

**Black carbon
hygroscopicity**

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Influences on the fraction of hydrophobic and hydrophilic black carbon in the atmosphere

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Abstract

Black carbon (BC) is a short term climate forcer that directly warms the atmosphere, slows convection, and hinders quantification of the effect of greenhouse gases on climate change. The atmospheric lifetime of BC particles with respect to nucleation scavenging in clouds is controlled by their ability to serve as cloud condensation nuclei (CCN). To serve as CCN under typical conditions hydrophobic BC particles must acquire hygroscopic coatings. However, the quantitative relationship between coatings and hygroscopic properties for ambient BC particles is not known nor is the time scale for hydrophobic-to-hydrophilic conversion. Here we introduce a method for measuring the hygroscopicity of externally and internally mixed BC particles by coupling a single particle soot photometer with a humidified tandem differential mobility analyzer. We test this technique using uncoated and coated laboratory generated model BC compounds and apply it to characterize the hygroscopicity distribution of ambient BC particles. From these data we derive that the observed number fraction of BC that is CCN active at 0.2% supersaturation is generally low in an urban area near sources and that it varies with the trajectory of the air mass. We anticipate that our method can be combined with measures of air parcel physical and photochemical age to provide the first quantitative estimates for characterizing hydrophobic-to-hydrophilic conversion rates in the atmosphere.

1 Introduction

Black carbon (BC) particles absorb solar radiation, leading to heating and suppression of convection in the atmosphere. Black carbon has an average lifetime of 1 ± 1 weeks (Rodhe et al., 1972) and contributed $\sim 0.9 \text{ W m}^{-2}$ to the top of atmosphere forcing during 2005 (Ramanathan and Carmichael, 2008). Forcing estimates such as these rely on up-to-date emission inventories and accurate description of the wet removal process. Freshly emitted BC particles are hydrophobic and generally not able to serve

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as cloud condensation nuclei (CCN) at atmospherically relevant critical supersaturations (Lammel and Novakov, 1995; Dusek et al., 2006; Koehler et al., 2009). Over time BC particles acquire coatings that lower the critical supersaturation (s) at which BC particles can undergo nucleation scavenging (Wyslouzil et al., 1994; Weingartner et al., 1997; Zhang et al., 2008). Some global models (Cooke and Wilson, 1996; Koch, 2001; Chung and Seinfeld, 2002; Koch et al., 2009) parameterize the hydrophobic-to-hydrophilic conversion as an exponential turnover with an e-folding time (τ) of 24–39 h (Kanakidou et al., 2005; Koch et al., 2009). The time scale appears to be controlled by BC interaction with more hydrophilic species such as sulfates, nitrates, and secondary organic aerosol via condensation and/or coagulation (Petters et al., 2006; Riemer et al., 2010). Detailed microphysical models predicting τ indicate that the time scale varies between day and night, and that aging proceeds rapidly during daytime (Riemer et al., 2010). Verifying these differences experimentally is important because hydrophobic-to-hydrophilic conversion time scales represent a major uncertainty in determining BC lifetime and predicting its distribution throughout the atmosphere.

The recent development of the single particle soot photometer (SP2) (Stephens et al., 2003; Baumgardner et al., 2004; Schwarz et al., 2006) has allowed characterization of the refractory BC (rBC) size distribution and mixing state in unprecedented detail. Briefly, the SP2 exposes individual particles to a 1064 nm laser beam. Particles that absorb light sufficiently at this wavelength are heated to their incandescence temperature and the emitted thermal radiation is measured by optical detectors and converted to mass. The instrument also measures light scattered by particles to determine coating and mixing state information for rBC. Combined, the system quantifies the refractory mass of the absorbing particle, provides coating information and resolves the rBC mixing state for an ensemble of particles.

The relationship between hygroscopic growth and coating material/thickness has been studied for laboratory generated BC particles (Wyslouzil et al., 1994; Weingartner et al., 1997; Gysel et al., 2003; Popovicheva et al., 2008b; Zhang et al., 2008). These studies show that water uptake is controlled by the amount of coating material

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and that agglomerated particles may restructure from a combination of water soluble coating and absorbed water. Several recent studies also investigated the CCN activity of various model soot particles (Lammel and Novakov, 1995; Dusek et al., 2006; Koehler et al., 2009; Snider et al., 2010), showing that untreated (i.e. uncoated) BC activates at sizes and supersaturations larger than those predicted by the Kelvin equation, effectively rendering most of these particles CCN inactive under atmospherically relevant conditions. The water uptake studies and CCN studies are related through theoretical descriptions that quantitatively link hygroscopic growth and CCN activity. Water adsorption may lead to the nucleation of cloud droplets in various ways for uncoated soot (Fletcher, 1958; Mahata and Alofs, 1975; Henson, 2007; Sorjamaa and Laaksonen, 2007; Popovicheva et al., 2008a), while modified Köhler theory that accounts for the insoluble core describes coated soot (see Junge, 1950; Pruppacher and Klett, 1997; Weingartner et al., 1997; Snider et al., 2003; Petters and Kreidenweis, 2007, 2008 for theoretical discussion and Henning et al., 2010 for experimental verification). These studies addressed the relationship between water uptake and CCN properties for laboratory generated model soot aerosol. The link has not yet been established for externally mixed ambient aerosol because water uptake measurements are generally not sensitive to specific particle types such as BC.

We address this gap by proposing a new method that combines the SP2 with the humidified tandem differential mobility analyzer (HTDMA) technique (Rader and McMurry, 1986). The HTDMA measures the wet size distribution by first selecting a nominal particle diameter based on electrical mobility, exposing the particles to a specified relative humidity, and then measuring the resulting wet size distribution using a second differential mobility analyzer and a condensation particle counter (CPC). The addition of the SP2 identifies rBC in the output of the humidified differential mobility analyser (DMA). The water uptake properties of BC particles can also be linked directly to the thickness of the coating measured by the SP2. Combined with Köhler theory this provides direct insights into the relationship between rBC size, mixing state, and the ability of the particles to undergo nucleation scavenging in clouds. The purpose of this work is

to describe the HTDMA-SP2 setup, present tests with laboratory generated pure and mixed model BC particles, explain the data processing procedures, report on initial ambient data collected in a major urban center (central Manchester in the UK), and discuss how data products from this technique can be used in future targeted campaigns to improve our understanding of rBC aging processes.

2 Methods

Model black carbon particles were generated by atomizing solutions of black carbon proxies suspended in ultrapure deionized water. The aerosol was diluted with particle-free air and dried prior to sampling by the HTDMA-SP2 instrument. Black carbon proxies included glassy carbon, aquadag and carbon black. Glassy carbon particles consist of monomers or aggregates of spherical non-graphitic carbon particles while aquadag consists of clumps of non-spherical graphite sheets (Moteki et al., 2010). The morphology and structure of carbon black particles is unknown. To generate coatings, ammonium sulfate or malonic acid was added to the BC suspensions. Since the shape of our particles was unknown, the relationship between mobility diameter and mass (effective density) was not clearly defined and consequently we refer to the diameter of particles classified by a DMA as mobility diameter (D_{mob}). Uncertainties introduced by this limitation are discussed later.

Ambient data was collected at the University of Manchester between 3 and 16 August 2010. Manchester is located at the center of the British Isles and prevailing winds are southerly/westerly resulting in a maritime climate. Manchester is situated on the urban east-west corridor that connects Leeds and Liverpool, so incoming air may have already acquired some BC. Aerosol was sampled through 3/8" copper tubing running from the instrument laboratory to the outside through a port in the window ~20 m a.g.l. The laboratory is located ~100 m from a major urban corridor (with a scheduled passenger bus frequency of one per minute during daytime) and around 2 km south of the Manchester city center. We therefore expect to have sampled a mixture of BC from

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local as well as regional sources.

2.1 The single particle soot photometer (SP2)

The SP2 instrument used in this study and the data processing and analysis procedures used to interpret the instrument output are described elsewhere (McMeeking et al., 2010). Briefly, the SP2 uses the maximum detected emission of thermal radiation (“incandescence”) to determine the rBC mass for individual rBC-containing particles. Moteki and Kondo (2010) showed that the response of the SP2 depends, in part, on the refractive index and shape of the particle, so the choice of calibration material is critical to accurately determine rBC mass. Here we calibrated the instrument using mobility-selected (TSI 3085) glassy carbon spheres with density = 1.42 g cm^{-3} (Liu et al., 2010) and $|(m^2 - 1)/(m^2 + 2)| = 0.81$, where m is the complex refractive index (Moteki et al., 2010). The nominal detection range of the SP2 is between $D = 70$ and 600 nm , although the lower detection range depends on the intensity of the intra-cavity laser (Schwarz et al., 2010). In this study we only sampled $D_{\text{mob}} = 147, 193$ and 286 nm , which are sufficiently large to ignore any laser-power related detection limitations.

The SP2 has two avalanche photodiodes (APDs) that measure incident light ($\lambda = 1064 \text{ nm}$) scattered by particles crossing the Gaussian profile cavity laser. One detector is a modified four-element APD that allows the Gaussian scattering function to be constructed from the leading edge of the regular APD signal prior to its distortion by any laser-induced heating (Gao et al., 2007). Non-absorbing particles can be sized simply from the peak of the unperturbed Gaussian profile scattering signal. The scattering response of the regular APD was calibrated with polystyrene latex spheres (PSL) over a range of sizes with refractive index $n = 1.58$.

2.2 The HTDMA-SP2 setup

The HTDMA used in this study is described in detail elsewhere (Cubison et al., 2005; Good et al., 2010). Briefly, particles are dried to $\sim 20\%$ RH inside a desiccant drier,

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charge equilibrated inside a ^{90}Sr neutralizer, size selected inside a DMA, followed by humidification to $\text{RH}=90\%$. The resulting humidified size distribution is scanned using a second DMA connected to a water based condensation particle counter (water-CPC, TSI 3782). The DMAs were operated with recirculating sheath flows and a sheath-to-sample flow rate of 10:1. A detailed flow schematic is presented in Fig. 1. The SP2 was used, in addition to the CPC, to measure the humidified size distribution of BC particles. We inverted the SP2 counts using the same method that is traditionally used to process CPC counts sampled by DMA2 of the setup. The traditional inversion is described in detail by Gysel et al. (2009).

Each particle detected by the SP2 was categorized and quantified according to the following scheme:

i. Purely scattering particles: If a particle was detected by the APD sensor but no thermal radiation was observed, the mass of rBC in the particle was either below the SP2 incandescence detection limit or the particle did not contain rBC. These particles were classified as purely scattering and assigned a size using the intensity of the APD detector signal and the PSL calibration curve.

ii. rBC core diameter: Particles with detectable incandescence signal were classified as rBC particles and assigned a volume equivalent rBC core diameter (D_{BC}) determined based on the calibration between incandescence signal and mass obtained from laboratory generated glassy carbon.

iii. Coating thickness: Coating thickness was estimated by comparing D_{BC} with other measures of unperturbed particle size, including mobility diameter from the DMA and optical diameter from the SP2. Both estimates are susceptible to measurement artifacts that will be discussed when we present the data.

iv. Thickly coated particles: The time required for the particle to reach its peak temperature was estimated from the time between peak scattering and thermal radiation signals or time delay (Shiraiwa et al., 2007). Particles having time delays longer than

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a critical time delay ($t_d > 1 \mu\text{s}$) were classified as thickly coated. The critical time delay was instrument setup dependent and was chosen based on the location of the minimum of the histogram of the time-delay response (see Fig. 2 in Shiraiwa et al., 2007).

2.3 The hygroscopicity framework and its relationship to aging

To analyze the growth factor data in terms of aging, the data were converted into an equivalent hygroscopicity parameter, κ , (Petters and Kreidenweis, 2007) using:

$$\kappa = \frac{(gf^3 - 1)(1 - a_w)}{a_w}$$
$$a_w = RH \exp\left(\frac{A}{gf D_d}\right) \quad (1)$$

where, $gf = D/D_d$ is the diameter growth factor, D is the diameter, D_d is the dry diameter, a_w is water activity, RH is the fractional relative humidity, $A = 8.69 \times 10^{-6}$, T [K] is temperature, and σ [J m^{-2}] is the surface tension of the aqueous solution/air interface. Here, $\sigma = 0.072 \text{ J m}^{-2}$ and $T = 298.15 \text{ K}$ are chosen as reference state. Physically, κ represents the amount of water associated per unit dry volume normalized by relative humidity.

For idealized multicomponent particles, e.g., a spherical rBC core with an ammonium sulfate coating, the overall κ of the particle can be computed using the following mixing rule

$$\kappa = \sum \epsilon_i \kappa_i \quad (2)$$

where ϵ_i is the volume fraction and κ_i is the hygroscopicity parameter of the i th component in the particle. For a non-hygroscopic and insoluble compound $\kappa = 0$. Equation (2) predicts that for a coating with a constant effective κ , coating thickness and observed overall κ , or growth factor, form a unique relationship that can be retrieved directly from the HTDMA-SP2 data.

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Models consider a BC particle to be “aged” if it has acquired sufficient coating material to serve as a CCN. Conceptually it is helpful to choose a typical maximum supersaturation for different cloud types, e.g. $s=0.2\%$ for stratus clouds and $s=1\%$ for cumulus clouds. The question of whether a particle is aged or not can then be addressed by computing the critical supersaturation of each particle and decide whether these threshold values are met. In practice, the critical supersaturation required for the particle to serve as CCN can be estimated from the measured dry size and overall κ by finding the maximum of Eq. (6) in Petters and Kreidenweis (2007). Thus BC aging can be understood in terms of coating thickness if the effective κ of the coating material is known. BC emitted with a coating or other hygroscopic inclusion will be considered aged by this definition. In practice, the number fraction of aged particles is computed by assigning a threshold growth factor for each dry size above which the particle is CCN active. The relative number fraction of aged particles is then computed by integrating the growth factor distribution above the threshold value and dividing by the total rBC number concentration detected during the scan. Deviations from this idealized model will be discussed in detail later.

3 Results

Example raw data scans with minimal processing applied are shown in Figs. 2 and 3. These figures correspond to a single scan over the humidified size distribution. Scan times depended on observed particle concentrations, but they were typically between 10 and 30 min. Figure 2 shows an example for ambient aerosol and contrasts a typical growth factor distribution measured by the CPC with the SP2-derived distributions for scattering and absorbing particles. The mean diameter of the rBC cores (D_{BC}) as a function of gf is superimposed. The D_{BC} calculations were restricted to the singly-charged particle mode, which was identified from the mass distributions produced by the SP2. The rBC core diameter decreased with increasing growth factor consistent

with the expectation that hygroscopic rBC was coated. For this particular scan the difference in rBC core diameter suggested a coating thickness ~ 20 nm (Fig. 2).

3.1 Pure rBC proxy materials

We characterized the HTDMA-SP2 system using three different rBC proxy materials (glassy carbon spheres, aquadag and carbon black) that have been used previously to evaluate SP2 measurements (Moteki et al., 2010; Schwarz et al., 2010). All three rBC proxy samples had a dominant non-hygroscopic mode that was centered at $gf \sim 1.0$ (Fig. 3a–c). The combination of rBC and non-rBC particles detected by the SP2 was in agreement with CPC measurements for all scans. The $gf=1$ mode was dominated by rBC particles for all three proxy materials.

3.2 Mixtures of rBC proxies, ammonium sulfate and malonic acid

To test the ability to detect coatings and mixing state we atomized mixtures of the carbon black rBC proxy particles and ammonium sulfate or malonic acid. Examples of two HTDMA-SP2 scans for the mixtures of carbon black with ammonium sulfate and carbon black mixed with malonic acid are shown in Fig. 3d,e, respectively. The hygroscopic mode dominated the non-hygroscopic mode for both cases, but the non-hygroscopic mode could still be observed, centered at $gf=1.0$. The non-hygroscopic mode was dominated by rBC particles and the hygroscopic mode dominated by non-BC particles. The sum of SP2-measured rBC and purely scattering particles was in agreement with the CPC concentrations. The gf 's measured for the hygroscopic modes (1.75 and 1.6) were consistent with what we expected for pure, 193 nm diameter ammonium sulfate ($gf=1.76$) and malonic acid ($gf=1.67$) particles at $RH=90\%$. Unlike the “pure” rBC proxy compounds shown in Fig. 3a–c, the mixture cases featured a small concentration of rBC-containing particles detected as a tail extending into the hygroscopic mode. We believe that these particles were coated with either ammonium sulfate or malonic acid.

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3.3 Manchester ambient sampling

Two ambient gf scans are shown in Fig. 3f, g. These scans exhibited a non-hygroscopic mode centered at $gf=1.0$ and a hygroscopic mode centered at $gf\sim 1.5$. Examination of the SP2 measurements revealed that the non-hygroscopic mode was dominated by rBC, but there was a substantial contribution by non-rBC particles to the non-hygroscopic mode. The results differ from our observations during the mixture and single component tests and indicated the presence of additional non-hygroscopic particles that do not contain rBC. The hygroscopic mode was dominated by purely scattering or non-rBC containing particles, however the 16 August measurements (Fig. 3g) showed an appreciable increase of rBC particles in the hygroscopic mode, similar to the mixed test case results, but even more pronounced.

Figure 4 shows aerosol hygroscopicity measured by the HTDMA-SP2 system during the entire ambient sampling period between 5 and 16 August 2010. Contrary to the data in Fig. 2, these data were inverted as described in the methods section. We converted measured gf into κ and separated the measurements of rBC-containing particles, purely scattering particles, and total particles identified by the SP2 (that were also in agreement with CPC results). The total particle results showed the near-continuous presence of non-hygroscopic and hygroscopic modes centered at $\kappa=0$ and 0.4. rBC-containing particles were found mostly in the non-hygroscopic mode, though we did observe periodic increases in hygroscopic rBC concentrations (e.g., 14–16 August). Purely scattering particles were primarily in the hygroscopic mode, but there was always a small contribution to the non-hygroscopic mode that for isolated periods became stronger. Overall concentrations fluctuated, reflecting changes in transport and local conditions.

We examined the meteorological conditions during the measurement period to provide a context for interpreting the HTDMA-SP2 ambient sampling results. Meteorological conditions during the ambient measurement period were unsettled, with frontal systems passing over the UK on the 3, 6, 9, and 12 August. As a result, Manchester

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experienced several days of cloudy, wet and windy weather. Ceilometer measurements taken from the roof of an adjacent university building indicated the nearly continuous presence of low-clouds (cloud deck beginning at 500–1500 m above the surface) between 6 and 14 August and several intermittent rain events. The pattern broke at roughly 12:00 UTC 14 August when a high-pressure ridge moved over the UK from the west, resulting in clear skies over Manchester.

Modeled backward trajectories, terminating at 500 m a.g.l. over the Manchester grid box, reflected the larger-scale flow. Several examples at selected times of interest are shown in Fig. 5. The two backward trajectories arriving on 3 and 7 August show typical flow patterns during the early portion of ambient measurements that featured frequent frontal passages and westerly flow. The flow pattern changes around the 14 August when flow over the Northern UK was influenced by the high pressure system and became easterly, as shown by the trajectories for 14 and 16 August. The backward trajectory for 12:00 UTC on 8 August shows a stronger northerly component compared to other trajectories during the westerly period.

Gridded carbon monoxide (CO) emissions from the UK National Atmospheric Emissions Inventory for 2008 are also shown in Fig. 5. Carbon monoxide and rBC are strongly correlated because both are emitted by incomplete combustion and previous SP2 measurements have shown strong rBC correlations with CO over the UK (McMeeking et al., 2010). In addition to Manchester itself, the largest CO (and rBC) emissions near Manchester are found in the Liverpool region to the west, the Leeds/Sheffield region to the east and the Birmingham and London urban areas to the south. The trajectories shown in Fig. 5 reaching Manchester from the west did not pass over large rBC/CO source regions, unlike those approaching from the east and south, which were also influenced by Continental Europe. Therefore we believe that samples taken towards the end of the study period contained BC that experienced longer processing times in the atmosphere.

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4 Discussion

4.1 Quantifying coating thickness

Our overall objective is to quantitatively relate coating thickness to the derived hygroscopicity. To do so we must discuss the uncertainties involved in coating thickness estimates. We now return to the pure model BC compounds (Fig. 3a–c). The mean rBC mass equivalent core diameters (D_{BC}) were near constant for $gf < 1.2$ and retrieved D_{BC} 's were slightly larger than the selected mobility diameter ($D_{mob} = 193$ nm). We calculated the effective density to convert D_{BC} to D_{mob} , finding $\sim 1\text{--}1.5$ g cm⁻³ for carbon black, aquadag, and glassy carbon. The same analysis for ambient samples suggested a much lower value of 0.6 g cm⁻³, suggesting a more fractal shape for ambient rBC. Moteki and Kondo (2010) reported a similar discrepancy between laboratory generated and ambient rBC measured in Tokyo. Constant density must be assumed in order to quantify a relative coating thickness (comparing uncoated vs. coated D_{BC}). However, it is likely that the rBC cores for thickly-coated particles collapsed to a more compact shape (Alexander et al., 2008; Zhang et al., 2008; Lewis et al., 2009). If this occurred, it would result in underestimation of rBC density translated into an overestimate of rBC core diameter and an underestimate of amount of coating present.

It is important to note that coatings do not affect D_{BC} (Slowik et al., 2007). Any decrease in rBC mass, or calculated diameter, must then be compensated by the presence of additional non-rBC material in order for the particle to have the same D_{mob} as a larger rBC particle (e.g., 193 nm). An alternative possibility is that the shape and therefore effective density of the rBC core changes, leading to a different inferred D_{BC} , but we do not expect this to occur for laboratory generated rBC proxies. Thus we treat the decrease in D_{BC} as a qualitative indicator for the presence of non-rBC material associated with the particle, i.e., a coating. The amount of non-rBC material was estimated by assuming it existed as a coating on a spherical rBC core and that the rBC density did not change with mobility diameter. Under these assumptions, the effective

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change in coating thickness is given as $\Delta D_{BC}/2$ as shown in Fig. 2.

According to Eq. (2), the gf 's of mixed particles should be proportional to the mass fraction of carbon black and ammonium sulfate in the particles. Here we calculated the non-rBC coating thickness and volume of material using the difference between $D_{mob}=193$ nm and D_{BC} , shown in Fig. 6. Superimposed are the expected relationships for ammonium sulfate, malonic acid and generic organic coatings assuming $\kappa_{BC}=0$, $\kappa_{AS}=0.53$, $\kappa_{MA}=0.44$, and $\kappa_{org}=0.1$ (Petters and Kreidenweis, 2007). We averaged the measured HTDMA κ values into hydrophobic and hygroscopic modes to account for the coarseness of the DMA transfer function. As expected, there was an increase in measured κ for increased rBC coating thickness, though measured κ exceeded the prediction. This may be due to increases in the core rBC density for coated particles leading to an underestimate of coating thickness as discussed earlier. There is no significant difference in the coating thickness versus κ relationship for the two different coating materials. However given their similar κ values of ammonium sulphate and malonic acid this is not too surprising.

4.2 Refractory black carbon “age”

Most of the ambient rBC cores were not coated and did not take up water. A relatively small fraction of the particles were coated with up to 20 nm thick layers as determined from the D_{BC} measurements (e.g., Fig. 2). These particles took up water and had a mode with an overall $\kappa \sim 0.2$ – 0.4 (Fig. 3). Should those particles be considered as aged, i.e. CCN active, in atmospheric models? Recalling our treatment of BC age from Sect. 2, we first quantify the relationship between the rBC core diameter, coating thickness, and critical supersaturation. The critical supersaturation required to activate a particle depends on the dry diameter and its κ . If a threshold supersaturation is defined (e.g. $s=0.2\%$ for stratus cloud conditions), the core diameter is known, and a value for κ of the coating is assumed, it is conceptually straightforward to find the critical coating thickness, defined as the thickness that is required to make the core CCN active. Note that coating a BC core will simultaneously increase the particle

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diameter and overall κ through the mixing rule given in Eq. (2), thereby necessitating an iterative procedure.

Calculated critical coating thicknesses are shown in Fig. 7 for a number of threshold supersaturations and assumed κ 's of the coating material. Also shown are two representative size distributions for rBC cores measured by Schwarz et al. (2008) to aid the interpretation. As expected from theory, smaller particles require larger coatings to meet the “aged” threshold. In the extreme case of $\{D_{\text{BC}}=50 \text{ nm}, s=0.1\%, \kappa=0.1\}$, the coating thickness that is required is $\sim 100 \text{ nm}$. Overall this corresponds to a 250 nm diameter particle which is completely dominated in mass by the coating material. In the other extreme $\{D_{\text{BC}}=300 \text{ nm}, s=1\%, \kappa=0.6\}$ a coating thickness of $\sim 0.1 \text{ nm}$ is sufficient to age the particle. Figure 7 can be used as state space to identify if a particular particle/coating combination is aged. For example consider an rBC particle with $gf=1.6$ shown in Fig. 2. Such a particle has $D_{\text{BC}}\sim 170 \text{ nm}$ and a coating thickness $\sim 20 \text{ nm}$ and its location in the state space suggests that this particular particle is sufficiently coated to activate at $s=0.1\text{--}0.2$, depending on the κ value of the coating. The critical coating thickness is surprisingly sensitive to the κ of the coating material, and hence the chemical composition of the coatings. The case study illustrates that taken in isolation neither coating thickness nor the measured rBC κ distributions are sufficient to diagnose the hydrophobic-to-hydrophilic conversion in the atmosphere.

4.3 Ambient rBC measurements

We calculated the number fraction of “aged” rBC particles (F_{aged}) using the previously discussed aging framework, treating all rBC particles with κ greater than that needed to activate at $s=0.2\%$ as aged. Figure 8 shows F_{aged} measured in Manchester during the ambient sampling period. F_{aged} remained low (<0.05) and relatively constant for the first eight days of measurements, which were dominated by westerly flow and featured several precipitation events. F_{aged} increased to ~ 0.25 during the last two days of measurements, starting at around midday on the 14 August. This coincided with the shift in wind direction from west to east and backwards trajectories passing over

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Continental Europe and North-Eastern England (Fig. 5). We attribute the increase in F_{aged} to the change in transport pattern. Previous airborne measurements over the UK have shown evidence of more aged aerosol associated with easterly transport from Continental Europe (e.g., Morgan et al., 2010).

The overall low fraction of F_{aged} observed throughout the observation period (typically less than 10%) reflected the importance of local urban rBC sources in close proximity to the measurement site. Even when long-range transport patterns shifted to bring continental pollution over the UK, it was super-imposed on the emissions from local sources in Manchester. The importance of local sources was also reflected by the nearly continuous presence of the non-hygroscopic rBC mode throughout the measurement campaign. There was more variability in the hygroscopic mode, which was dominated by non-rBC particles and reflected contributions by both primary and secondary sources. Riemer et al. (2010) characterized F_{aged} inferred aging time scales using a plume model. The HTDMA-SP2 method can be used in principle to validate this type of model if a lagrangian experiment design is implemented or the age of the black carbon particles could be ascertained.

The HTDMA-SP2 measurements also provided the first opportunity to examine the composition of hydrophobic particles. The HTDMA-SP2 measurements in urban Manchester showed that ~25% of the hydrophobic particles do not contain any detectable concentrations of rBC (Fig. 8). We suspect these particles were composed primarily of hydrocarbon-like organic aerosol (HOA), which has been measured by aerosol mass spectrometer at a number of urban locations, including Manchester (Zhang et al., 2005). This was expected because combustion processes that are responsible for BC emissions also emit particles that are composed of hydrophobic non-polar non-absorbing high molecular weight hydrocarbons (Saxena and Hildemann, 1996; Simoneit, 2002) which are typically described by $\kappa=0$. It is encouraging that the HTDMA-SP2 measurements may be able to probe the mechanisms by which these non-hygroscopic, but non-rBC particles are processed.

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4.4 Implications for SP2-only rBC measurements

The SP2 is also capable of obtaining independent information regarding the rBC mixing state through the analysis of the scattering and incandescence signals for single rBC-containing particles (e.g., Gao et al., 2007; Shiraiwa et al., 2007). These approaches have widely been used in the SP2 community to evaluate the mixing state of rBC (Schwarz et al., 2006, 2008; Baumgardner et al., 2007; Shiraiwa et al., 2007; Subramanian et al., 2010). Schwarz et al. (2008) used the SP2 to contrast rBC in urban and biomass burning dominated rural airsheds and found thinner coatings and smaller number fractions of coated particles in the urban sample. The number fraction of coated particles also increases by $\sim 1.9\% \text{ hr}^{-1}$ in the plume downwind of Tokyo, Japan (Shiraiwa et al., 2007), with sulfate and organics being the main contributors to the coatings.

We investigated whether the traditional SP2-only mixing state measurements could be related to rBC hygroscopicity. We calculated the average number fraction of “thickly coated” particles (see methods) for different growth factors. Figure 9 shows an example of the SP2 coating information for a single HTDMA-SP2 scan from the 16 August 07:00 BST, which was also shown in Fig. 2. We excluded multiply-charged particles from the coating analysis. Nearly all of the rBC particles detected in the hygroscopic mode ($gf > 1.2$) were classified as “thickly coated” using the time delay criterion, consistent with the need for additional material to compensate for the reduced rBC mass while maintaining a $D_{\text{mob}} = 193 \text{ nm}$. The coating thickness also remained constant for $gf < 1.2$ before increasing to approximately 40–100 nm for higher gf . The coating thickness inferred from the decrease in rBC mean diameter for the scan was approximately 15–20 nm. The presence of the water on the particles may also lead to an overestimate of the coating thickness, but this could be eliminated by adding an active drying system between the HTDMA and SP2 inlet which was missing in our setup.

Previous studies involving the SP2 have speculated that the addition of hygroscopic material to rBC particles during aging processes would increase the rBC hygroscopic-

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ity. The good relationship between different SP2-derived indicators of coatings shows that SP2 measurements may provide an independent measure of rBC hygroscopicity, if size/coating relationships such as presented in Fig. 7 are taken into account.

5 Conclusions

We have developed and tested a coupled HTDMA-SP2 system for measuring refractory black carbon (rBC) aerosol hygroscopicity. The HTDMA-SP2 distinguished rBC from “purely scattering” particles in laboratory and ambient sampling. We found that three different laboratory-generated rBC proxy materials, glassy carbon spheres, aquadag and carbon black, had $gf \sim 1$ and higher gf for carbon black mixed with two different hygroscopic compounds. Ambient sampling near Central Manchester showed the majority of rBC-containing particles were non-hygroscopic, with only 5–10% having $gf > 1.2$. The hygroscopic fraction increased following a change in transport pattern from the west (maritime Atlantic) to the east (continental polluted). Three independent qualitative measures of rBC mixing state (mean rBC core size, number fraction of “thickly coated” particles, and leading edge only inferred coating thickness) showed clear differences between hygroscopic and non-hygroscopic rBC particles for both laboratory-generated and ambient samples. We used the single parameter framework to estimate the number fraction of aged particles, i.e. particles that can undergo nucleation scavenging in clouds, and found that the aged fraction seemed to be controlled by the history of the air mass and was consistent with a mixture of local and regional sources. Future studies should combine this method with a measure of physical or photochemical age to provide quantitative estimates for characterizing hydrophobic-to-hydrophilic conversion rates in the atmosphere.

Acknowledgement. This work was supported by the NERC grant Multiscale Chemical Composition of Carbonaceous particles and Coatings (MC4), NE/H008136/1. Author contributions: M.D.P. and G.R.M. designed research; N.G. and G.R.M. performed research; H.C. and G.M.

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supported the research, provided equipment and guidance; N.G., G.R.M. and M.D.P. analyzed data and G.R.M., M.D.P., N.G., H.C. and G.M. wrote the paper. We thank Michael Flynn for providing ceilometer data, his input on the experiments and general support for the SP2 and James Whitehead for his assistance during the ambient sampling. Carbon monoxide emission data were provided by the UK National Atmospheric Emission Inventory website (<http://www.naei.org.uk/index.php>), which is supported in part by the UK Department for Environment, Food and Rural Affairs.

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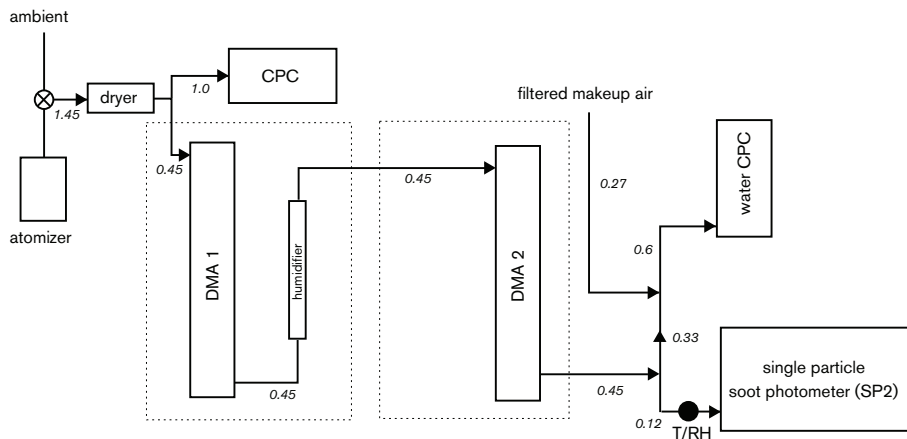


Fig. 1. Schematic of the instrument setup.

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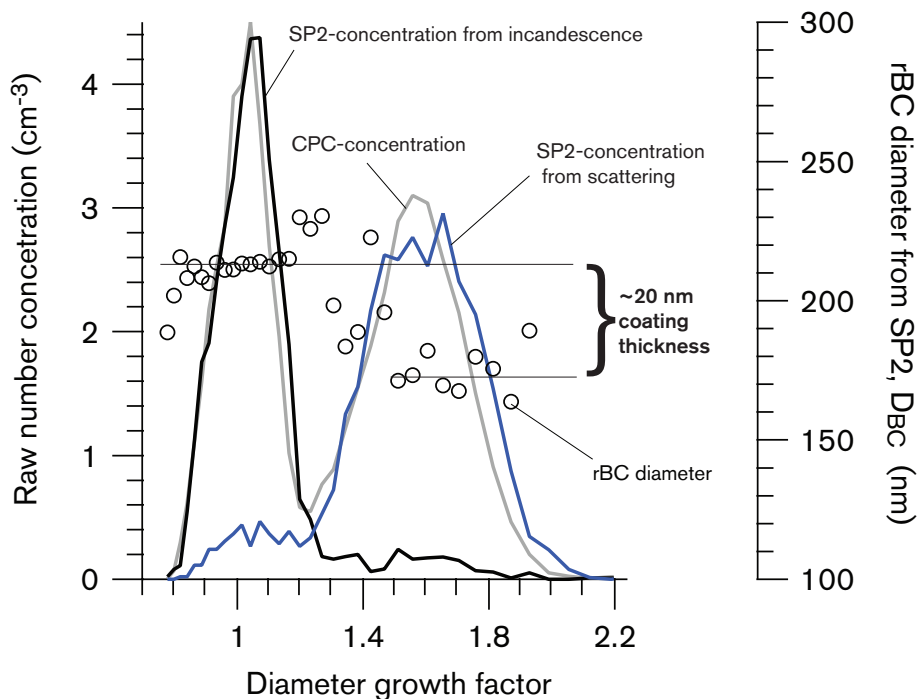


Fig. 2. Concentrations of total particles measured by the CPC, rBC and purely scattering particles measured by the SP2 and the mean rBC diameter determined from SP2 mass measurements plotted as a function of growth factor.

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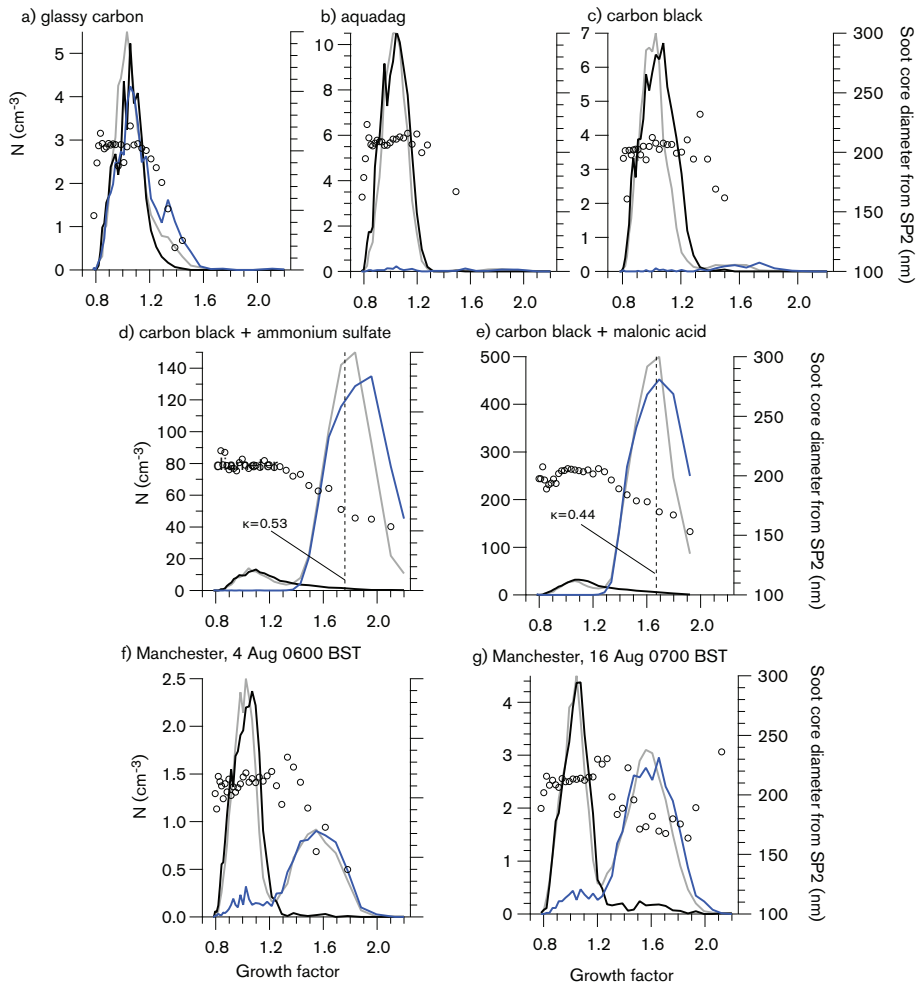


Fig. 3.

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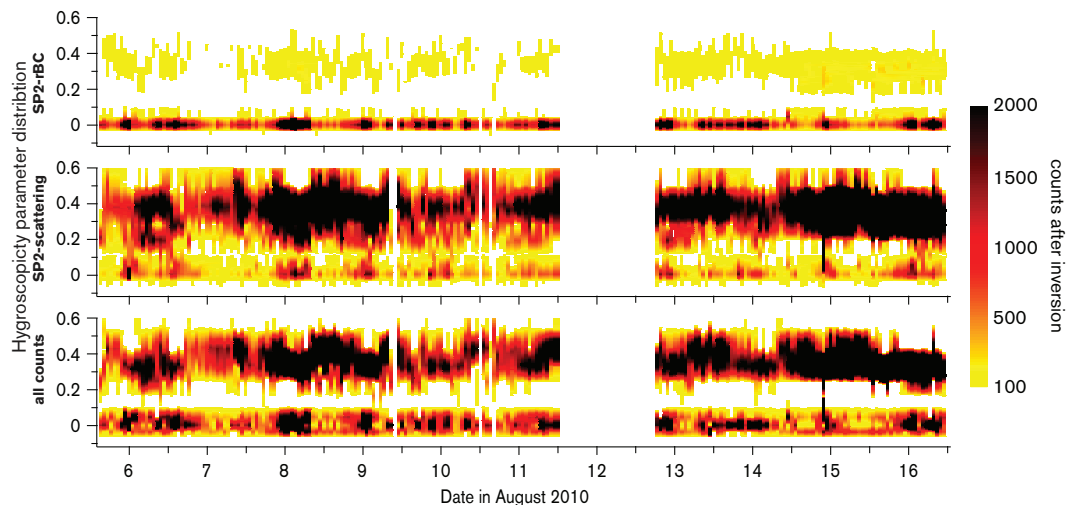


Fig. 4. Hygroscopicity parameters for mixed particle mobility dry diameter 193 nm ambient aerosol measured for approximately two weeks in central Manchester by the HTDMA-SP2. The top panel shows κ for rBC-containing particles only, the middle panel shows κ values for purely scattering particles and the bottom panel shows κ of the sum of rBC and purely scattering particle.

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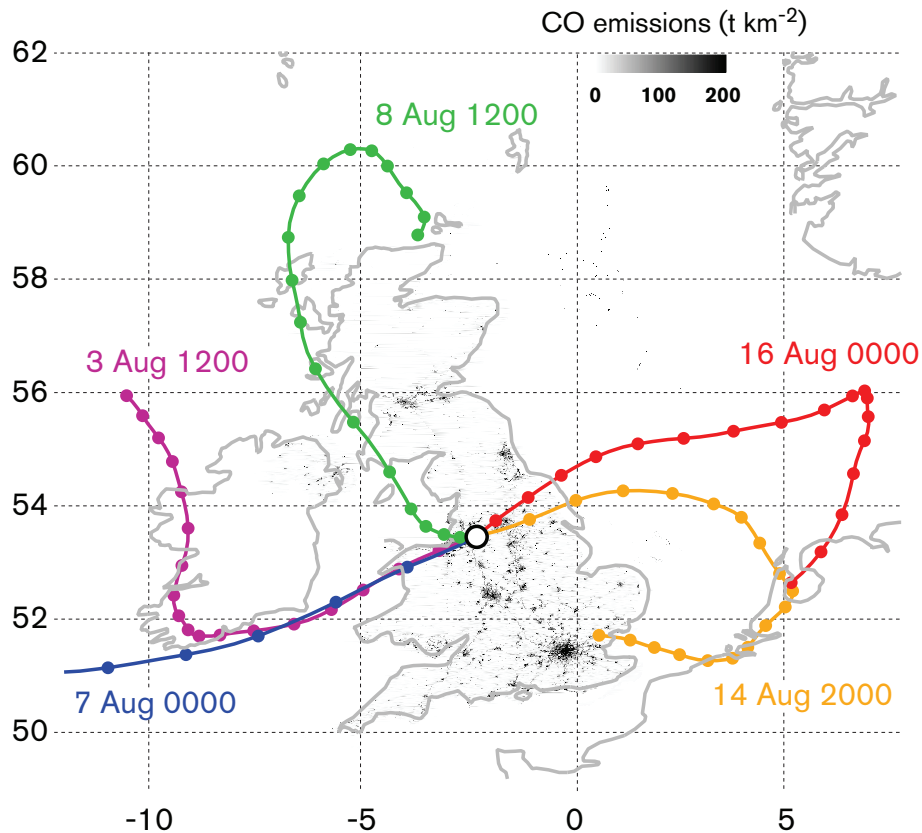


Fig. 5. Selected air parcel backwards trajectories computed from the NOAA HYSPLIT model (Draxler and Rolph, 2010) during ambient Manchester sampling in 2010 superimposed on the UK National Atmospheric Emissions Inventory carbon monoxide emissions inventory for year 2008.

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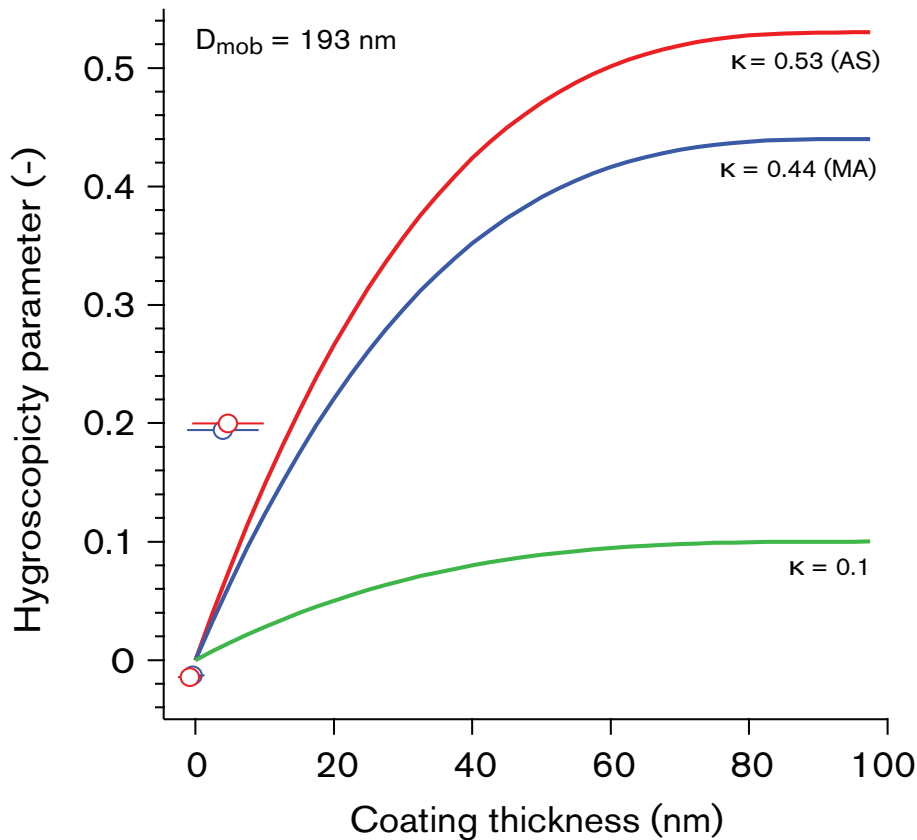


Fig. 6. Measured and predicted kappa for a two-component mixture of rBC (carbon black; $\kappa=0$) and coating with assumed κ value as a function of coating thickness derived from DMA dry diameter and SP2 derived rBC diameter.

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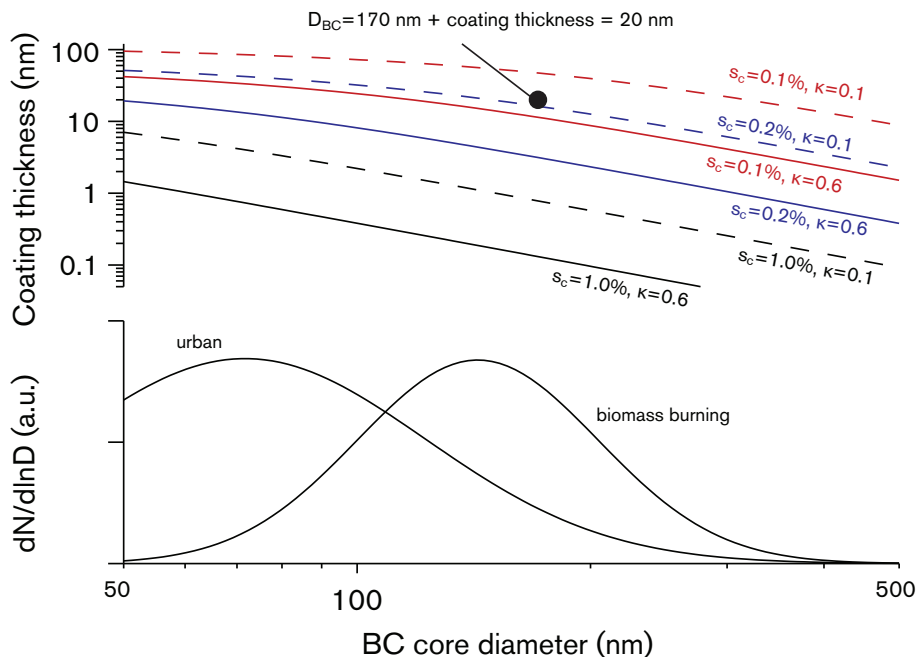


Fig. 7. Bottom plot: number distribution of refractory BC cores size distribution measured in fresh urban and biomass burning plumes reported by Schwarz et al. (2008). Top plot: coating thickness that a soot core must acquire before it can serve as CCN. Black, blue and red colors indicate the 1%, 0.2%, and 0.1% supersaturation threshold. Solid lines and dashed lines are computed assuming that κ of the coating material is 0.6 or 0.1, respectively.

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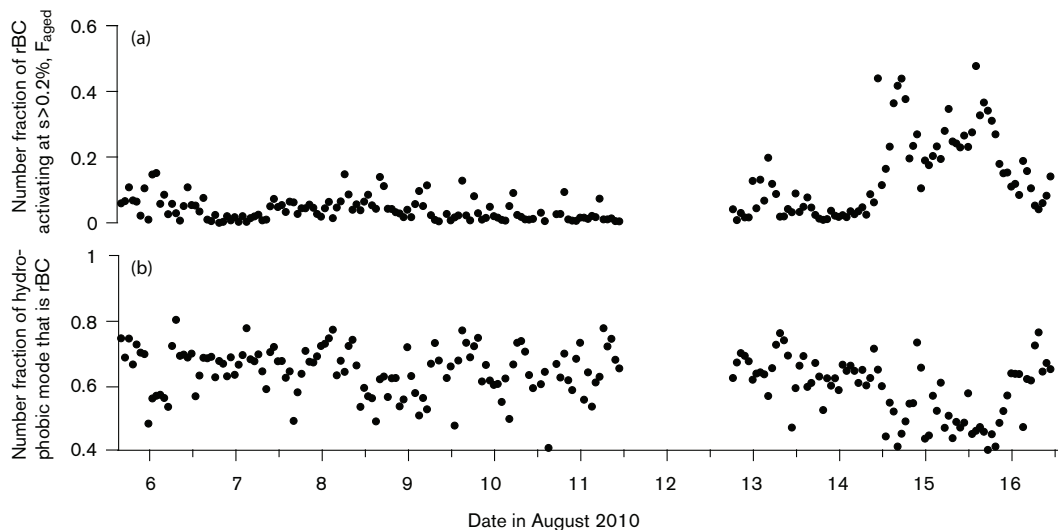


Fig. 8. Number fraction of rBC-containing particles that are CCN active at a supersaturation 0.2% for mixed particle dry mobility diameters of 193 nm as a function of time **(a)** and the number fraction of 193 nm non-CCN active particles that contain rBC **(b)** observed during the ambient Manchester sampling between 5 and 16 August 2010. Only periods when the HTDMA-SP2 system was operating at 90% RH are shown.

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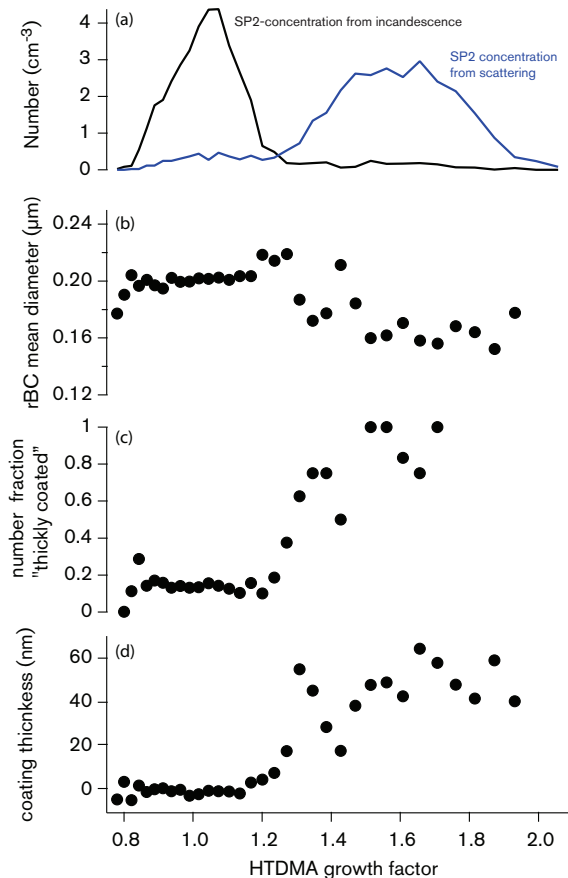


Fig. 9. SP2-derived coating information for a single HTDMA-SP2 scan starting at 07:00 BST on 16 August 2010. Shown are number concentration from scattering and incandescence detector **(a)**, rBC mean diameter **(b)**, number fraction of thickly coated rBC particles **(c)**, and coating thickness as a function of growth factor derived from mobility diameter and D_{BC} **(d)**.

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