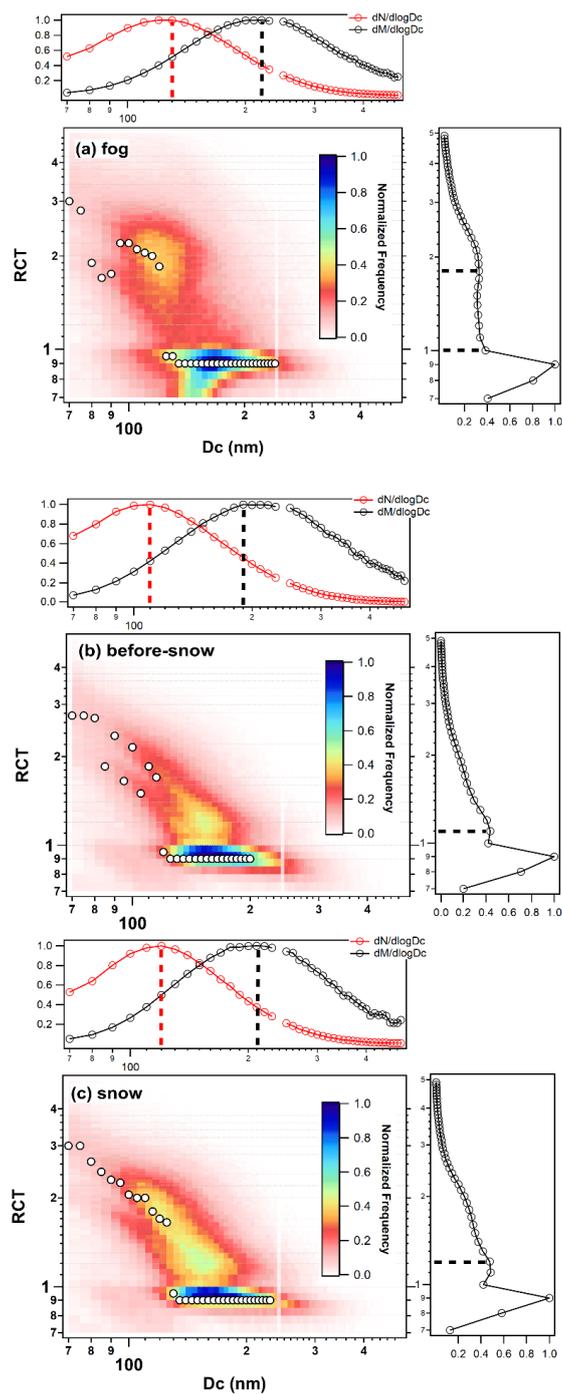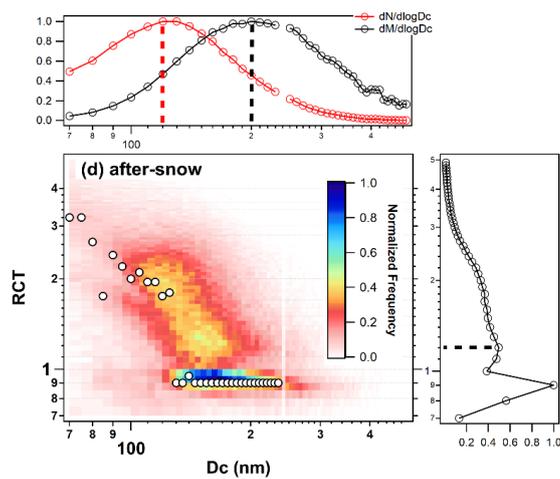
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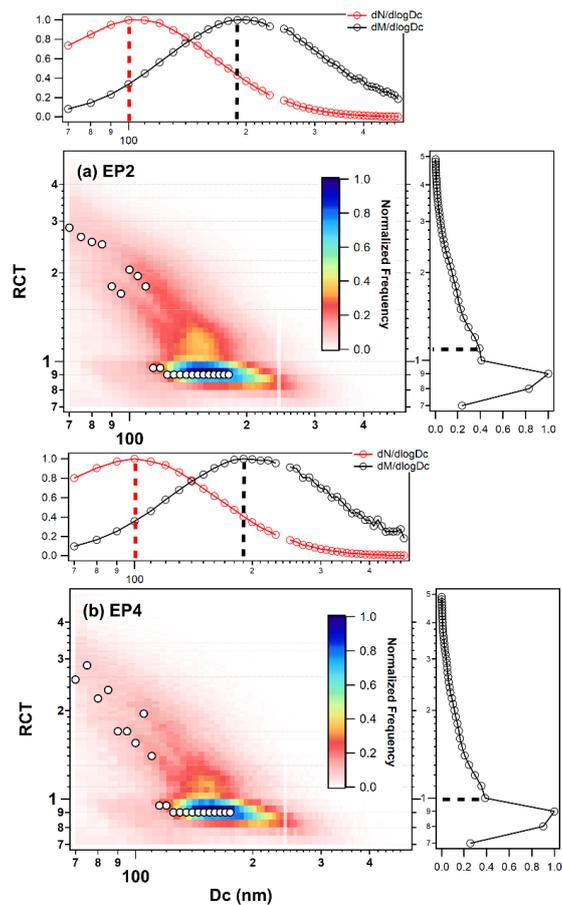
Figure 5: The RCT as a function of the *r*BC core diameter during (a) fog, (b) before–snow, (c) snow, and (d) after–snow events. The image plot is a 2D histogram, with the color denoting the normalized frequency in each bin. The right panel denotes the normalized (maximum=1) histogram of RCTs. The upper panel illustrates the number and mass size distribution of the *r*BC core.

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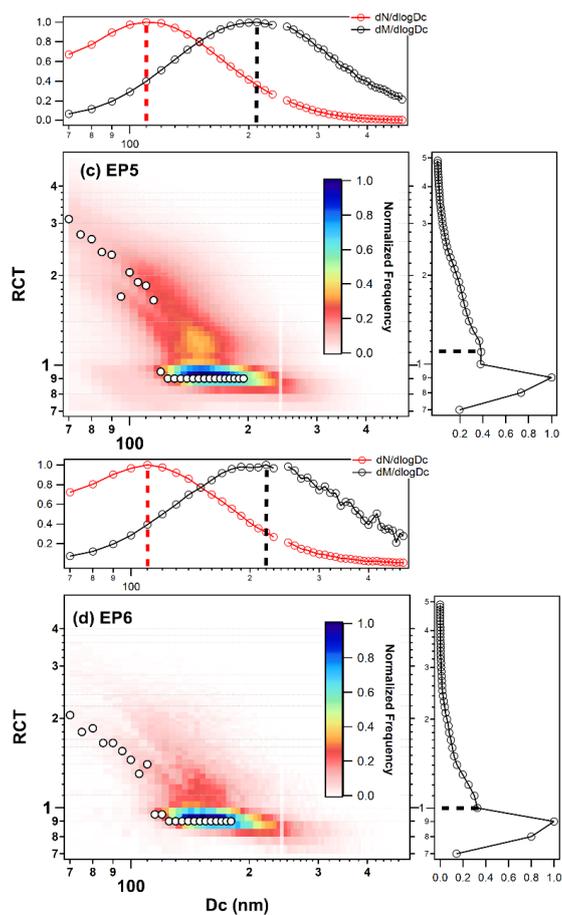
Figure 6: The RCT as a function of the *r*BC core diameter during (a) EP2, (b) EP4, (c) EP5, and (d) EP6 events. The image plot is a 2D histogram, with the color denoting the normalized frequency in each bin. The right panel denotes the normalized (maximum=1) histogram of RCTs. The upper panel illustrates the number and mass size distribution of the *r*BC core.

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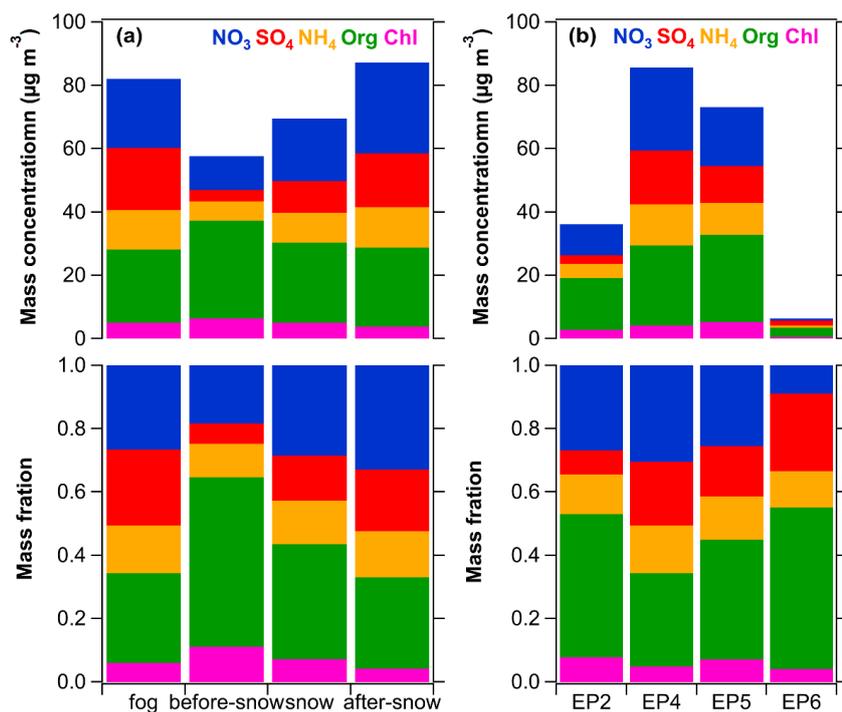


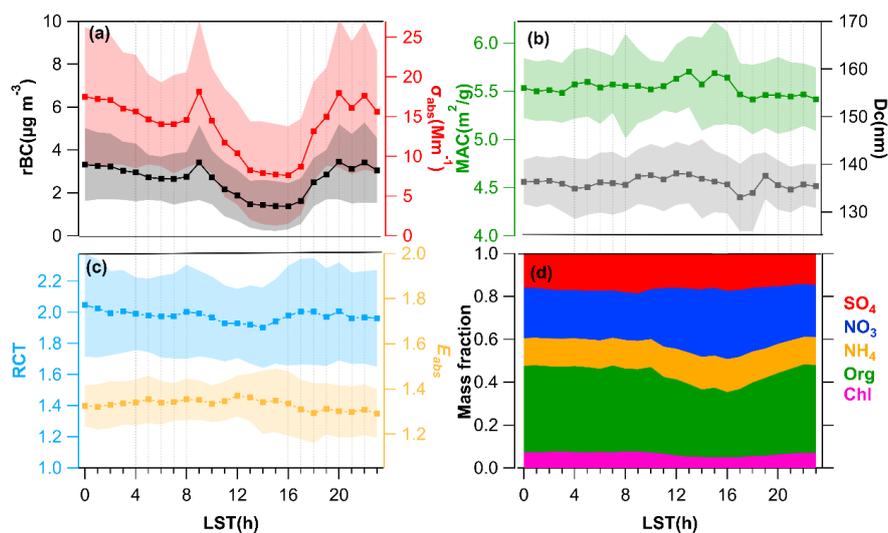
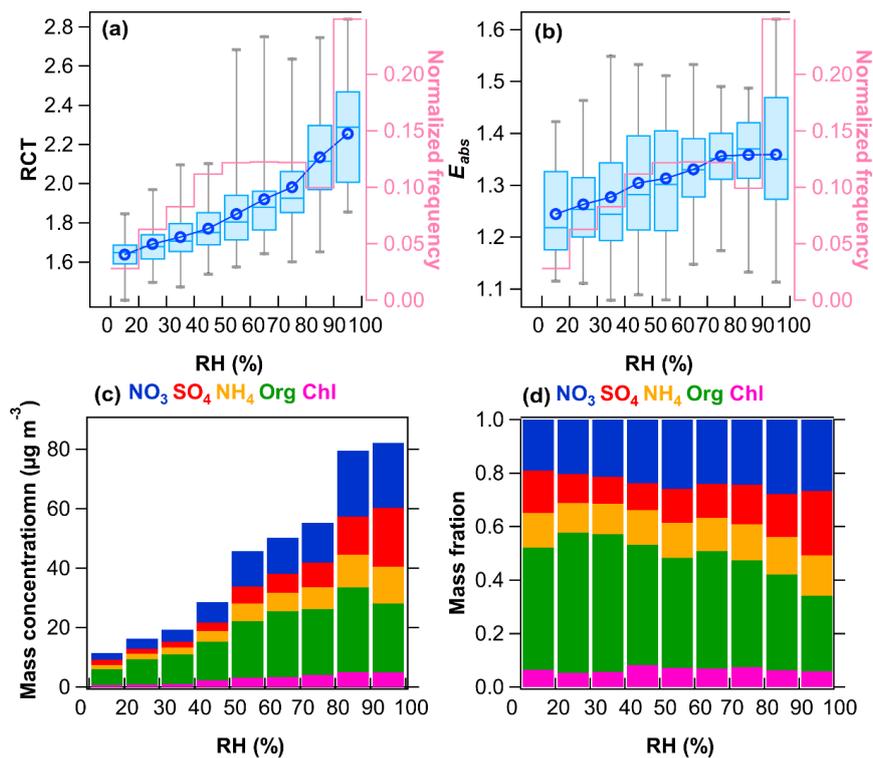
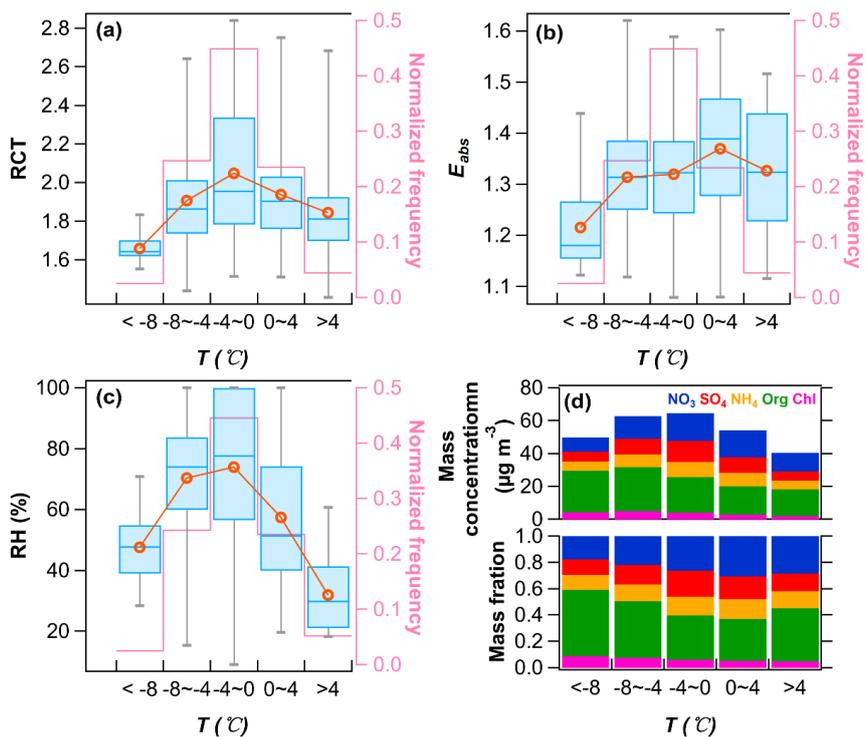
Figure 7: Changes in mass concentration and mass fractions of aerosol species during different periods.

845 **Figure 8: Diurnal variation in (a) rBC mass loading and absorption coefficients (σ_{abs}) of rBC–containing particles, (b) the mass absorption cross–section (MAC) of rBC–containing particles and the MMD, (c) relative coating thickness and absorption enhancement (E_{abs}) of rBC. The shaded aera denote the standard deviation. (d) Mass fraction of aerosol species.**

850   **Figure 9: (a–b) RCT, E_{abs} dependency on RH. Blue circles represent the average values. The line inside the box indicates the median. The upper and lower boundaries of the box represent the 75th and 25th percentiles; the whiskers above and below each box represent the max and min values. The pink lines represent the normalized frequency of data points in each bin. (c–d) Mass concentration and mass fractions of aerosol species dependency on RH.**

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Figure 10: (a–c) RCT, E_{abs}, RH dependency on temperature. Red circles represent the average values. The line inside the box indicates the median. The upper and lower boundaries of the box represent the 75th and the 25th percentiles; the whiskers above and below each box represent the max and min values. The pink lines represent the normalized frequency of data points in each bin. **(d)** Mass concentration and mass fractions of

860   aerosol species dependency on temperature.