

Dear Editor and Referee,

We thank the referee once again for the comprehensive comments. We have addressed the comments as follows. Our replies are in blue.

The authors have done a generally good job responding to the reviewer comments. I do still find that the paper could be easier to follow, but as the other reviewer did not seem to have the same difficulty I do not wish to belabour my suggestion about organizational structure. I would ask the authors to address the below additional concerns.

L320: I guess I don't see the need to state "While none of our other analyses indicate the presence of such a source...". I actually don't think it's consistent with the rest of the paper. The authors discuss explicitly that there are likely increased emissions in the winter when concentrations are high. This undoubtedly results in a shift in the relative contributions from different source types (e.g. vehicle versus home heating versus energy production, etc.). This is evident in the supplementary figure S1. The residential is substantially larger in winter. There is absolutely a shift in sources between summer and winter. And within a season there is absolutely a dependence on which regions contribute with BC concentration (Fig. 5), and the relative balance of sources differs between regions. These issues are even discussed in the previous section of the paper. I suggest this is removed.

We have adopted the referee's suggestion and this part has been removed in the revised version.

Line 320.

Fig. S2: While I find the revised Fig. S2 improved, it is still evident that in many cases the distributions are not log normal, in contrast to the statements in the manuscript. There are not three "log normal modes". The sm+lg,uncoat distribution itself has at least two modes in nearly every case. Is there a need to argue for log normality? Or am I missing something?

We have reworded this part and removed the "lognormal".

line 367.

Previous Reviewer Comment: OOA: Per the complementary Wang et al. paper, the OOA2/BC ratio is notably larger than the OOA1/BC ratio. Yet the OOA2\_BC factor is more correlated with "moderately" coated BC while the OOA1\_BC is more correlated with "thickly" coated BC. Can these be reconciled?

Clarified comment: The authors indicate they are unsure what I am asking for with this comment. Basically, I am saying that if OOA1/BC is larger than OOA2/BC, then why does "thickly" coated BC correlate well with OOA2\_BC while the "moderately" coated BC correlates with OOA1\_BC. Wouldn't one expect the more "thickly" coated BC to correlate better with the factor where the coating/BC is larger?

We have more explicitly made this statement in the revised version.

“Note that the absolute values of rBC mass from SP-AMS or SP2 had not necessarily corresponded with each other for the correlated factors, e.g. the OOA2\_BC is higher than OOA1\_BC but vice versa for the SP2 factors. This may result from different responses and sensitivities for the measurement techniques of both instruments at different levels of BC mixing state.”

Line 418-422.

L492: The comma after “material” should be a period.  
corrected.

L494: How do high concentrations of precursors “exacerbate” coagulation? What matters is not the precursors, but the particles. Are the authors trying to say that there may be more particles when the precursor concentrations are high? If this is the case they should just say this. Also, implicit in this is the idea that this will lead to nucleation and formation of new particles. Without nucleation, the precursors will form new secondary material on particles, but not influence the particle number concentration, which is what matters for coagulation. They might also consider including data (if they have it) or a reference indicating that higher mass concentrations are also correlated with higher number concentrations in the region. It is not a given that they will (although I suspect this is the case).

We thank for the suggestions and the discussions have been added in the revised version.

“High concentrations of secondary precursor during higher pollution episode in the gas phase may lead to nucleation and new particle formation, or size growth on pre-existing particles. A further analysis shows high number concentration of particles also corresponded with higher mass concentrations, indicating that the new particle formation and primary emission coincided with particle size growth. These processes will in turn promote the high coatings on BC.”

Line 497-502.

L504: I have some difficulty understanding the argument that the different BC types have differing contributions due to their varying absorption efficiency alone, which is what is implied as stated. I think the authors should also indicate that variations in absolute contributions of these types will also matter and, likely, dominate the behavior here.

The discussion has been revised:

“implying that different BC types have varying absorption efficiency but the contribution on absorption is determined by both mass loading and MAC”.

Line 512-513.

L507: It should be noted that there is no strong experimental evidence (or at least none that I'm aware of) that the absorptivity of atmospheric BC falls off at large sizes. This is something that happens in Mie theory, to be sure, but it's not clear that this actually occurs, or if it does that it occurs to nearly the same extent as Mie theory predicts. (This has to do with atmospheric BC not actually being spherical.)

We agree with referee and the related discussion has been added.

"BC<sub>lg,uncoat</sub> had a lower MAC because of its larger core size which is consistent with Mie calculation."

Line 515.

L505: It should be stated explicitly here that these are calculations, and not measurements, of the MAC. Also, given the shift to 870 nm in Fig. 13 (the wavelength of the measurements), it is not clear why the authors have retained using 550 nm here. They should also state explicitly that they assume non-absorbing coatings. I realize these points are made in the "methods" section but they should be repeated here.

The MAC<sub>550</sub> is used here in order to be compared with many other studies. This information is now added in both method section and the discussions here:

"The contribution of absorption coefficient is calculated based on single particle information shown in Fig. S4 (note that the coating is assumed to be non-absorbing here)."

Line 509-510.

L511: The authors should state these not as ~, but with the mean and a meaningful metric such as the standard deviation.

Corrected.

Line 519-522.

L514: An estimated uncertainty for the 1.4 and 1.6 should be provided. As noted previously, the calculated MAC values may be low, since it is known that Mie theory often underestimates MAC values relative to measurements. Consequently, the Eabs values here, determined as a ratio between a measurement and a calculation, have a decent chance of being biased high.

The uncertainty is now calculated based on the calculated uncertainty of uncoated BC, and this information is added in the revised version.

Line 523.

L524: It is not "particularly" when the coating is absorbing. It is only when the coating is absorbing.

Corrected.

Table A1 is a welcome addition, but missing many of the abbreviations used throughout.

This is double checked and added in the new table.

Page 19.

# Contrasting physical properties of black carbon in urban Beijing between winter and summer

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## Abstract

25 Black carbon (BC) is known to have major impacts on both human health and climate. The populated megacity represents the most complex anthropogenic BC emissions where the sources and related impacts are very uncertain. This study provides source attribution and characterization of BC in the Beijing urban environment during the joint UK-China APHH (Air Pollution and Human Health) project, in both winter (Nov. - Dec. 2016) and summer (May - Jun. 2017). The size-resolved mixing state of BC-containing particles was characterized by a single particle soot  
30 photometer (SP2) and their mass spectra was measured by a soot particle mass spectrometer (SP-AMS). The refractory BC (rBC) mass loading was around a factor of 2 higher in winter relative to summer and more variable coatings were present, likely as a result of additional surface emissions from the residential sector and favourable condensation in cold season. The characteristics of the BC were relatively independent of air mass direction in summer; whereas in winter airmasses from the Northern Plateau were considerably cleaner and contained less-coated  
35 and smaller BC, whereas the BC from the Southern Plateau had the largest core size and coatings.

We compare two online source apportionment methods using simultaneous measurements made by the SP2, which measures physical properties of BC, and the chemical approach using the positive matrix factorization (PMF) of mass spectra from the SP-AMS for the first time. A method is proposed to isolate the BC from the transportation sector using a mode of small BC particles (core diameter  $D_c < 0.18 \mu\text{m}$  and coating thickness  $ct < 50\text{nm}$ ). This mode of BC  
40 highly correlated with  $\text{NO}_x$  concentration in both seasons ( $\sim 14 \text{ ng m}^{-3} \text{ BC ppb}^{-1} \text{ NO}_x$ ) and corresponded with the morning traffic rush hour, contributing about 30% and 40% of the total rBC mass (35% and 55% in number) in winter and summer respectively. The BC from coal burning or biomass burning was characterized by moderate coatings ( $ct = 50\text{--}200\text{nm}$ ) contributing  $\sim 20\text{--}25\%$  of rBC mass. Large uncoated BC particles ( $D_c > 0.18 \mu\text{m}$  and  $ct < 50\text{nm}$ ) was more likely to be contributed by coal combustion, as these particles were not present in urban London. This mode  
45 was present in Beijing in both winter ( $\sim 30\text{--}40\%$  rBC mass) and summer ( $\sim 40\%$  rBC mass) but may be dominated by residential and industrial sector respectively. The contribution of BC thickly-coated with secondary species ( $ct > 200\text{nm}$ ) to the total rBC mass increased with pollution level in winter, but was minor in summer. These large BC importantly enhanced the absorption efficiency at high pollution levels - in winter when  $\text{PM}_{10} > 100 \mu\text{g m}^{-3}$  or  $\text{BC} > 2 \mu\text{g m}^{-3}$ , the absorption efficiency of BC increased by 25-70%. Reduction of emissions of these large BC particles and  
50 the precursors of the associated secondary coating will be an effective way of mitigating the heating effect of BC in urban environments.

# 1 Introduction

55 Black carbon aerosol (BC) has a significant impact on both climate (Bond et al., 2013) and human health (Baumgartner et al., 2014). Its regional impact in the atmosphere may be very large, especially close to polluted hotspots such as in South and East Asia, where anthropogenic emissions are high and population exposure is severe (Ramanathan and Carmichael, 2008). It has been estimated that BC over China could contribute up to 14% of the global radiative forcing budget (Li et al., 2016). Reducing BC has been postulated as a win-win policy intervention  
60 because of the shorter atmospheric lifetime of BC compared to the greenhouse gases, delivering immediate mitigation, while at the same time improving air quality (Kopp and Mauzerall, 2010).

Beijing, as one of the most populated megacities in the world has experienced severe air pollution (Yang et al., 2005; Xu et al., 1994). The complexity of emissions from multiple sectors that are often co-located (Li et al., 2017) make it extremely challenging to attribute source contributions to the BC load, hindering policy making on emission  
65 regulations. The source apportionment of BC in urban environments has been studied using both online and offline measurements and using site receptor models (Cao et al., 2005; Viana et al., 2008 and refs therein). Most of the techniques separate the fossil fuel BC, such as that from traffic sources from the solid fuel burning fraction (such as that from wood burning (Srandadewi et al., 2008; Healy et al., 2012) or open biomass burning (Schwarz et al., 2008). These techniques include using biomass burning tracers in aerosol (Puxbaum et al., 2007), or using individual organic  
70 tracer compounds to attribute the sources and provide time series representing the different sources. These are then used to segregate the different BC emission contributions by multi-linear regression (Liu et al., 2011; Laborde et al., 2013). An approach using Aethalometer measurements has been widely used based on the spectral dependence of absorption (Srandadewi et al., 2008). This technique needs to assume a prescribed absorption spectrum from traffic or wood burning sources which may be subject to variation under different burning conditions (Zotter et al., 2017).  
75 Isotope analysis of elemental carbon, in conjunction with thermal separation, allows identification of modern carbon (e.g. from biomass) from fossil fuel (from diesel or coal) based on the  $^{14}\text{C}$  abundance (Bernardoni et al., 2013; Zhang et al., 2012). This method has been considered to be relatively unambiguous in isolating wood burning sources from traffic source, and has been used to validate the other methods in attributing elemental carbon (Liu et al., 2013; Zotter et al., 2017).

80 These techniques, mostly use distinct features in the chemistry or physical properties to isolate one BC source from the other, and to do so requires that there are unique characteristics that are separable. The BC sources in Beijing are combinations of residential, industrial and transport sectors (Li et al., 2017), and the fuel use could be rather more complex than two distinct sources which most techniques are based on. For example, both coal burning and diesel fuel could emit fossil fuel BC, which may not be isolated through isotope analysis, and also the absorption spectrum  
85 of BC from different sources may vary considerably and to assume a single pattern based on Aethalometer measurements may not be suitable to attribute multiple sources. The fast secondary processing of aerosols in Beijing (Sun et al., 2016b) may make the source attribution of primary BC even more challenging as the secondary coating formed on BC may alter its original source-dependent features. Given these difficulties it is unlikely that any single

methodology will give unambiguous results, but a combination of different methods may improve the understanding on the source attribution because source-specific physio-chemical properties of BC may be reflected in different ways by different methods.

It is also necessary to gain knowledge on the microphysical structure and mixing state of the soot, namely its size and what other materials are present on the individual particles, as these dictate its impact on the wider atmosphere. Other material present on a BC particle (a ‘coating’) may alter its optical properties (Liu et al., 2017), affecting the direct radiative effect on the local atmosphere, and it may also make it more susceptible to in-cloud scavenging, meaning that it can perturb the cloud properties or experience a shortened atmospheric lifetime through wet deposition (Hodnebrog et al., 2014). The source profile of size-resolved mixing state of BC is desired for the evaluation of BC properties in process models (Riemer et al., 2009) especially for environments with combined sources (Fierce et al., 2016).

This study quantifies the source attribution of BC-containing particles in urban Beijing and delivers source-specific information on their properties by combining two techniques, both of which directly characterize BC-containing particles but are based on physical and chemical techniques respectively. The physical technique uses a single particle soot photometer (DMT, SP2), which was previously used for source apportionment of BC in urban London (Liu et al., 2014b). This approach is to examine mixing state of BC particles as a function of their core size and this has been used to attribute the BC from traffic diesel and wood burning source. The chemical approach uses the soot particle aerosol mass spectrometer (Aerodyne, SP-AMS) which has been previously used to identify the chemical compositions of coatings associated with BC (Onasch et al., 2012a), which may be used to determine primary sources or secondary processing of BC. The combination of both techniques in this study will give the detailed physio-chemical properties of BC influenced by mixed sources. In particular, by combining the approaches the contribution of different emission sources to the optical properties of BC can be quantified and so an attribution of different sources to the BC heating in the atmospheric column can be made.

## 2 The site, meteorology and air mass classification

The experiments were conducted at the tower site of Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (39°58'28"N, 116°22'16"E) in Beijing during both winter (Nov.-Dec. 2016) and summer (May-Jun. 2017) periods, as part of the Air Pollution and Human Health-Beijing campaign. This site represents the typical urban Beijing environment with pollution influences from surrounding traffic, commercial activities, residential activities such as cooking and home heating and regional transport (Sun et al., 2016a).

Fig. 1a shows the terrain of the North China Plain (NCP) region to the north of Beijing and Fig. 1b shows the surface emission inventory of BC for the year 2010 (Li et al., 2017). The high anthropogenic BC emission can be generally divided by the border along Taihang and Yanshan Mountain Ridges, beyond which the region from northwest Beijing has relatively lower emissions. Considerably higher emissions are also present across the southern Plateau region. In



order to investigate the regional influence of pollutants in Beijing, the regions over the NCP and the Plateau are classified according to the terrain and BC surface emission, shown in Fig. 1c. The regions are firstly classified as the plateau and plain according to the terrain height below and above 800m, then for the region <800m, 116.5°E (the longitude of central Beijing) is used to separate the Eastern and Western NCP (E and W are used as the abbreviations during the following discussion); the region >800m is separated as Northern and Southern Plateau (N and S are used as abbreviations for the following discussion) using the border along 41.5°N; the Ocean is defined as the terrain height below zero. The Northern Plateau has significantly lower emission, meaning north-westerly air mass will bring clean air into Beijing and are likely to reduce pollution levels in the city, whereas westerlies may bring pollutants from the Western Plateau and south-westerlies could transport the high emissions from central China to the NCP. The local area is defined in this work as the area within the square  $\pm 0.25^\circ$  away from the measurement site. BC emission inventories from different sectors are shown in Fig. S1. In winter the residential sector, which is mainly composed of residential coal burning, contributes the vast majority of BC emissions; whereas the emissions from the industrial (which also contains significant coal consumption) and transportation sectors are maintained throughout the year. This means the differences in BC emissions between winter and summer will mainly result from changes in the residential sector.

The HYSPLIT backtrajectory model (Draxler and Hess, 1998) was run using the  $1^\circ \times 1^\circ$  horizontal and vertical wind fields provided by the GDAS1 reanalysis meteorology. Given the emissions are intensive around the immediate Beijing area, air mass back trajectories were only followed for the previous 24-hours to examine the influence from the most recent air masses. The back trajectories are then mapped onto the classified regions (Fig. 1c) to investigate variations in the potential regional source influence. The back trajectories have a 1h time resolution and each point along a single 24 hour trajectory is assigned to one of the four regional classifications. All the points along a single trajectory are then used to determine the fraction of time during the previous day that the air mass spent above each of the classified regions as shown in the bottom panel of Fig. 3a and Fig. 3b. This method has been applied previously in the western Africa region to identify the potential source contributions (Liu et al., 2018). Note that the HYSPLIT analysis is not able to reproduce the dispersion of the air mass, but such effects are likely to be minimal since the trajectories are only investigated over the previous 24 hours.

Each back trajectory is assigned to be predominately from one of the regions based on a ranked classification scheme that takes account of the likely greater influence on the pollution at the receptor from closer regions with large emissions. The methodology considers each region in turn, beginning with the western NCP air mass because it represents the mostly polluted region and a relatively lower air mass fraction of western NCP will make an important contribution to the pollutants measured at the receptor. If the back trajectory spent more than 10% of the previous 24 hours over the western NCP it was classified as being from that sector. The 10% threshold was somewhat arbitrarily set based on an iteration over a range of values – too low a threshold biased air masses towards the very near field, whereas too high a value failed to classify a large fraction of air masses. The sensitivity of the threshold was tested by varying it between 9 and 11% ( $\pm 10\%$ ) and the classification was shown to be insensitive to change. The following regions are then considered in a similar way in turn based on the following order: eastern NCP, southern Plateau and

northern Plateau with each above 10% air mass fraction. Lastly if the air mass spent more than 20% in the local area it is defined as having significant local influence.

The meteorological parameters such as wind, relative humidity (RH) and temperature were measured at ground level ( $z=10\text{m}$ ) and also on the tower at  $z=120\text{m}$ . The temperature and RH at  $z=10\text{m}$  is used, but the wind at  $120\text{m}$  is used to avoid the surface friction effect. In addition, the planetary boundary layer height (PBLH) spanning the experimental period was determined using Lidar and Ceilometer measurements (Kotthaus and Grimmond, 2018).

### 3 Instrumentation and data analysis

#### 3.1 The physical properties of BC

The physical properties of individual refractory BC particles were characterized using a single particle soot photometer (SP2) manufactured by DMT Inc (Boulder, CO, USA). The instrument operation and data interpretation procedures are described elsewhere (Liu et al., 2010; McMeeking et al., 2010). The SP2 incandescence signal was calibrated for rBC mass using Aquadag® black carbon particle standards (Aqueous Deflocculated Acheson Graphite, manufactured by Acheson Inc., USA) and corrected for ambient rBC with a factor of 0.75 (Laborde et al., 2012). The mass-equivalent diameter of the rBC core ( $D_c$ ) is obtained from the measured rBC mass assuming a density of  $1.8 \text{ g cm}^{-3}$  (Bond and Bergstrom, 2006). For a given time window, the mass median diameter (MMD) of rBC core is calculated from the  $D_c$  distribution below and above which the rBC mass was equal.

The scattering signal of each BC particle measured by the SP2 is determined using a leading edge only (LEO) technique to reconstruct the distorted scattering signal when the particle passes through the SP2 laser beam (Gao et al., 2007). This was used to determine the scattering enhancement ( $E_{sca}$ ) for each single particle which is defined as the ratio between the measured scattering intensity resulting from the entire BC containing particle, including any coating, and the calculated scattering intensity resulting from the uncoated BC core of that particle (Liu et al., 2014a; Taylor et al., 2015), expressed as:

$$E_{sca} = \frac{S_{measured, coated BC}}{S_{calculated, uncoated BC}} \quad (1),$$

where the numerator is the scattered light intensity of the coated BC particle measured by the SP2 and the denominator is the calculated scattering intensity of the uncoated BC core based on the measured mass and using a refractive index of BC  $2.26+1.26i$  at the SP2 laser wavelength,  $\lambda=1064\text{nm}$  (Moteki et al., 2010). For a given  $D_c$ , a higher  $E_{sca}$  means a thicker coating and  $E_{sca}=1$  means there is no coating. The coated BC particle size ( $D_p$ ) is then determined by matching the modelled scattering with the measured scattering by applying a Mie core-shell lookup table (Taylor et al., 2015). For the current SP2 configuration (Liu et al., 2017), the detection efficiency for the coating, taking into account only particles with sufficient signal to noise in the two-element APD detector signal to perform

190 reliable LEO fitting, is >80% for  $D_c=0.12-0.45\mu\text{m}$ , >60% for  $D_c >0.45\mu\text{m}$  (due to partly saturated signal) and >50% for  $D_c=0.08-0.12\mu\text{m}$ .

The bulk relative coating thickness ( $D_p/D_c$ ) in a given time window is calculated as the total volume of coated BC particles divided by the total volume of the rBC cores (Liu et al., 2014a), expressed as:

$$\frac{D_p}{D_c} = \sqrt[3]{\frac{\sum_i D_{p,i}^3}{\sum_i D_{c,i}^3}} \quad (2),$$

195 where  $D_{p,i}$  and  $D_{c,i}$  are the coated and rBC diameters for each single particle respectively (the abbreviations using subscript  $i$  refer to the single particle, variables without a subscript refer to the bulk information). Note that 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.

The volume-weighted coated BC size ( $D_{p,v}$ ) is then calculated as the product of the bulk relative coating thickness  
200 and the MMD of the BC cores, to indicate the mean coated BC size (Equation 3). The bulk mixing ratio of coating mass over rBC mass ( $M_{R,bulk}$ ) can be also derived from  $D_p/D_c$  assuming densities for the bulk coating and rBC core (Equation 4):

$$D_{p,v} = \frac{D_p}{D_c} \times MMD \quad (3),$$

$$M_{R,bulk} = \left( \left( \frac{D_p}{D_c} \right)^3 - 1 \right) \times \frac{\rho_{coating}}{\rho_{rBC}} \quad (4),$$

205 The mass absorption cross section at  $\lambda=550\text{nm}$  ( $MAC_{550}$ ) is calculated for each single particle by assuming the refractive index of rBC core  $1.95+0.79i$  (Bond and Bergstrom, 2006) and coating refractive index  $1.50+0i$  (Liu et al., 2015), using the Mie core-shell approach (Bohren and Huffman, 2008). Note that the absorption enhancement due to coating is considered to only occur when the coating mass over rBC mass is larger than 3 according to the recent study of (Liu et al., 2017) and the coating here is assumed to be non-absorbing. Fig. S3 gives the calculated  $MAC_{550}$   
210 mapped on the  $E_{sca}-D_c$  plot. The  $MAC_{550}$  in bulk for a given time window is calculated as the integrated absorption coefficient ( $MAC \times m_{rBC}$ ) for all particles divided by the integrated particle masses, expressed by Equation (5),

$$MAC = \frac{\sum_i MAC_i \times m_{rBC,i}}{\sum_i m_{rBC,i}} \quad (5),$$

where  $MAC_i$  and  $m_{rBC,i}$  are the MAC and rBC mass for each single particle respectively. This calculation is performed for each type of BC.

215 A PAX (Droplet Measurement Technologies, Boulder, CO, USA) (Wang et al., 2014; Selimovic et al., 2018) was deployed to directly measure the in-situ aerosol light absorption every minute using photoacoustic technology. The

light-absorbing particles are heated by a laser in the acoustic chamber, and this heating produces pressure waves which are detected by a microphone. The calibration of scattering and absorption for PAX was performed using the polystyrene latex spheres and fullerene soot respectively. The absorption coefficient at  $\lambda=870\text{nm}$  ( $\sigma_{\text{abs},870}$ ) is measured by the PAX. The mass absorption cross section (MAC) is determined as the absorption coefficient per unit rBC mass. Note that in this study  $\sigma_{\text{abs},870}$  values for rBC mass loadings  $<0.5 \mu\text{g m}^{-3}$  were not used for MAC calculations due to the large uncertainty of absorption measurement at low concentration.

## 3.2 BC chemical composition

The chemical composition of black carbon containing particles, including the refractory BC and coating compositions, are measured by a soot particle mass spectrometer (SP-AMS) (Onasch et al., 2012a; Wang et al., 2017). The results from SP-AMS measurement during APHH are detailed in (Wang et al., 2019). The SP-AMS was run in laser-only mode and so only detected compositions for BC-containing particles. In this mode the non-refractory components were not detected if they are not contained within a BC particle. The ionization efficiency (IE) and relative ionization efficiency (RIE) of sulphate and nitrate were calibrated by using ammonium nitrate and ammonium sulphate (Jayne et al., 2000). RIE of rBC was calibrated by using Regal Black (RB, REGAL 400R pigment black, Cabot Corp.) (Onasch et al., 2012b). Positive matrix factorization (PMF) (Paatero and Tapper, 1994) was applied to the mass spectra of the organic and rBC components to attribute the source contribution of BC-containing particle mass, as detailed in (Wang et al., 2019). Four types of BC-containing particle associated with different organic coatings were identified: fossil fuel combustion OA (FOA), biomass burning OA (BBOA), low-volatile organics (OOA1) and semi-volatile organics (OOA2) were identified. In addition, a PAH factor was also derived from the SP-AMS measurement, which is associated with coal combustion (Sun et al., 2016a).

## 4 Results

### 4.1 Overview of BC physical properties

The following section describes the measured BC properties in both the winter and the summer seasons. Each property is discussed in turn and the similarities and differences between the seasons highlighted to clearly identify property changes that can be linked to changes in sources or processes in summer and winter.

Fig. 3 shows the temporal variation of the physical properties of BC, associated gaseous pollutants and meteorological parameters and their association with the air mass classifications. As the bottom panels show, the site was mostly influenced by northerly and westerly air masses in winter, and very few air masses came from the eastern NCP. The first half of the winter campaign up to 20<sup>th</sup> Nov. was periodically influenced by air masses from western NCP, and during the second half the synoptic meteorology shifted appreciably and was dominated by northerly (from the

northern Plateau) or westerly (from the southern Plateau) air masses, with the period between 02/12 and 04/12 dominated by air from the southern Plateau. The temperature dropped from  $\sim 10^{\circ}\text{C}$  to below  $5^{\circ}\text{C}$  when the air mass type shifted to deliver air from the plateau. In summer, Beijing received air from the western NCP, the eastern NCP and the northern plateau with southerly air masses more dominant than those from the north.

The classified air mass types are generally consistent with the local wind directions measured at 120m for both seasons (Fig. 4). In winter, the northern Plateau air masses were characterised by high speed, dry NW winds, in summer the flow was not as strong. Air masses from the southern plateau were associated with both northerly and southerly winds but with much lower wind speed and systematically higher RH than the northern plateau air masses. The south-westerly air masses also had the highest RH, which is consistent with previous observations that show air masses from lower latitudes contained more moisture in wintertime (Tao et al., 2012). In summer, air masses from the western NCP showed lower RH. The site showed lower wind speed and wider variation of RH when influenced by local air masses.

BC properties associated with different air mass types in both the winter and summer seasons are compared in Fig. 5. rBC mass loadings were higher in winter than in summer by around a factor of 2 for both local and regionally transported air masses, mostly likely due to a combination of higher surface emissions from both the local Beijing region and the surrounding area in the cold season, and also the increased frequency of lower boundary layer heights in winter (section 4.4). However, air masses from the northern Plateau during periods of strong and dry wind had notable effect on the rBC mass in winter, greatly reducing the rBC mass in Beijing. This air mass type contributed to over 90% of the cleaner days ( $\text{rBC mass concentration} < 1\mu\text{g m}^{-3}$ ) in winter. This is consistent with the emission inventory that the northwest Beijing is dominated by lower surface emissions over Mongolia. The dilution of Beijing pollution by high wind speeds during NW air flow has been widely observed (Sun et al., 2015; Zhang et al., 2013; Zhang et al., 2015). The BC particles during these periods had systematically lower core sizes (Fig. 5b1) and lower coatings (Fig. 5c1) and therefore smaller total particle sizes. This may result from more efficient removal processes for the more coated and larger BC particles in winter.

No significant differences ( $p < 0.01$ ) in the physical properties of BC particles were observed between the different air mass types in summer, e.g. there is a consistent peak of  $D_p/D_c \sim 1.4$  for all air mass types, which may suggest an almost homogenous mixture or consistent BC sources across a large region around Beijing in China. In winter, the range of  $D_p/D_c$  values extended from similar values to those in the summer up to 2.5. The MMD of BC cores was most often observed to be  $\sim 180\text{nm}$  for both seasons, but it is noted that the air mass from the southern Plateau (as the green lines show) had systematically larger MMD, and BC particles in air masses from this region also had the highest coatings and largest coated BC size compared to other air masses. The large BC core size and coatings observed during westerly air masses may arise from ageing of sources in central and western China during transport, though it should be noted that the trajectories presented are only for the previous 24 hours. However, the BC core size was significantly higher ( $p < 0.01$ ) in winter than in summer during periods when Beijing received air from the

southern plateau. This may result from a large contribution of residential heating activities in southern Plateau in winter which were not present in summer.

As Fig. 6 shows, the diurnal variation of rBC mass loading in winter showed a strong anti-correlation ( $R^2=0.73$ ) with the mixing layer height (MLH). In winter, surface cooling during the night leads to a shallow nocturnal boundary when coupled with increased emissions from heating activities greatly enhances surface pollution. During the day, a deeper boundary layer is re-established, resulting a much larger volume for emissions to mix into. The diurnal variation in rBC is a combination of both diurnal variations in emissions and marked changes in the boundary layer structure. In summer, the night-time peak of rBC mass loading was absent but peaked during the morning rush hour which may reflect the important contribution from traffic. Fig. 6 shows an evident increase of BC coatings around 10 am in winter and a slight increase around 9 am in summer, and the coatings in winter were notably higher at night than in the day. In general, larger variations in the physical properties of BC were observed in winter compared to summer.

## 4.2 The size distribution and mixing state of BC

Fig. 7a gives examples of BC core size distributions for typical periods in both seasons. The BC core size distribution could be modelled as a single lognormal distribution fitted for  $D_c=100-400\text{nm}$ ,

$$\frac{dM}{d\log D_c} = A e^{\left(\frac{\log^2(D_c/D_0)}{2\log^2\sigma_g}\right)} \quad (6),$$

where  $A$  is the peak concentration,  $D_c$  is the BC core size measured by the SP2,  $D_0$  is the core MMD,  $\sigma_g$  is the geometric standard deviation (GSD) for the lognormal distribution. The red lines in Fig. 7a show the lognormal fitting to the observations. It is noted that some fraction of the distribution at the larger end is not fitted within the single lognormal distribution, which may require an additional moment of lognormal distribution to be accounted for, as has been shown during previous urban studies (Huang et al., 2011). However, fitting a second lognormal mode will be subject to large uncertainty due to the saturation of the SP2 detector which has an upper cut off at  $D_c=550\text{nm}$ , leading to insufficient data points to constrain such a fit. The additional rBC mass distribution above 550nm may exist but would require instrument reconfiguration to be fully detected. The two-moment lognormal fitting is thus not performed in this study. The extrapolated rBC mass accounted for 5-8% of the total rBC mass loading which is included for the rBC mass loading reported in this study.

Fig. 7b shows the fitting parameters of BC core size distribution at different levels of rBC mass concentration. The core size generally increased at higher rBC mass concentration but demonstrated considerable variability ranging between 150-220nm. BC particles were observed to have systematically larger core sizes in winter than in summer at the same rBC mass concentration. In winter, the significant increase of core MMD when the rBC mass concentration  $>5\mu\text{g m}^{-3}$  may indicate that coagulation is taking place at high concentration. The increased BC coating thickness observed under these conditions is also consistent with BC coagulating with non-BC particles (Fig. 8). The

width of the core size distribution  $\sigma_g$  in winter showed a decreasing trend at higher rBC mass concentration, again this is consistent with the view that coagulation may occur at high rBC mass concentration reducing the width of the size distribution (Pratsinis, 1988). However, these effects may also reflect a shift in the range of sources present during periods of higher pollution levels that produces proportionally more rBC particles with large core sizes. ~~While none of our other analyses indicate the presence of such a source, we cannot rule out this latter possibility and so are unable to unequivocally identify coagulation as the reason for these changes.~~ In summer  $\sigma_g$  showed an increasing trend with rBC mass concentration, which may result from more diverse source contributions at higher rBC mass concentration. The higher  $\sigma_g$  in winter than in summer at the same rBC mass concentration suggests a greater complexity of sources in winter.

The core sizes observed in Beijing are significantly larger ( $p < 0.01$ ) than those observed in London even when the BC source profile was dominated by wood burning (170nm), which may result from other sources of BC. Fig. 8 shows the coating content of BC was similar between seasons with  $M_{R,bulk}$  1-2 when the rBC mass concentration  $< 2 \mu\text{g m}^{-3}$ . During summer the coating thickness only periodically increased ( $M_{R,bulk} > 2$ ); but in winter the coating increased particularly when the rBC mass concentration  $> 3 \mu\text{g m}^{-3}$ , showing a highly variable  $M_{R,bulk}$  ranging between 1.5-10 (bulk  $D_p/D_c \sim 1.4$ -2.6). Accordingly, the coated BC size  $D_{p,v}$  peaked at 220-310nm when rBC mass concentration  $< 2 \mu\text{g m}^{-3}$  in both seasons, however it reached values as high as 550nm under highly polluted conditions. The large variation of BC mixing state during winter-time when the rBC mass concentration  $> 3 \mu\text{g m}^{-3}$ , may reflect the additional primary sources such as the large contribution from residential sources during the cold season. However, secondary processing of the complex source mixtures under highly polluted conditions may also play an important role in increasing the coatings. Possible reasons for these differences are investigated in more detail in sections 4.4 and 4.6 where the rBC is segregated into characteristic types and compared with PMF results from the SP-AMS and PM1 respectively.

### 4.3 BC segregation by size-resolved mixing state

Fig. 9 shows the BC core size-resolved mixing state during typical periods in both seasons, and the results obtained in London are also shown as a reference (Liu et al., 2014b). It is noted that  $E_{sca}$  appears to be  $< 1$  at larger  $D_c$ . This arises for two reasons. Firstly, the assumption of sphericity used in the Mie calculations to derive  $E_{sca}$  introduces significant bias for larger BC cores with little or no coating. The resulting scattering for uncoated BC will be lower than that derived by Mie-scattering due to geometrical influences as has been shown when comparing with T-matrix calculations (He et al., 2015; Wu et al., 2018) and this increases with rBC core size. Secondly, the BC at larger  $D_c$  largely results from coal combustion (section 4.4), and this may have a refractive index (RI) that is different from rBC from traffic sources (2.26, 1.26). Both factors will lead to lower estimated scattering cross section for uncoated rBC, and hence  $E_{sca} < 1$ . Since no measurements of BC morphology or source-dependent RI of rBC are available in this study, we are only able to state that these BC with larger  $D_c$  is likely to be very thinly-coated and assume the particles with  $E_{sca} < 1$  had a  $D_p/D_c = 1$ . This assumption is not likely to lead to major biases since the BC at large  $D_c$

values has a lower MAC (Fig. S5) and adding material to these particles will only lead to the presence of a thin coating that will not significantly influence the resulting overall MAC (less than 8%).

The BC particles were segregated according to the discontinuous distribution in  $E_{sca}-D_e$  during different periods. The criteria used is shown by the thick dashed lines in Fig. 9a. Four modes of BC could be segregated: small BC ( $BC_{sm}$ ) with BC cores smaller than 180nm and coating thicknesses <50nm (assuming a core-shell structure); moderately coated BC ( $BC_{mod}$ ) - moderate coating with coating thicknesses of 50-200nm; thickly coated BC ( $BC_{thick}$ ) with coating thicknesses >200nm, and large uncoated BC ( $BC_{lg,uncoat}$ ) with BC core sizes >180nm and thicknesses <50nm. The contribution of these four modes of BC particles to the total rBC number varied during different periods. In summer, the  $BC_{thick}$  only contributed a minor fraction of the total number throughout the experiment. The small, moderately coated and  $BC_{lg,uncoat}$  fractions are all present in both seasons. Compared with the results in London (Fig. 9e and f), the  $BC_{sm}$  fraction was consistent with traffic influences with small core and thin coatings, and the  $BC_{mod}$  was broadly consistent with the wood burning observed in urban London. It is noted that the  $BC_{lg,uncoat}$  was not important in urban London under the different air masses or source influences observed, with the mass fraction of  $BC_{lg,uncoat}$  <8% and number fraction <3% throughout the experimental period. This means  $BC_{lg,uncoat}$  may represent a source which was uniquely present in urban Beijing, however not in the UK or surrounding area.

A further analysis on the segregated BC core and coated size distribution (Fig. S2) shows the total size distribution of BC core and coated size distribution could be generally separated as two or three lognormal-size distributions with  $BC_{sm}+BC_{lg,uncoat}$ ,  $BC_{mod}$  and  $BC_{thick}$ , representing the thinly, moderately and thickly coated BC respectively. In particular, the thickly coated BC could well explain the additional mode observed in the coated BC size distribution. This in turn suggests the apportioned BC modes may represent discernible primary sources or sources subject to secondary processing.

#### 4.4 Comparison of BC source estimation

Fig. 10 shows the temporal evolution of rBC mass in winter determined by the SP2 and SP-AMS categorized according to the different source contributions derived in section 4.3 and as explored in (Wang et al., 2019) respectively. PMF analysis on SP-AMS detected mass spectra identified four factors for BC-containing particles (Wang et al., 2019): fossil fuel BC (FOA\_BC) containing BC from vehicle sources and coal burning; BC coated with biomass burning organics (BBOA\_BC); BC associated with less-volatile organic coatings (OOA1\_BC); and BC associated with semi-volatile organic coatings (OOA2\_BC). Note that each PMF factor includes the refractory BC ( $C_x$ ) and the non-refractory coatings associated with it. In order to directly compare with the rBC mass measured by the SP2, only the mass of the  $C_x$  fragments in the PMF factors are used. Table 1 shows the linear correlation coefficient between the different PMF factors and the SP2 segregated BC types, with green shading highlighting the high correlation ( $r^2>0.6$ ).

The FOA\_BC was not able to be further apportioned via the PMF analysis, and so this factor contains both mobile



sources such as from diesel or gasoline engines, and importantly the coal burning emissions. Coal burning could result from both the residential and industrial sectors (Finkelman and Tian, 2018), with the former sector overwhelmingly dominating in winter but the contribution from the latter maintained throughout the year (Fig. S1). The small BC particle component is shown to be solely correlated with FOA\_BC ( $r^2=0.68$ ), but FOA\_BC is also correlated with moderately coated and BC<sub>lg,uncoat</sub>. The multiple correlations of FOA\_BC with BC at different core sizes and coating thicknesses means the fossil fuel related BC could exhibit a range of mixing states, however the BC<sub>sm</sub> particle fraction that has smaller core sizes and thinner coatings tends to be only associated with and contribute to the fossil fuel BC fraction.

BBOA\_BC which mostly resulted from open cooking sources in Beijing (He et al., 2010), is correlated with BC<sub>mod</sub> and the BC<sub>lg,uncoat</sub> from the SP2 ( $r^2>0.6$ ). Both BC types had high correlation with FOA and BBOA ( $r^2>0.6$ ) since the fossil fuel (excluding the part correlated with BC<sub>sm</sub>) and biomass burning BC particles have similar core sizes and coating contents. The potential contribution from coal burning sources are further investigated by correlating the SP-AMS measured PAH with the SP2-segregated BC types, as the PAH is considered to be an ideal marker for coal burning (Xu et al., 2006; Sun et al., 2016a). The moderately coated and BC<sub>lg,uncoat</sub> fractions are found to have the highest correlation with PAH ( $r^2>0.8$ ). This means the BC from coal burning tended to contribute to both the moderately coated and the BC<sub>lg,uncoat</sub> fractions (Zhang et al., 2018b), but not the BC<sub>sm</sub>, which in turn indicates that the BC<sub>sm</sub> is mainly a result of mobile sources (such as traffic) rather than coal burning. Previous studies found that the coal emission in urban China may have a larger BC core size compared to traffic sources (Wang et al., 2016). This is also consistent with the lack of the BC<sub>lg,uncoat</sub> mode in urban London where there was no coal burning present in the city (Fig. 9). Given biomass burning was also correlated with moderately coated and BC<sub>lg,uncoat</sub> fractions ( $r^2>0.6$ ), analyses limited to the size-resolved mixing state alone may not be able to distinguish the BC particles derived from coal and biomass burning in urban Beijing. This may be because the contribution of biomass burning to BC was significantly lower ( $p<0.01$ ) than that from fossil fuel in Beijing (Zhang et al., 2017), and the open biomass burning was only sporadically significant during spring and autumn harvest time over the NCP region (Chen et al., 2017). In addition, even some of the coal burning contribution, especially for the coal from residential use may be attributed as biomass burning if using levoglucosan as a marker (Yan et al., 2018), which may lead to some fraction of BBOA identified by the SP-AMS containing some fraction of coal burning. BC<sub>mod</sub> is consistent with wood burning in urban London but BC<sub>lg,uncoat</sub> are not present from these sources (Fig. 9e and f). It is therefore more likely that the BC<sub>lg,uncoat</sub> was mainly contributed by coal combustion.

The BC<sub>thick</sub> or BC<sub>mod</sub> fraction is well correlated ( $r^2>0.6$ ) with the BC coated with less-volatile organics (OOA1\_BC) or semi-volatile organics (OOA2\_BC), respectively. This means the coating composition would mostly contain less-volatile organic species when BC was thickly coated, whereas the moderate coating BC particle fraction mainly contained semi-volatile species. The coal burning or biomass burning contributions are also significant in the BC<sub>mod</sub> fraction, which means these primary sources may also emit considerable semi-volatile species internally mixed with BC. Note that the absolute values of rBC mass from SP-AMS or SP2 had not necessarily corresponded with each other for the correlated factors, e.g. the OOA2\_BC is higher than OOA1\_BC but vice versa for the SP2 factors. This

may result from different responses and sensitivities for the measurement techniques of both instruments at different levels of BC mixing state.

#### 4.5 Diurnal variation of different types of BC

Fig. 11 shows that the diurnal variation of the four different rBC types classified by the SP2. In winter all BC types anticorrelated with the diurnal evolution of MLH, whereas in summer all BC types exhibited a morning rush hour peak. For BC<sub>thick</sub> in winter, the average was significantly higher ( $p < 0.01$ ) than the median, indicating the sporadic occurrence of the thickly coated BC. There was no discernible difference in the diurnal patterns of the absolute mass loadings of the different BC types, which means similar emission sources and the PBL development may have controlled the diurnal pattern of different BC types to a similar extent. Nevertheless, differences could be identified by relative abundances of different BC types as discussed in the following section.

The diurnal variation of the number or mass fraction of BC<sub>sm</sub> (Fig. 11c) peaked at 8am and 7am in the winter and summer respectively, which corresponded with the morning rush hour. This is consistent with the identified possible traffic contribution to the BC<sub>sm</sub> fraction by comparison with the SP-AMS factors (section 4.4). The diurnal variation of this BC mode also had high correlation with NO<sub>x</sub> in both seasons ( $r^2 > 0.7$ ), with the morning rush hour occurring slightly later in winter than in summer, which further confirms the likely origin of traffic source. The correlation between the NO<sub>x</sub> concentration and different BC types is further evaluated by a multi-linear regression function, expressed as Equation (7). The fitting parameters are summarized in Table 2.

$$[NO_x] = a_0 + a_1 * [BC_{sm}] + a_2 * [BC_{mod}] + a_3 * [BC_{thick}] + a_4 * [BC_{lg,uncoat}] \quad (7)$$

Among all BC types,  $a_1$  shows the highest value in both seasons, which indicates the strong correlation ( $r^2 > 0.7$ ) between the BC<sub>sm</sub> mass fraction and the NO<sub>x</sub> concentration, with almost identical emission factor of 68-72 ppbv NO<sub>x</sub>/μg m<sup>-3</sup> of BC<sub>sm</sub>. In winter, the BC<sub>mod</sub> also contributed some fraction of NO<sub>x</sub>, whereas in summer the contribution of this BC type to NO<sub>x</sub> was almost negligible. The BC<sub>lg,uncoat</sub> was not correlated with NO<sub>x</sub> emission ( $r^2 < 0.3$ ), which in turn suggests the coal combustion may not emit significant NO<sub>x</sub> (Zhao et al., 2013; Wang and Hao, 2012). The BC<sub>sm</sub> fraction contributed the most in summer (50-60% in number and 40% in mass) and the second most in winter (30-40% in number and 30% in mass). These BC particles had smaller core size and thin coatings, and thus they contributed more significantly to the number than the mass. A similar number fraction of the BC was also present in urban London (Liu et al., 2014b) and Paris (Laborde et al., 2013) and had also been identified to be dominated by traffic sources.

BC<sub>mod</sub> showed comparable contribution in both seasons (40-50% in mass or 20-25% in number). The fraction of these particles slightly increased throughout the afternoon for both seasons, and this may partly result from daytime photochemical processing, though this BC type was also significantly associated with primary sources (section 4.4). The BC<sub>thick</sub> fraction showed no apparent diurnal pattern (note that BC<sub>thick</sub> mass fraction in summer was minor ~5%)

and only made a significant contribution at higher pollution levels (section 4.6).

455  $BC_{lg,uncoat}$  contributed a significant mass fraction (30-40% in winter and 40% in summer) but contributed little to the number (<10%) because of the large core sizes. The mass fraction of these BC particles had a pronounced night-time peak in winter, consistent with the view that this BC type may be contributed by coal burning (also identified by comparing with the PAH factor in section 4.4), because in the cold season there was significant residential heating activities at night which may use coal as fuel (Chen et al., 2006). This night-time peak in the mass fraction of  $BC_{lg,uncoat}$  460 was missing in summer due to lack of these heating activities. Nevertheless, the  $BC_{lg,uncoat}$  mass fraction remained substantial in summer, comparable with that of the  $BC_{sm}$  fraction at around 40%. This may be because the coal consumption from the industrial sector that is maintained throughout the year (Fig. S1).

To account for the dilution effect resulting from the development of the PBL, the rBC mass loading was multiplied by the MLH for every half hour throughout the day. The MLH-corrected rBC mass for each BC type is shown in Fig. 465 11b and provides a way of assessing the influence of BC emissions, although there are uncertainties associated with the MLH determination from ceilometer measurement (Kotthaus and Grimmond, 2018). All BC types showed a peak in the MLH corrected concentration at night in winter but showed a night-time minimum in summer, which may reflect a generally higher emission during night-time in winter but not in the summer. During the daytime between the hours of 6:00 and 19:00,  $BC_{sm}$  mass corrected for the MLH was similar in both seasons, suggesting that  $BC_{sm}$  may 470 have comparable emission rates between seasons, consistent with the view that these BC may be dominated by transportation sector (section 4.4).  $BC_{lg,uncoat}$  had significantly higher ( $p < 0.01$ ) emission at night in winter than in summer by a factor of 2.5, also consistent with the higher coal consumption from the residential sector in winter.

## 4.6 BC at different pollution levels

475 Given the complexity of the sources contributing to BC in Beijing, the relative primary source contributions and its interaction with other aerosol species may vary with the overall level of pollution and this in turn may change both the mixing state and the optical properties of BC. Fig. 12 shows mass fractions of different BC types at different  $PM_{10}$  level determined by the total mass of AMS+SP2. The traffic-like  $BC_{sm}$  (Fig. 12a) were a constant fraction of the total mass at lower pollution levels (when  $PM_{10} < 50 \mu g m^{-3}$ ) that was around 30% and 40% in winter and summer 480 respectively. The decreased mass fraction of  $BC_{sm}$  at higher pollution levels occurs in both seasons but is particularly marked in winter, and matched by an equal and opposite increase in the mass fraction of  $BC_{thick}$  under high pollution loadings.. The  $BC_{lg,uncoat}$  fraction (Fig. 12b) was similar in magnitude to the  $BC_{sm}$  fraction in summer across all levels of pollution, which means the coal-burning like BC was almost as important as the traffic source. In winter, the contribution of  $BC_{lg,uncoat}$  mass was slightly higher than the traffic-like  $BC_{sm}$  mass fraction whereas in summer the 485  $BC_{sm}$  mass was more significant. At the higher pollution levels in winter, some of the  $BC_{lg,uncoat}$  may be also contributed by coagulation.

The increase in the mass fraction of  $BC_{thick}$  at higher pollution levels (Fig. 12d) and the commensurate reduction in the mass fraction of  $BC_{sm}$  (Fig. 12a) is very striking, especially when  $PM_1 > 100 \mu g m^{-3}$  with rBC mass loading  $> \sim 2 \mu g m^{-3}$ . Under these conditions,  $BC_{thick}$  may be up to 50% of the total rBC mass. The coatings on these  $BC_{thick}$  particles were largely contributed by secondary species according to the SP-AMS analysis (section 4.4). In summer, there were no periods of very high pollution in excess of  $100 \mu g m^{-3}$  and the  $BC_{thick}$  mass fraction was less than 10%, though the trends in the fraction of  $BC_{sm}$  and  $BC_{thick}$  with pollution loading is the same in both seasons. This is entirely consistent with coagulation of particulate under very high concentrations. Under such conditions the very high numbers of  $BC_{sm}$  may coagulate rapidly with the large numbers of non-BC accumulation mode pollution aerosol that is composed largely of secondary material, this process can happen rapidly at high number concentrations and lead to the small BC particles gaining very thick coatings with no change in the core mass distribution (see also Fig. 9). High concentrations of secondary precursor during higher pollution episode in the gas phase ~~will exacerbate this process, may lead to nucleation and new particle formation, or size growth on pre-existing particles. A further analysis shows high number concentration of particles also corresponded with higher mass concentrations, indicating that the new particle formation and primary emission coincided with particle size growth. These processes will in turn promote the high coatings on BC.~~

At higher  $PM_1$  level in winter, the increased mass fraction of  $BC_{thick}$  also led to a decrease of  $BC_{mod}$ . However, in summer the  $BC_{mod}$  fraction increased when  $PM_1 > 50 \mu g m^{-3}$ , this high pollution event has previously been shown to be dominated by secondary species (Sun et al., 2015). The higher fraction of  $BC_{mod}$  in winter than in summer at the same pollution level may result from greater primary emissions (i.e. more residential coal burning in the cold season) or more condensable semi-volatile species at colder temperatures. The mass contribution of  $BC_{mod}$  and  $BC_{thick}$  in summer was lower than in winter at the same pollution level, possibly as a result of higher ambient temperatures in summer reducing the amount of semi-volatile material partitioning to the particles.

The contribution of absorption coefficient is calculated based on single particle information shown in Fig. S4 (note that the coating is assumed to be non-absorbing here). The right axis of Fig. 12 shows the mean contribution of absorption corresponding to the mass fraction for each BC type, implying that different BC types have ~~different absorption contribution because of their~~ varying absorption efficiency but the contribution on absorption is determined by both mass loading and MAC. Fig. S5 shows that the histogram of occurrence for  $MAC_{550}$  of each BC type during the experimental period: the  $BC_{sm}$  and largely uncoated BC had average  $MAC_{550}$  about  $7.3 m^2 g^{-1}$  and  $5.3 m^2 g^{-1}$  respectively, and  $BC_{lg,uncoat}$  had a lower MAC because of its larger core size which is consistent with Mie calculation. The moderately and  $BC_{thick}$  had average MAC of  $11.2 m^2 g^{-1}$  and  $12.4 m^2 g^{-1}$  respectively.

Fig. 13 shows both modelled and PAX-measured  $MAC_{870}$  at different pollution levels, the results agree to within 15%. For both seasons, when  $PM_1 < 50 \mu g m^{-3}$ , the measured absorption efficiency of BC showed little dependence on the concentration of particulate matter with  $MAC_{870}$   $\sim 4.9 \pm 0.4 m^2 g^{-1}$  and  $4.7 \pm 0.3 m^2 g^{-1}$  in winter and summer respectively. The absorption at  $\lambda = 870 nm$  is deemed to be unaffected by brown carbon (Sun et al., 2007). The  $MAC_{870}$

for uncoated BC was calculated to be  $-4.3 \pm 0.2 \text{ m}^2 \text{g}^{-1}$  for both seasons so the enhancement of absorption efficiency ( $E_{abs}$ ) is calculated as the modelled  $\text{MAC}_{870}$  normalized by this value.  $E_{abs,870}$  significantly increased at  $\text{PM1} > 50 \mu\text{g m}^{-3}$  up to  $1.4 \pm 0.1$  and  $1.6 \pm 0.1$  for summer and winter respectively. This increase in absorbing capacity of BC at higher pollution levels implies that both primary emission and secondary processing may both contribute to the coatings and subsequent increased absorption. It also highlights the potential for additional feedback between pollution and radiation under very high pollution loadings (Zhang et al., 2018c). There was a wide variability in  $\text{MAC}$  or  $E_{abs}$  at  $\text{PM1}$  concentrations of between 100 and  $200 \mu\text{g m}^{-3}$ . In addition, the mean PAX-measured  $\text{MAC}_{870}$  was higher than the modelled results by 20% at this pollution level. This suggests complex processes at this moderate pollution level where a large variability of BC coating content was present, but a single mixing scenario based on Mie-calculation is not able to fully explain the measurements of absorption. The  $\text{MAC}_{870}$  slightly decreased at very high  $\text{PM1}$ , i.e.  $> 300 \mu\text{g m}^{-3}$ , and this decrease is more pronounced for measurement (the grey line shows) than Mie-based modelling. This may result from the shadowing effect that very thick coatings may shield incident photons from the absorbing core, particularly when the coating is absorbing (He et al., 2015; Zhang et al., 2018a).

## 5 Conclusion

In order to probe the sources and processes governing atmospheric black carbon in Beijing, measurements were performed in both winter and summer using an SP2 and the core size and coating thickness were examined using the single particle data. Higher rBC mass loading with more variable coatings was found in winter than in summer. The air mass from the Southern Plateau brought BC with the largest core size and coatings in winter, indicating the appreciable regional influence, whereas in summer the characteristics of BC were relatively independent of air mass direction. In contrast to equivalent measurements in London, where two particle types were observed corresponding to traffic and wood burning, other types were observed in Beijing, probably reflecting a more complex mixture of sources. rBC number and mass concentrations were quantified according to the following four particle types: small thinly-coated BC, moderately-coated BC, thickly-coated BC and large thinly-coated BC. By comparison with other measurements, in particular a factorisation of coating materials from the SP-AMS, these were assigned to different soot sources.

The small thinly-coated rBC fraction was associated with traffic emissions and made up for 30% and 40% of the rBC mass in winter and summer respectively. This particle fraction was strongly associated with  $\text{NO}_x$ , though the implied ratio of  $14 \text{ ng m}^{-3} \text{ ppb}^{-1}$  was lower than the values of  $18\text{--}28 \text{ ng m}^{-3} \text{ ppb}^{-1}$  reported for London, likely due to differences in the emissions fleet, such as a more widely used gasoline engine in Beijing (Wang et al., 2009). The large thinly-coated rBC could be associated with coal combustion and corresponded to around 30–40% and 40% of the rBC mass in winter and summer respectively.

The moderately-coated particle fraction made up 40–50% of the rBC mass and was associated with both emissions and atmospheric processes. As a result, the original source of these particles is currently ambiguous; it is possible

555 that this class has multiple contributions. The thickly-coated particle fraction was mainly present during the winter heavy haze events when PM1 was greater than 200  $\mu\text{g m}^{-3}$  or the rBC mass loading was greater than 4  $\mu\text{g m}^{-3}$ . During these events, these particles made up for around 20-45% of the rBC mass and the coatings could be associated with secondary species, implying that these are rBC particles that have undergone some form of atmospheric processing. Given the thick coatings, it would be expected that these particles would exhibit higher mass absorption and scattering  
560 coefficients, higher hygroscopicities (thus high optical thickness in the upper boundary layer) and greater scavenging potential (thus shorter atmospheric lifetime). These large BC importantly enhanced the absorption efficiency at high pollution levels, and reduction of emissions of these large BC particles and the precursors of the associated secondary coating will be an effective way of mitigating the heating effect of BC in urban environments.

565

## Data availability

Processed data is available through the APHH project archive at the Centre for Environmental Data Analysis (<http://data.ceda.ac.uk/badc/aphh/data/beijing/>). Raw data is archived at the University of Manchester and is available on request.

## Author contributions

D.L., J.D.A., M.J.F designed the research; J.D.A., D.L. R.J. J.W. C.Y. J.D.A. H.C. M.J.F, C.X., J.L. F.S. X.G. Y.S. and P.F. performed experiments; D.L. performed the data analysis; J.W. and X.G. analysed the SP-AMS data; S.K. and S.G. analysed the MLH data; J.L. and F.S. analysed the NO<sub>x</sub> and CO data; D.L., J.W. J.D.A., and H.C. wrote the paper.

## Acknowledgments

This work was supported through the UK Natural Environment Research Council (grant refs. NE/N007123/1, NE/N00695X/1, NE/N00700X/1), the National Natural Science Foundation of China (41571130024, 41571130034, 21777073).

**Table A1. Symbols and abbreviations**

Symbols/abbreviations	Meaning
BC <sub>sm</sub>	Small BC
BC <sub>mod</sub>	Moderately coated BC
BC <sub>thick</sub>	Thickly coated BC
BC <sub>lg,uncoat</sub>	Large and uncoated BC
FFOA	Fossil fuel organic aerosol
BBOA	Biomass burning organic aerosol
OOA1	Low-volatile organic aerosol
OOA2	Semi-volatile organic aerosol
<u>PBL</u>	<u>Planetary boundary layer</u>
<u>PMF</u>	<u>Positive matrix factorization</u>
<u>rBC</u>	<u>Refractory BC</u>
SP2	Single particle soot photometer
D <sub>c</sub>	BC core diameter
D <sub>p</sub>	Coated BC diameter
rBC	Refractory BC
<u>MAC</u>	<u>Mass absorption cross section</u>
MMD	Mass median diameter

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$r^2$ (N=1406)	FOA_BC (fossil fuel)	BBOA_BC (biomass burning)	OOA1_BC (less volatile)	OOA2_BC (semi-volatile)	PAH_BC
Small BC	0.68	0.55	0.10	0.12	0.47
Moderately coated BC	0.61	0.66	0.40	0.63	0.81
Thickly coated BC	0.31	0.54	0.61	0.47	0.59
Large uncoated BC	0.79	0.85	0.42	0.34	0.82
BCmass total	0.74	0.85	0.51	0.51	0.89

Table 1. (a) Pearson's correlation coefficients between the time series of SP2 and SP-AMS segregated rBC mass and PAH. The correlations with Pearson  $r^2 > 0.6$  are shaded in green. All correlations are significant at the 0.01 level (2-tailed).

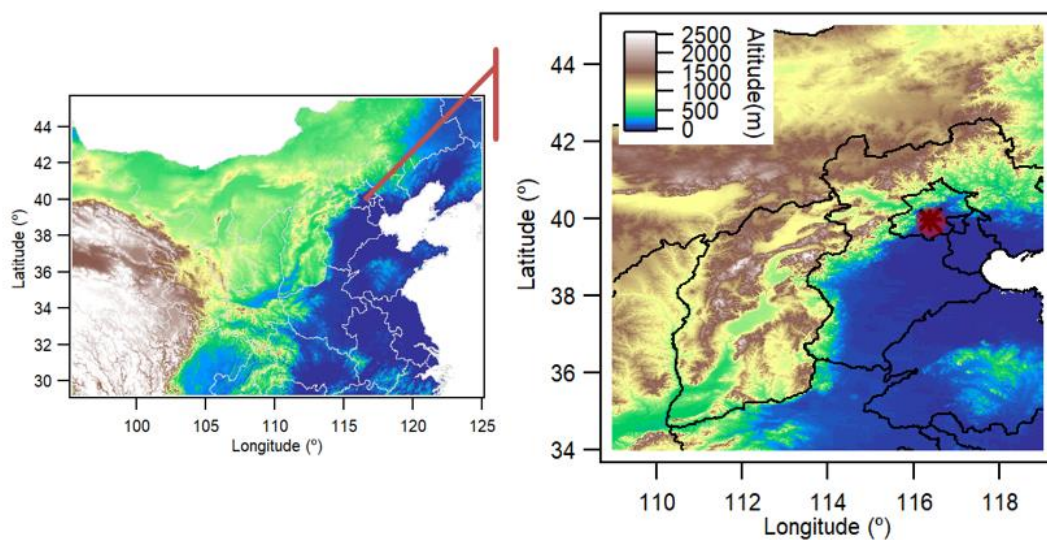
780

NO <sub>x</sub> with BC types	a1	a2	a3	a4	a0
winter	72.3 ± 3.2	21.3 ± 3.0	16.3 ± 2.1	0	8.8 ± 1.3
summer	68.4 ± 4.7	0	0	0	1.15 ± 0.77

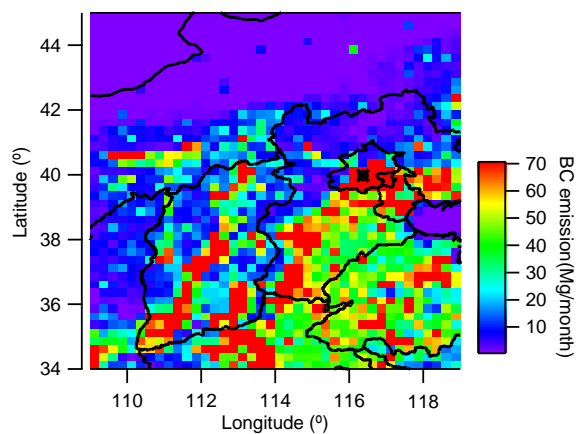
Table 2. Multi-linear regression for Equation (7) among NO<sub>x</sub> and different BC types.

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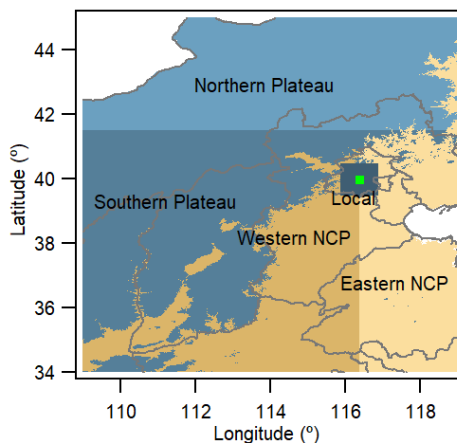
(a)



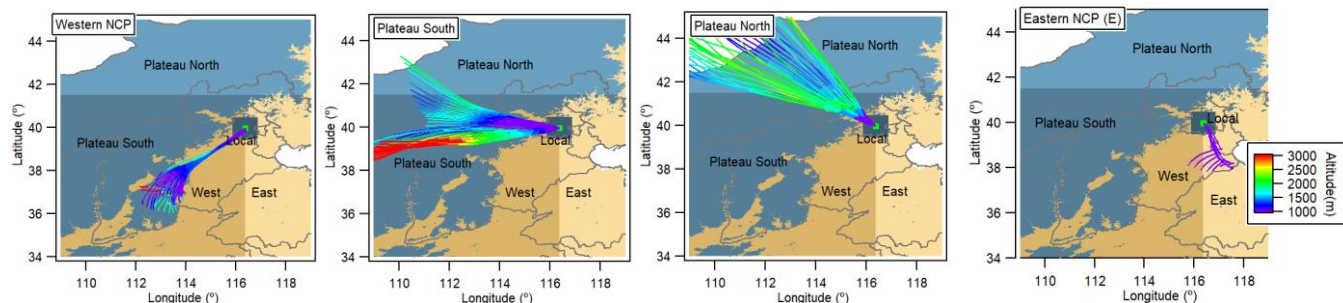
(b)



(c)



790 Figure 1. (a) Terrain height for the North China Plain (NCP) and the Plateau; (b) BC emissions from all sectors in  
 795 2010; (c) the regional classification according to terrain height and emission.



795 Figure 2. Classified air mass origins based on back trajectory analysis: western NCP, Southern Plateau, Northern  
 800 Plateau and Eastern NCP.

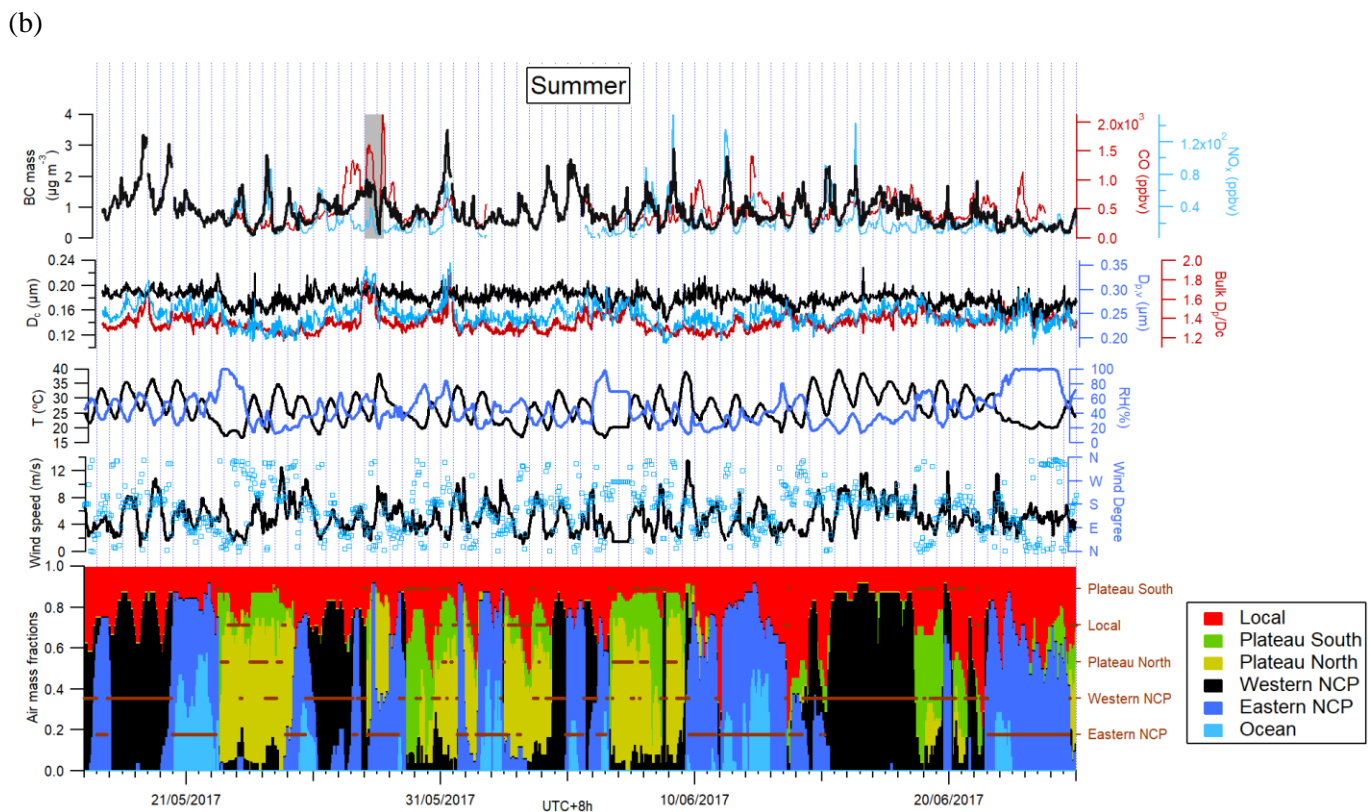
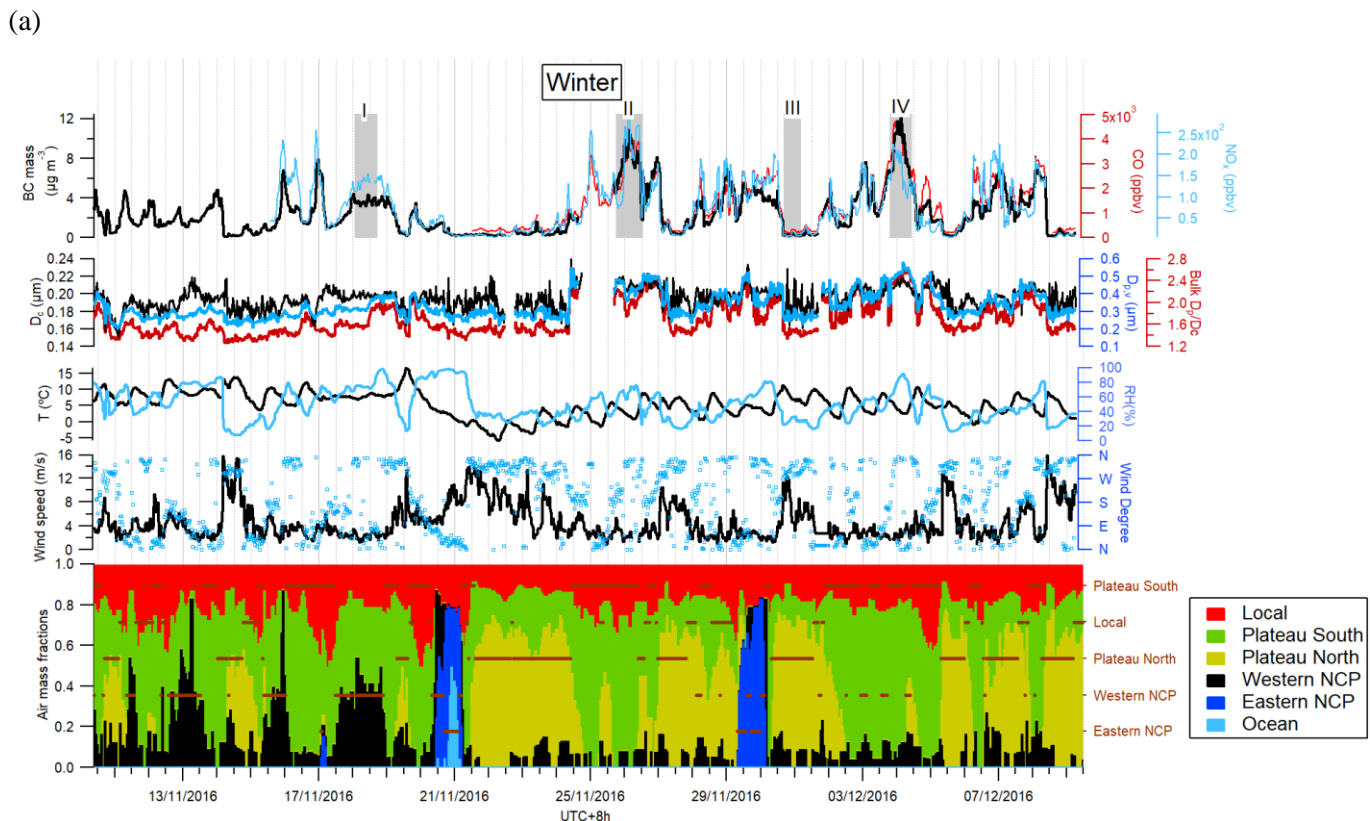


Figure 3. Time series of BC-related properties in the winter (a) and summer (b) experiments. From top to bottom subpanels: BC mass loading, CO and  $\text{NO}_x$ ; BC bulk  $D_p/D_c$ , core MMD and coated volume-equivalent diameter; ambient temperature and RH at  $z=8$  m; wind speed and direction at  $z=120$  m; air mass fractions from different origins



based on back trajectory analysis, with the brown horizontal lines indicating the classified air mass types. The vertical grey shades mark the periods for the detailed mixing state analysis in Fig. 9.

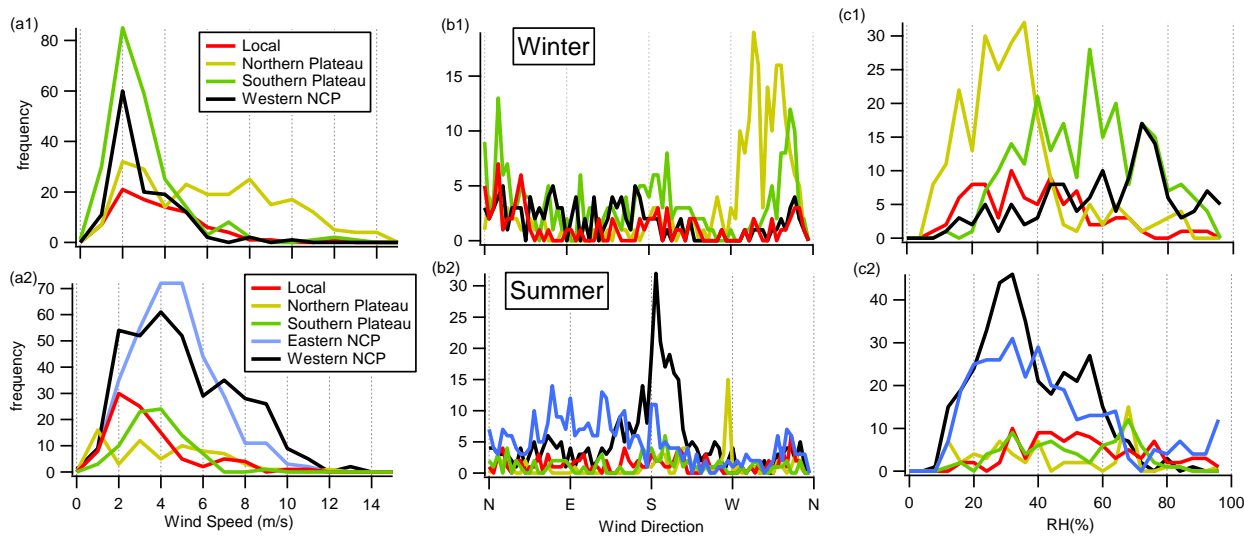


Figure 4. Frequency distributions of wind speed and direction ( $z=120$  m) and RH ( $z=8$  m) for classified air mass types in both seasons.

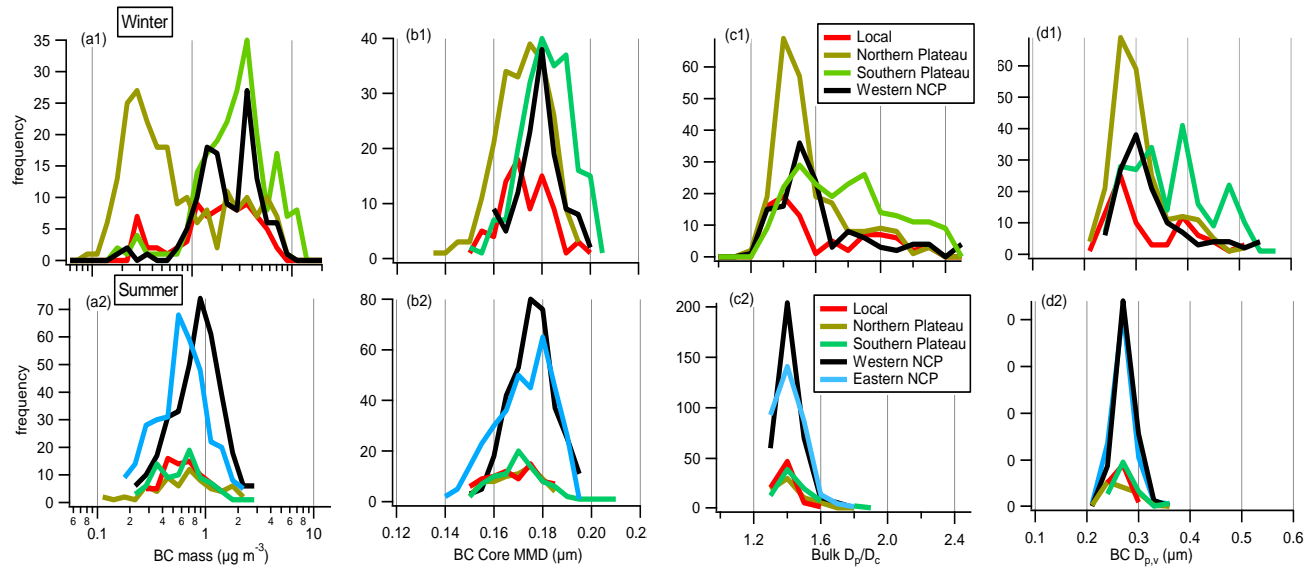
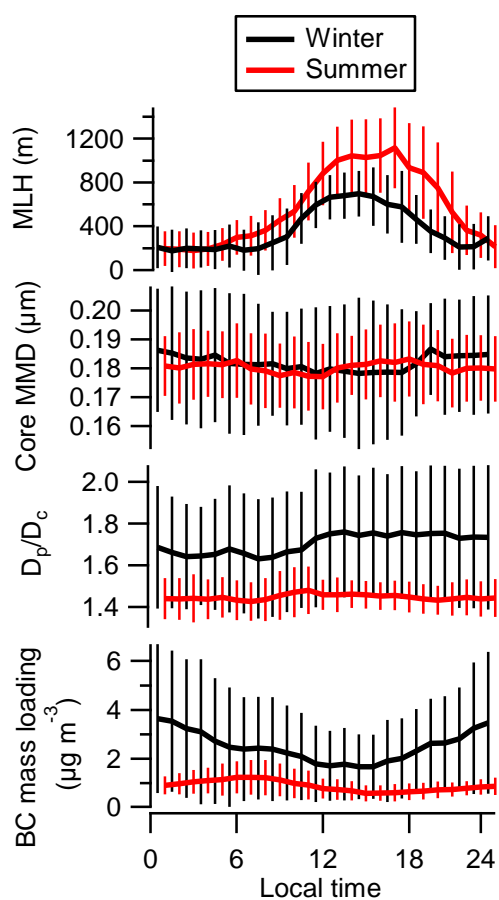
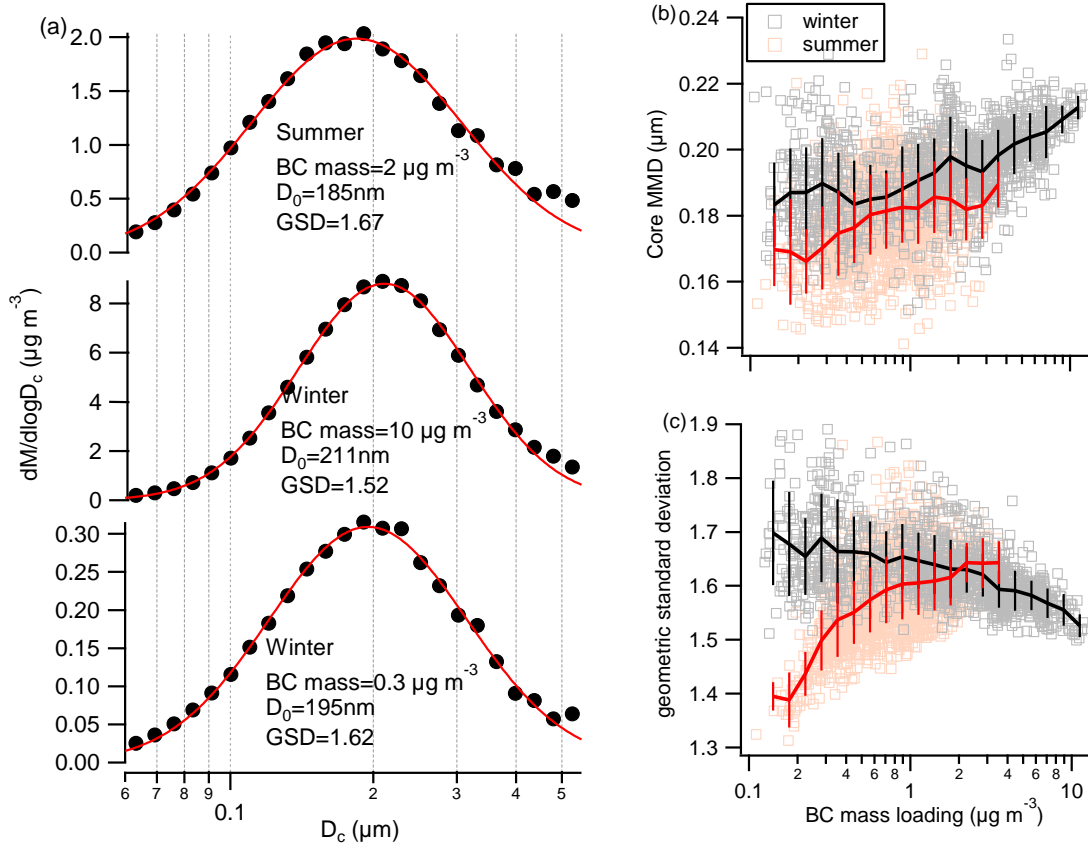


Figure 5. Histograms of BC mass loading, core size MMD,  $D_p/D_c$  and  $D_{p,v}$  for different air masses in both seasons.

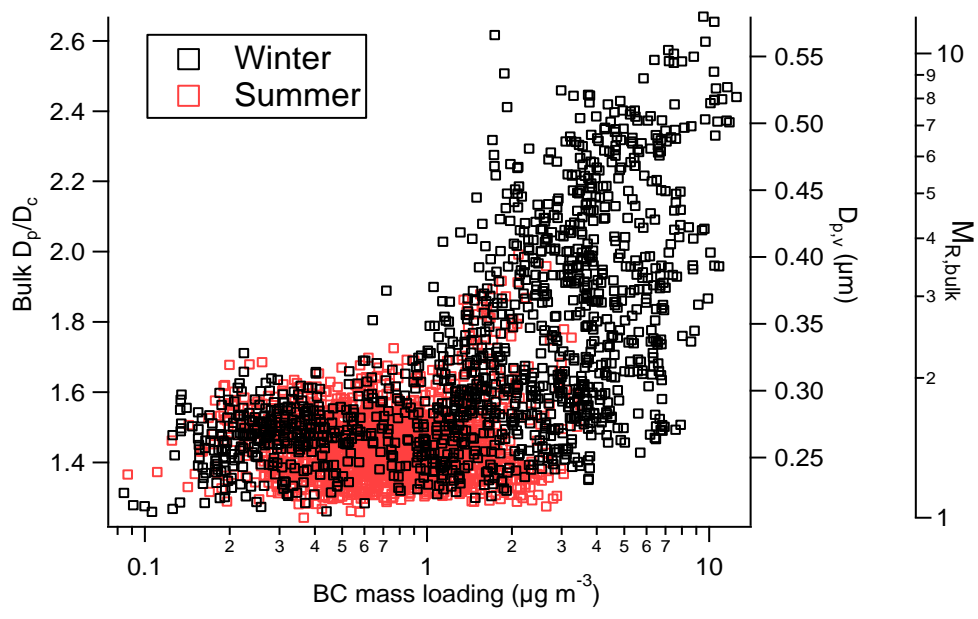


815 Figure 6. Diurnal variations of mixing layer height (MLH) and BC-related properties in winter and summer. The lines show the mean at each hour and error bars denote  $\pm 1\sigma$ . The x-value for summer is shifted by 0.5h to avoid the overlap.





820 Figure 7. (a) BC core size distribution averaged over different rBC mass loading conditions in both seasons, showing the lognormal fitting and the fitted peak diameter ( $D_0$ ) and geometric standard deviation (GSD); (b) BC core MMD as a function of BC mass loading and parameterization; (c) BC core GSD (from the fitting) as a function of BC mass loading and their fitting functions. The line and error bars show the mean $\pm\sigma$  at each rBC mass bin.



825 Figure 8. Mixing status of BC at different levels of BC mass loading in both seasons, with different y-axes showing bulk  $D_p/D_c$ , volume-weighted coated particle size ( $D_{p,v}$ ) and bulk mass mixing ratio of coating/rBC.

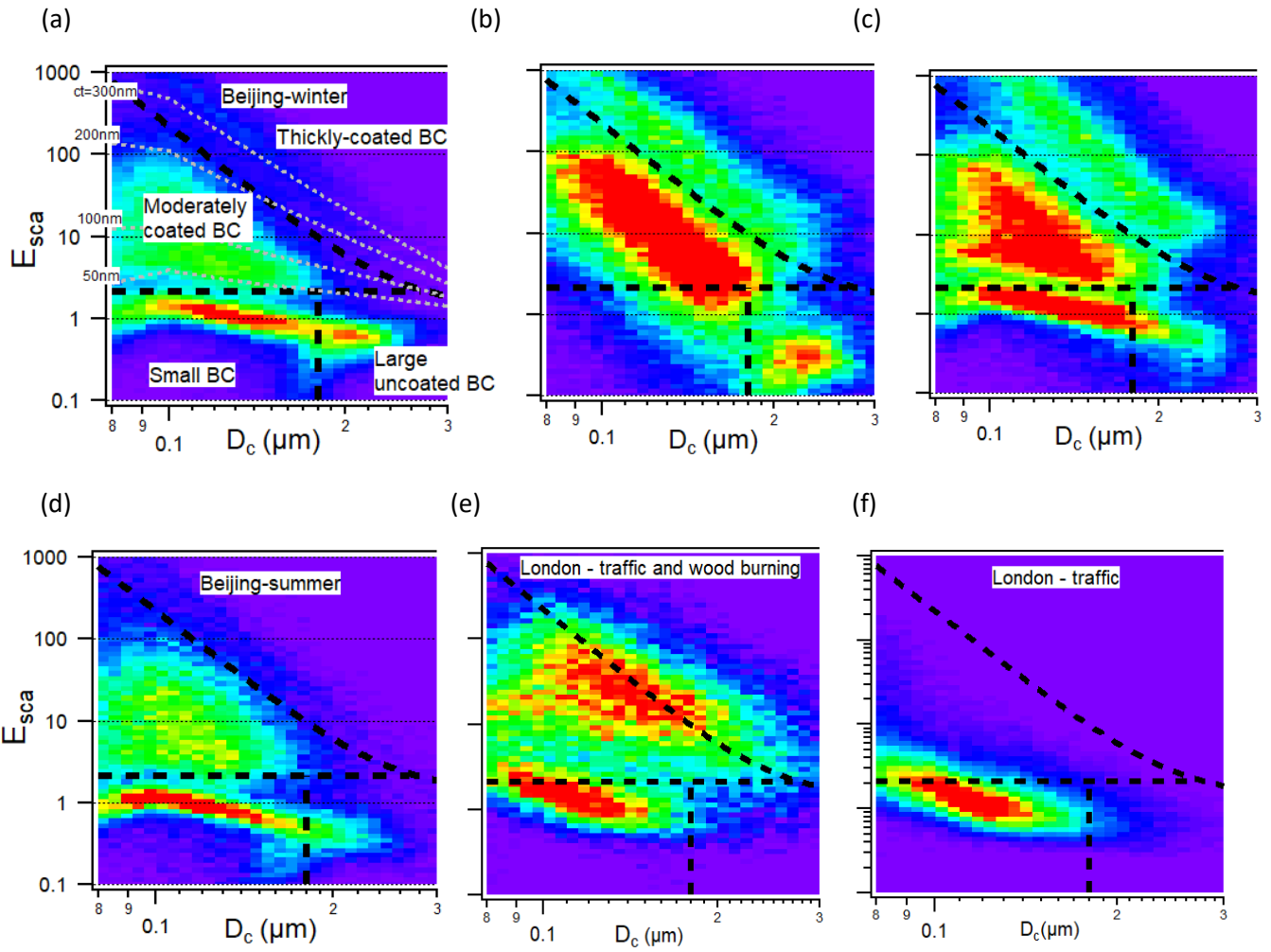


Figure 9. Scattering enhancement ( $E_{sca}$ ) as a function of BC core size ( $D_c$ ) for the three periods (as period I-III indicated in Fig. 3) in Beijing winter (a-c), Beijing summer (d), London with mixed sources (e) and London with traffic source (f). Each plot is coloured by particle number density (the colour scale is set to be red when the number density is above 70% of the maxima in each panel). The particles are separated as four groups using the borders (from top to bottom) at  $y=3.38+0.000436*x^{-5.7}$ ,  $y=2.1$ ,  $x=0.18$ , as shown by dashed lines on each plot. The grey dashed lines on (a) denote coating thicknesses mapped on  $E_{sca}$ - $D_c$  plot.

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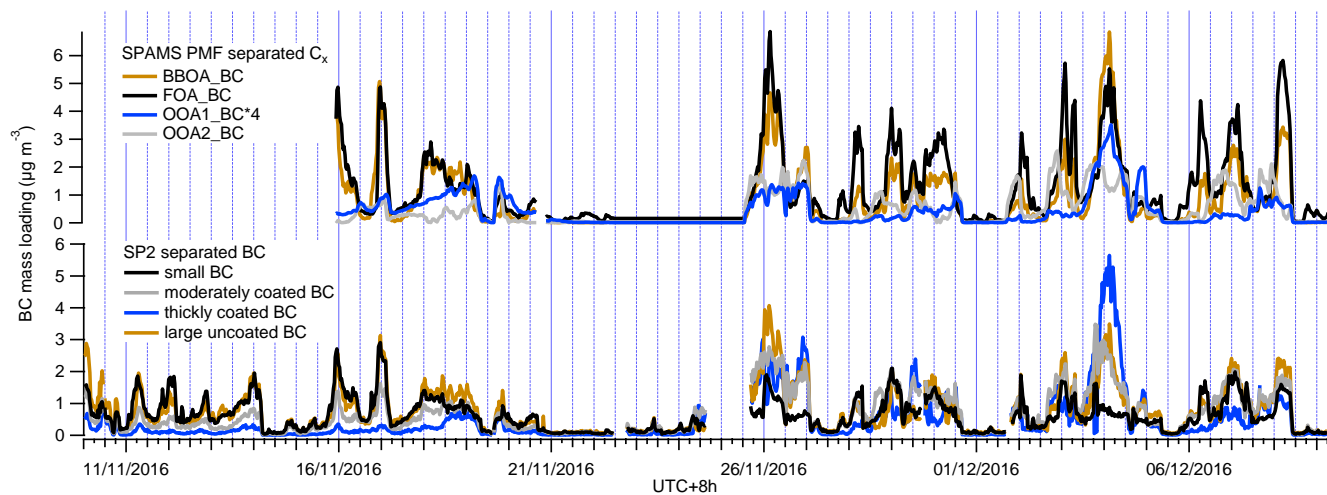


Figure 10. Time series of SP2-separated rBC mass and SP-AMS separated  $C_x$  mass by PMF analysis.

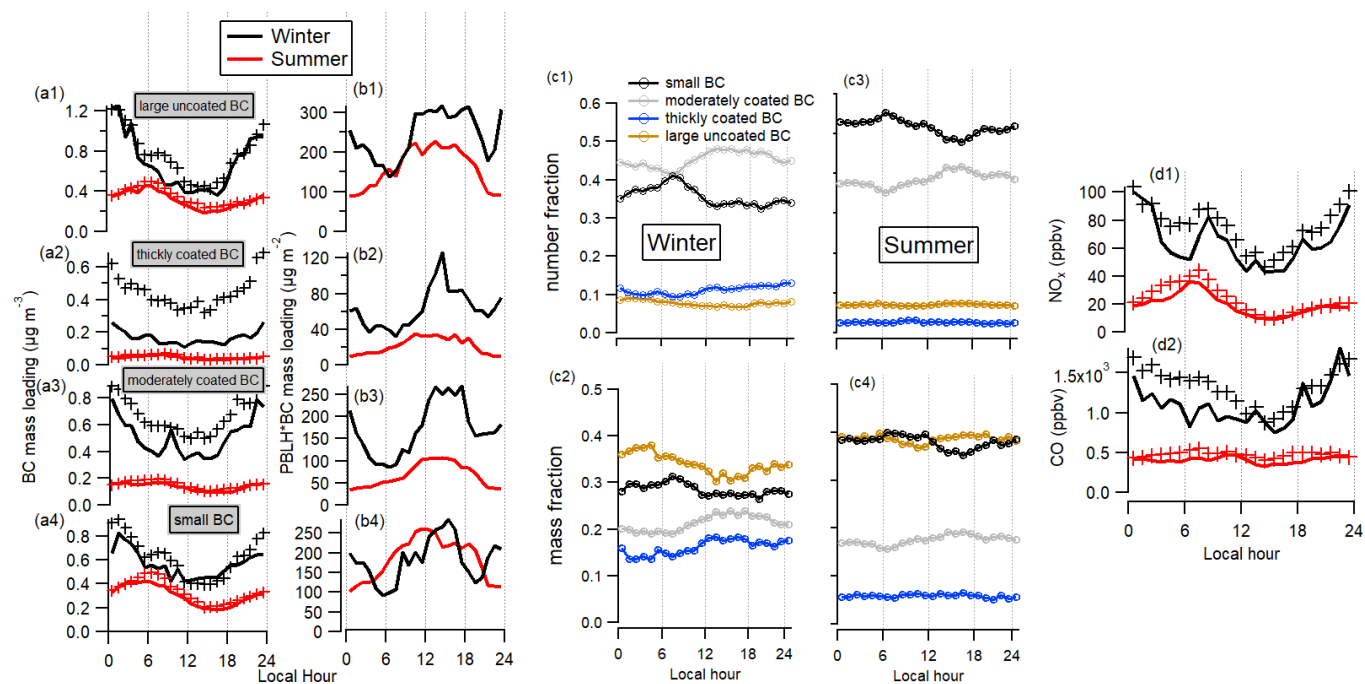
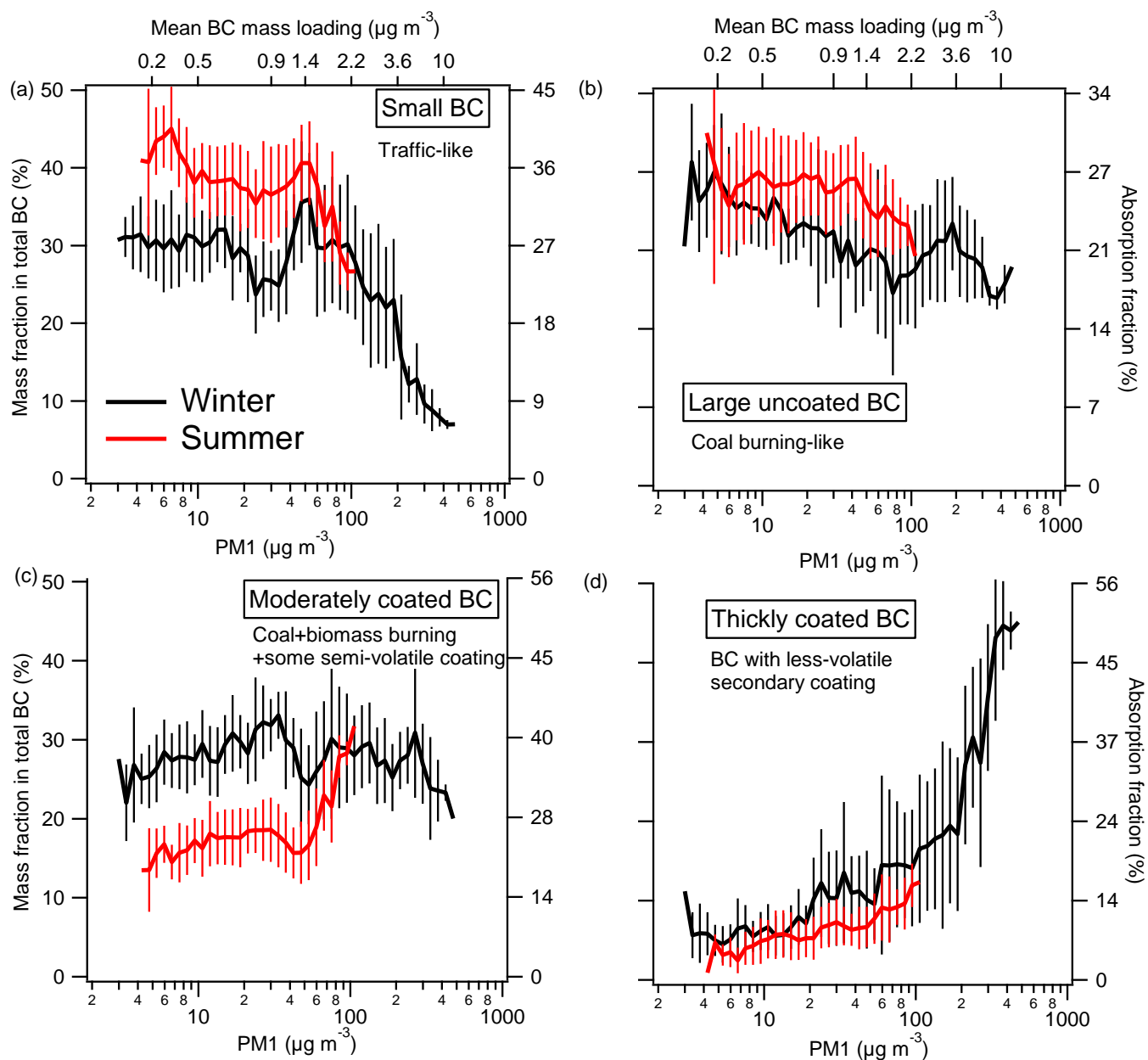


Figure 11. Diurnal variation of the rBC mass segregated by their SP2 characteristics in both seasons. a) shows the median (solid line) and mean (markers) at each hour; b) the median value of PBLH-corrected rBC mass; c) the number and mass fractions for each BC type; d) the  $\text{NO}_x$  and CO.

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850 Fig. 12. The mass (left y-axis) contributions of different BC types at different pollution levels during winter and summer. The mean contribution of the absorption corresponding to the mass fraction for each BC type is shown on the right y-axis. The mass fraction of each BC type is the average  $\pm$  standard deviation at each PM<sub>1</sub> bin. The top axis shows the averaged rBC mass loading at each PM<sub>1</sub> bin, and the right axis indicates the average absorption fraction corresponding with each rBC mass fraction.

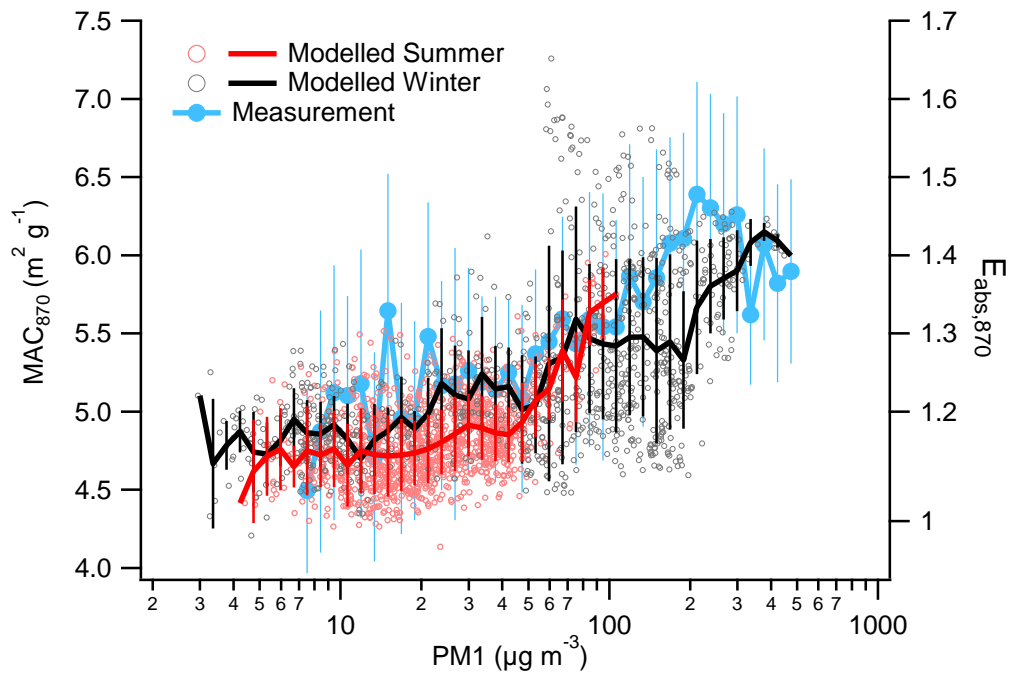


Fig. 13. The modelled and measured MAC<sub>870</sub> and E<sub>abs</sub> at different pollution level.