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Black carbon absorption enhancement in the atmosphere determined by particle mixing state

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Atmospheric black carbon makes an important but poorly quantified contribution to the warming of the global atmosphere. Laboratory and modelling studies have shown that the addition of non-black carbon materials to black carbon particles may enhance the particles' light absorption by 50 to 60% by refracting and reflecting light. Real world experimental evidence for this 'lensing' effect is scant and conflicting, showing that absorption enhancements can be less than 5% or as large as 140%. Here we present simultaneous quantifications of the composition and optical properties of individual atmospheric black carbon particles. We show that particles with a mass ratio of non-black carbon to black carbon of less than 1.5, which is typical of fresh traffic sources, are best represented as having no absorption enhancement. In contrast, black carbon particles with a ratio greater than 3, which is typical of biomass burning emissions, are best described assuming optical lensing leading to an absorption enhancement. We introduce a generalised hybrid model approach for estimating scattering and absorption enhancements based on laboratory and atmospheric observations. We conclude that the occurrence of the absorption enhancement of black carbon particles is determined by the particles' mass ratio of non-black carbon to black carbon.

Atmospheric black carbon (BC) makes the second largest single contribution after CO_2 to climate forcing in the present-day atmosphere[1]. Previous detailed modelling and laboratory studies have shown that weakly absorbing non-BC materials contained within the same particles as BC can significantly enhance the absorption per unit mass of the latter through refraction and internal reflections, sometimes referred to as the 'lensing effect'[2,3]. A "core-shell" description[4] has often been applied to describe this effect when coatings envelop the central BC core, but this oversimplifies the complex particle morphologies[5]. The non-BC

components may not be evenly distributed and the BC core is not necessarily completely enclosed, and as such the absorption enhancement predicted using the core-shell approach could greatly overestimate the real value[3]. Microscopy[5,6] can examine BC microphysical properties but has limited quantitative capability and may evaporate semi-volatile materials. By detecting the remaining non-BC fragment after laser induced incandescence with a single particle soot photometer (SP2[7], DMT inc.), Sedlacek et al.[8] and Moteki et al.[9] reported the non-core-shell structure of some BC particles, however they did not provide an appropriate model approach to estimate optical properties.

Measurement of single BC particle mass ratio

In this study, for the first time we quantify the mixing state of individual BC particles using morphology-independent measurements of the total particle mass (M_p) and the mass of the refractory black carbon, rBC (M_{rBC}) from a variety of laboratory and field experiments. We determined the mass ratio, M_R (= $M_{non\text{-}BC}/M_{rBC}$), where $M_{non\text{-}BC}$ is the mass of non-BC material in a BC containing particle:

$$M_{non\text{-}BC} = M_p - M_{rBC} \quad (1).$$

We then challenge different models of the BC optical properties and in so doing, determine the optimum model description.

Fig. 1 shows the ambient traffic BC number has a maximum at a M_R of 0.3. The peak in the laboratory diesel BC number distribution during normal engine running conditions (NR) is at M_R=1, consistent with volatility measurements from diesel engines[10]. The higher M_R measured in the laboratory compared with ambient traffic could result from evaporation of coatings in the ambient or differences in sources. Diesel generated under cold idle conditions in the laboratory (CI) generates particles with a range of M_R after injection in the chamber as

a result of coagulation effects. Ambient BC dominated by solid fuel (SF) burning exhibits a much higher M_R. Data taken during bonfire night (BN) has a higher M_R than SF.

The transitional behaviour of BC optical properties

The single particle scattering cross section of BC at 1064 nm (S_{model}) is estimated using a number of models and compared with direct measurements ($S_{measure}$), integrated over the collection solid angle of the detector. The model approaches (see Methods) make different assumptions about the physical configuration of BC containing particles. These are that the BC and non-BC components are mixed: (a) effectively externally, with BC and non-BC components contributing independently to the total scattering; (b) such that the BC is enveloped by non-BC materials in a core-shell arrangement; (c) homogenously and modelled using either the Maxwell-Garnett or Bruggemann mixing rules, and (d) the different components exist as an agglomeration of smaller, independent particles in a core-shell configuration, according to a simplified Rayleigh-Debye-Gans (RDG) model[11]. The refractive index of rBC, m_{rBC}, at 1064nm is 2.26+1.26i[12,13] and coating refractive index is 1.5+0i[11]. The material density (used to calculate volume) of rBC (ρ_{rBC}) is set as 1.8 g cm^{-3} [14], the calculation of the associated non-BC density (ρ_{nonBC}) is described in Methods.

If the BC is not at the centre of the particle, the particle will scatter less than the ideal core-shell prediction [3]. We present an extreme hypothetical case of this situation using a model that treats the BC and non-BC components as independent but coincident optical scattering elements, in other words as externally mixed particles (although still part of the same detection event). In the following comparisons, the concentric core-shell approach (S_{c-s}) is used as a reference for modelling the absorption enhancement[3], and both $S_{measure}$ and S_{model} are normalized to S_{c-s}. When $S_{measure}/S_{c-s}$ is less than unity, it is likely that the 'lensing' effect is reduced. Fig. 1 shows $S_{measure}/S_{c-s}$ and S_{model}/S_{c-s} as a function of M_R for 2fg mass selected

particles from different sources (this mass chosen as it presented the best data coverage across all values of M_R, see top panel of Fig. 1). When M_R<0.1, $S_{measure}/S_{s\text{-}c}$ is close to unity and all models are in close agreement. This indicates that Mie calculations are appropriate for the light scattering of uncoated BC, validating the choice of m_{rBC} and the insensitivity of the Mie calculations to the morphology of largely externally mixed BC at 1064 nm.

When M_R is between 0.1 and 1.5, $S_{measure}/S_{s\text{-}c}$ is consistent with the $S_{model}/S_{s\text{-}c}$ values derived using an externally mixed model. This could be because the non-BC material is not sufficient to encapsulate the BC, but is instead partially filling in the voids between BC spherules or attached to them, consistent with Moteki et al.[9]. For M_R > 3, we find the measured scattering cross section is best reproduced by the core-shell model. The sensitivity of S_{model} to the assumed non-BC density may partly explain $S_{measure}/S_{c\text{-}s}$ >1 in this region. Some individual particles with high non-BC content may not be core-shell-like[6], however this has not affected the statistics derived here. When M_R is above ~20, all models tend to agree, as the behaviour converges on that of almost pure non-BC material. Similar phenomena are found at other particle masses (Supplementary Fig. 7). The range of M_R values over which neither the external nor internal mixing assumptions effectively describe light scattering by BC particles is relatively narrow for all particle sizes. Models with different representations of internal mixing do not yield significantly different values of S_{model} compared to that of the core-shell model.

The additional non-BC material causes the measured light scattering cross section to be greater than that calculated for the bare BC core and we term this ratio the scattering enhancement (E_{sca}) (Supplementary Fig. 8A). The large fraction of the scattering in the near infrared results from the high real refractive index of rBC, and as such in the majority of scattering occurs within the core. Thus we expect that the phenomenon that causes E_{sca} will

have a similar effect on absorption enhancement (E_{abs}), defined as the ratio of the absorption cross section of the measured particle to that of the BC core in isolation.

The measured and calculated BC absorption enhancement

Our single particle measurements of M_p and M_{rBC} show that M_R can be directly related to E_{sca} (Supplementary Fig. 8B) and hence we can derive M_R values for experiments (see supplementary section S9) where particles were not selected by mass prior to measurement (Fig. 2A). A hybrid optical model is introduced, where it is assumed there is no E_{abs} for a single particle when M_R is below the lower transition threshold, and is linearly interpolated to the upper threshold, where the enhancements are modelled using core-shell. In the experiments conducted with no mass selection, the E_{abs} for single particles in each experiment were determined and used to estimate M_R and derive the bulk E_{abs} for the ensemble of particles. To make the results directly comparable with recent literatures reporting bulk properties, we have also used the measured single particle M_R to derive an average M_R of the particle population ($M_{R,bulk}$, see Methods) and conducted direct measurements of the absorption of the ensemble. Our experiments using laboratory diesel clearly exhibit the transitional behaviour of E_{abs} with increased M_R and are well predicted by our hybrid model (Fig. 2C). This contrasts with the calculations using the core-shell model, which overestimates E_{abs}. A repeat experiment to that (shown as star markers in Fig. 2C) was conducted and showed consistent behaviour. The ambient results (see Methods, Supplementary Table 3) also demonstrate good agreement between the hybrid model and the measured E_{abs} and improved performance of the model compared to other approaches.

The calculated bulk E_{abs} for other datasets using this approach are shown in Fig. 2B and are in good agreement with E_{abs} derived from our measurements where these are available. The majority of BC from urban traffic sources is best described as externally mixed, with overall

calculated bulk E_{abs} <1.2; the relatively wide range of M_R for traffic sources in rural or semi-rural environments may reflect different ages of BC and this may account for differences between our near-field values and those previously reported from processed traffic sources[15]. The ambient solid fuel BC has not been isolated because of the ubiquity of traffic sources in the urban environment. The BC from mixed traffic and solid fuel burning has a bulk E_{abs} of 1.2-1.4, consistent with a recent study[16], though the $M_{R,bulk}$ in our study is lower because of the high influence of fresher urban traffic sources. Bimodal behaviour is likely when sampling mixed sources as traffic BC dominates at low E_{sca} and solid fuel or biomass burning sources show high E_{sca}[17] since the BC is largely mixed with non-BC materials. The latter significantly contributes to enhanced bulk E_{abs}. Such transitional behaviour in E_{abs} has previously been reported in the literature for laboratory-generated BC from biomass burning[18] and controlled flames[19]. The E_{abs} derived from $M_{R,bulk}$ measurements may differ significantly because of the different distributions of M_R in single BC particles and the nonlinear effects this introduces.

Global model application

The approach we have presented provides a robust and generic method for determining when absorption of BC is significantly enhanced by non-BC material based solely on the relative abundance of the mass of BC and non-BC within a single particle. To assess its implications, we use the global model of Mann et al., (2010)[20] that represents aerosol using a modal scheme. Fresh BC is considered 'insoluble' until particles have undergone sufficient atmospheric processing. The M_R was calculated for each aerosol mode in each grid box of the model. Fig. 3 shows that the mixing state varies dramatically depending on source (Supplementary Fig. 12) and region. The frequency distributions of M_R in the main pollution regions show consistent behaviour with our measurements (Fig. 2), specifically high M_R

values in biomass burning regions and lower M_R values in regions dominated by fossil fuel emissions. Biomass burning BC has significant associated non-BC material and should be represented as internally mixed but fresh BC from traffic should be treated as effectively externally mixed with no absorption enhancement. These model results highlight that there is a need to consider the effect of the variation of mixing state on the particle optical properties and point to a consistent approach to examine the role of optical enhancement of atmospheric BC absorption in global models.

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Data availability. Processed data is available through the archive at the British Atmospheric Data Centre (http://badc.nerc.ac.uk/browse/badc/), with search term “COMPART”. Raw data is archived at the University of Manchester and is available on request.

Competing financial interests

The authors declare no competing financial interests.

Figure captions

Fig. 1. The measured and modelled optical properties as a function of mass ratio. Panel A shows the particle number distribution against M_R under environments; Panel B shows the single particle scattering cross section (at 2fg mass) derived from various optical models and from direct observation, relative to the core-shell model. Each point represents the median value of single particle data in each M_R bin. The bars represent the variation from varying non-BC density between 1.0-1.2 g cm^{-3} (BN and SF) and 0.9-1.1 g cm^{-3} (cold idle). The grey bar shows the range of M_R when transition occurs.

Fig. 2. The BC optical properties and mass ratios from a wide range of sources. A) Histograms of E_{sca} for poly-dispersed BC particles. The top axis shows the corresponding M_R. The grey column denotes the transition of optical properties. B) The calculated bulk E_{abs} using the hybrid model, solid round markers apply for the internal mixing fraction at transition with bars showing the variation by varying the lower threshold of M_R. The green triangle markers are direct observation. C) The measured and modelled (Mie core-shell and hybrid model) bulk E_{abs} as a function of $M_{R,bulk}$, the bars are standard deviation over mean.

Fig. 3. The annually averaged global distributions of M_R at the surface for insoluble and soluble Aitken mode aerosol modelled using GLOMAP. The subpanels show the BC M_R histograms of both modes representing the regions with greatest BC emissions. The grey bar in each histogram shows the range of M_R values below which the optical properties of BC

particles should be treated as externally mixed and above which they should be treated as internally mixed.

Methods

Data and analysis methods. The laboratory study was conducted as part of the Combustion Particles in the Atmosphere: Properties, Transformations, Fate & Impacts (COM-PART) project. The experimental configuration is schematically shown in Supplementary Fig. 1. The diesel soot is sampled from the Manchester Aerosol Chamber (18 m^3 collapsible teflon bag) after the injection of exhaust from an automotive VW 1.9L SDI diesel engine on a dynamometer rig (CM12; Armfield Ltd., Hampshire, UK) that was fitted with an oxidising catalytic converter. This is considered representative of emissions from EURO 4 light-duty diesel engines, which are in widespread use throughout Europe. A normal running condition (2000rpm, 30% load and 10 minutes warm up, referred as NR) and a cold idle condition (CI) without warm up or engine load were investigated.

The ambient experiment was conducted in the Manchester urban environment from 29/10-10/11 in 2014, covering the UK festival known as Guy Fawkes' or bonfire night (BN), marked by a large number of intensive open wood fires and fireworks across the country. In addition, solid fuel burning (principally wood) is a significant source of fuel for residential heating during the winter season in the UK[21,22]. All measurements are performed on dry particles.

The source contribution was found by applying the Multilinear regression (ME-2) factorization[23] to the organic aerosol (OA) mass spectra measured by the aerosol mass spectrometer (AMS). This method uses target profiles (TP) as inputs to the model. Five OA sources were identified: solid fuel burning OA (SFOA), hydrocarbon-like OA (HOA, related to traffic emissions), cooking OA (COA), semi-volatile oxygenated OA (SVOOA) and low volatility oxygenated OA (LVOOA). The bonfire period is identified by the strong enhancements of the aerosol loading from 18:30, 05/11/2014 to 03:30, 06/11/2014

(Supplementary Fig. 2A). The first is to determine a solution representing the non-bonfire period. The best fit (total local minima Q/Q_{exp} = 3.4) is obtained by constraining the solution using the Paris TP [24], which constrains traffic OA with an a-value of 0.1 and cooking OA with an a-value of 0.5; and a total Q/Q_{exp} of 4.4 was obtained using London TP. The second step included data from the entire period and extrapolated the solution space for SFOA, HOA and COA from the first analysis. The best fit is obtained with a-values of 0.3 for SFOA and 0.1 for HOA and a total Q/Q_{exp} of 3.9 (Supplementary Fig. 2B). Wood and solid fuel burning sources of organic matter during BN cannot be separated by ME-2, but the two distinct time periods are presented separately as BC may feature differently. Supplementary Fig. 2C shows that during the morning rush-hour (07:30-10:00) traffic represents the major source, whereas between 20:00-23:00 solid fuel burning significantly contributed in addition to the traffic source.

We measured M_p and M_{rBC} of the same individual particles in each experiment by novel coupling of a Centrifugal Particle Mass Analyser (CPMA, Cambustion Ltd) [25], which selects particles of known and quantifiable charge-to-mass ratios across a narrow and well-defined distribution, and a single particle soot photometer (SP2, DMT Inc.), which is introduced downstream of CPMA and determines M_{rBC} and the intensity of scattered light at 1064nm for each BC particle sampled.

The incandescence signal of the SP2 is proportional to the M_{rBC} but independent of the particle morphology and coatings [26], which is calibrated using the material considered to only contain rBC, after all of the coatings have been removed. This is best represented by the laboratory-generated diesel soot that has not undergone photochemistry. We tested the SP2 response to soot produced from the diesel engine under normal running (NR) and cold idle conditions after particles had passed through a thermodenuder at 400°C and were mass-selected using a CPMA. At the same particle mass, a higher incandescence signal of the SP2

means the particle contains a higher mass fraction of rBC. As Supplementary Fig. 3 shows, the thermodenuded NR contains a higher fraction of rBC whereas the coatings of cold idle BC may have not been completely removed. We therefore used the thermodenuded BC core mass from the NR experiment as the calibration when determining rBC mass. The uncertainty of the measured M_{rBC} is <3% (from calibration). Note that for all CPMA data presented here, the default M/dM resolution of 5 was used, according to the FWHM of the transfer function described by Olfert and Collins [25]. While this translates to a precision of 20% for single particles, we should note that the average masses (and mass ratios) of the particle ensembles should be considerably more accurate, as these are the averages of many different particles. The multiply charged and neutral particles exiting CPMA are screened out through SP2 data processing (rejecting particles whose M_{rBC} or measured scattering cross section are outside of a plausible range) and M_R is only calculated for singly charged particles.

The detection efficiency of the SP2 was determined by measuring the NR diesel soot downstream of the CPMA in parallel with a condensation particle counter (CPC). The volume equivalent diameter (D_{ve}) of rBC is obtained by assuming an rBC density of 1.8 g cm^{-3} [27]. By assuming the CPC is detecting particles with 100% efficiency, the SP2/CPC ratio can be considered to be the detection efficiency of the SP2 (Supplementary Fig. 4). An increase in the laser power of the SP2 can increase the detection efficiency of the smaller rBC. The scattering cross section of 200nm PSL at λ=1064nm integrated over the detectable solid angle of the SP2 ($C_{sca,PSL200}$) is 314.16nm^2, and the laser power is measured as the SP2 scattering signal relative to the $C_{sca,PSL200}$. In this study, a laser power of 14.76*$C_{sca,PSL200}$ (laser current 3000mA) is used for the laboratory study and a laser power of 12.32*$C_{sca,PSL200}$ (laser current 2800mA) is used for the ambient experiment. Both laser powers give a collection efficiency of over 80% for rBC mass >0.2fg. Considering that the size of primary spherules of soot are

30-50nm [28], equivalent to D_{ve} in the range 0.02-0.1fg, this SP2 detection efficiency is sufficient to measure the small rBC.

The scattering signal of BC measured by the SP2 is processed using a leading edge only (LEO) technique to reconstruct the distorted scattering signal when BC passes through the SP2 laser beam [29]. The LEO methodology is detailed in Liu et al.[22]: briefly, the scattering signals for the last 200 non-BC scattering-only particles are used to determine the laser profile; the number of data points used for LEO is optimised to represent the scattering signal before the onset of particle volatilisation, and is automatically obtained by comparing the measured signal and laser profile, with uncertainty <12% (from the parametrization of the LEO fitting). Only single particles with successful LEO fitting are included in the calculation of optical properties.

Wavelength-dependent absorption coefficient (in Mm^{-1}) was measured by a photoacoustic soot spectrometer (PASS-3, DMT). The PASS-3 green (532 nm) channel was calibrated using absorbing polystyrene spheres referenced to a certified NO_2 standard [30]. The blue (405 nm) and red (781 nm) channels were matched to the green using thermally denuded diesel particles, assuming an absorption Ångström exponent (AAE) of unity [31].

The effective density (ρ_{eff}) of soot particles was obtained from equation (2) by measurements of the mobility diameter (D_{mob}) using an SMPS downstream of the CPMA which determined the particle mass (M_p),

$$M_p = \frac{1}{6}\pi D_{mob}^3 \times \rho_{eff}, \qquad (2),$$

At the same mass, a lower ρ_{eff} indicates a more fractal particle shape [32]. The NR diesel soot particles have a more fractal shape compared to Cold Idle (Supplementary Fig. 5). The lack of dependence of ρ_{eff} for Cold Idle implies that the particle shape is approaching spherical,

and so the D_{mob} under Cold Idle conditions represents its geometric diameter. The density of coating ($\rho_{non\text{-}BC}$) can then be obtained from Equation (3),

$$(M_p-M_{rBC})/\rho_{non\text{-}BC}+M_{rBC}/\rho_{rBC}=M_p/\rho_{eff}, \quad (3),$$

Using a ρ_{rBC}=1.8 gcm^{-3} and the SP2 measured M_{rBC}, the $\rho_{non\text{-}BC}$ is calculated to be 1.04-1.07gcm^{-3} for CI diesel soot. The NR diesel soot may have a different $\rho_{non\text{-}BC}$ due to different composition of the non-BC fraction. The density of oxidised organic aerosol has previously been determined to be approximately 1.3 g cm^{-3} [33]. Given that in wintertime the non-BC materials associated with ambient BC are mainly composed of primary organic matter with a lower degree of oxidation [34], a range of $\rho_{non\text{-}BC}$=1-1.2 g cm^{-3} [35] has been used here. The laboratory-generated soot is freshly formed and contains little associated secondary materials, thus a lower range of $\rho_{non\text{-}BC}$=0.9-1.1 g cm^{-3} is used.

Note that this variation in effective density will cause changes to the transfer function of the CPMA (according to the equations in Appendix A3 of the CPMA manual), effectively causing the M/dM resolution to vary from the nominal 5 by approximately ±20% - in the case of 2 fg undenuded particles, depending on the source. However, because we do not report CPMA-selected number concentrations and the effective density does not influence the median mass delivered, the effect of the resolution function here is limited to a 'smoothing' of the data in Fig. 1 and supplementary Fig. 7. For example, in the 2 fg case, this will be a smoothing in M_R space of between 17 and 25% (relative FWHM of a pseudo-triangular function), which is small compared to the overall trends presented here.

Modelling methods. The different model approaches for single BC particle optical properties are shown in Supplementary Fig. 6. The term externally mixed assumes the BC component (black sphere) is physically separated from the non-BC component (blue sphere), and the BC and non-BC will scatter the light independently. The idealised core-shell assumes the BC core is concentrically located inside the non-BC but remains in a separate phase to it. The

homogenous mixing model assumes the BC component has been well mixed with the non-BC at the molecular level. The Rayleigh-Debye-Gans (RDG) approximation simplifies the particle morphology by assuming the black carbon core is composed of many small primary spherules. The scattering is integrated over the specific collection solid angle of the SP2 detector thus the asymmetry parameter of scattering is not relevant for this study.

Modelled scattering cross sections are compared to measured values for different particle masses in Supplementary Fig. 7. The grey bars show the M_R for the transition of optical properties. The BC is considered to be effectively externally or internally mixed when the externally mixing (S_{ext}) or core-shell model ($S_{c\text{-}s}$) can reproduce the measured scattering within 20%; the BC with measured scattering above 20% of the S_{ext} but below 20% of the $S_{c\text{-}s}$ is considered to be within transition region. The results are summarized in Supplementary Table 2. At small particle masses, such as 1fg, the transition occurs at a lower threshold M_R compared to that at particle mass 2fg (Fig. 1), because a proportionally smaller non-BC mass is necessary to encapsulate a smaller BC core. A fraction of the particle number population from the diesel engine emission may include particles with mass below 1fg, however the M_R is not determined for the smaller masses as a result of instrument limitations. The masses of these small particles are not significant and are therefore not thought to be important for the bulk optical properties. Large particle mass also decreases the threshold M_R, possibly resulting from the increased absolute amount of non-BC material for larger particles. For particle masses of 5fg and 10fg, at the same M_R, the BN source has a higher measured scattering compared to TR source. This may result from different formation mechanisms of BC from different sources.

The model-calculated scattering enhancement (E_{sca}) at 1064nm using the Mie-core-shell and external mixing approaches at different particle masses is shown in Supplementary Fig. 8A. The modelled results, which will be used as references, are to large extent independent of

total particle mass. Supplementary Fig. 8B replicates these modelled curves and compares them with the SP2 measured E_{sca} for the different BC types in the experiments presented in this paper. The observationally derived E_{sca} shows a clear transition from agreement with the optical model assuming externally mixed BC and non-BC components for $M_R<1.5$ to agreement with the optical model assuming a core-shell arrangement with the BC at the centre of a non-BC coating for $M_R>3$. We have determined an average curve based on the data from all BC sources shown and used this to convert the measured E_{sca} to M_R for our much wider set of data when only the SP2 data were available.

In the transition regime, an internally mixed fraction (F_{in}) is derived using a combination of the Mie-core-shell and the external mixing model that best matches the relationship between M_R and E_{sca} from the average of the observations in that region (Supplementary Fig. 8B, top panel). The E_{abs} in the transition regime can be calculated as:

$E_{abs}=E_{abs,c\text{-}s}\times F_{in}+(1-F_{in})\times 1$ (4), where

$F_{in}=0.57\times M_R-0.74$ (when $1.5<M_R<3$) (5),

Where $E_{abs,c\text{-}s}$ is the E_{abs} calculated by Mie core-shell model. There is no absorption enhancement in the model when the components are assumed to be externally mixed so $E_{abs}=1$ in this case.

Supplementary Fig. 9A shows the evolution of BC properties since the engine emission injection. For the laboratory diesel engine experiments conducted under cold idle conditions, an increase of BC coatings was observed due to coagulation in the aerosol chamber over time, whereby rBC-containing particles coalesced with those that contained no rBC (Supplementary Fig. 9A). The rBC mass and absorption coefficient (B_{abs}) were measured by the SP2 and PASS-3 respectively. The PASS-3 periodically samples internally filtered air to determine the instrument baseline. The gap in the data was due to an external filter test

carried out on all of the instruments. The mass absorption cross section (MAC) is calculated as the mass absorption per unit mass of rBC. The MAC for uncoated bulk rBC core is calculated using Mie theory (with a refractive index 1.85+0.71i [27]) over the rBC core size distribution for each timestamp. The calculated MAC for uncoated BC in the green is lower than the previously reported value 7.5 g m^{-2} [27], which may be because the latter is from BC measurements that have ubiquitous coatings associated with them. The absorption enhancement (E_{abs}) is calculated as the measured MAC over the MAC of the uncoated rBC. The absolute MAC values rely on the PASS calibration but the trends in E_{abs} will be manifest regardless of the absolute calibration.

The mass median diameter (MMD) of the rBC core is almost constant throughout the experiment, but with increased BC coatings added. To directly compare the measured E_{abs} in the bulk, the M_R in single particles is converted to M_R in bulk ($M_{R,bulk}$) by summation of the total non-BC and rBC single particle masses over a given period, expressed as:

$$M_{R,bulk} = \frac{\sum_i M_{R,i} \times M_{rBC,i}}{\sum_i M_{rBC,i}} \qquad (6),$$

Where i denotes the i^{th} single particle.

In the ambient, we measured the absorption coefficient switching between a direct inlet line and one through a catalytic stripper [36] (held at 400°C) every 30 mins (Supplementary Fig. 10A). The heated line is corrected for thermophoretic losses by comparing the SP2-measured rBC mass between direct and heated line. The E_{abs} is determined as the ratio of absorption between direct line and averaged heated line adjacent to the direct line. Supplementary Fig. 10B shows the absorption coefficient (B_{abs}) at 532nm measured through the direct and heated lines when ambient was influenced by different sources for the entire experiment. The E_{abs} is

obtained by orthogonal distance regression (ODR), constrained through the origin. The E_{abs} observed at 781nm is similar (TR 1.05±0.02; SF 1.14±0.02; BN 1.20±0.06).

We apply the hybrid model to calculate the absorption for single particles and then work out the bulk E_{abs} by summation of the absorption of arising from all the single particles detected for each source (summarized in Supplementary Table 3). The hybrid model has higher agreement with observation whereas only applying the core-shell model largely overestimates E_{abs}. Though for all sources the 2-3fg core mass range is a major contribution to the BC particle core mass distribution (Fig. 1), the larger particles also contribute an important fraction in SF and BN environments. For these sources, we also tested the sensitivity in our calculated E_{abs} to the change in M_R values bounding the transition regime at different core mass sizes. We have applied the M_R values bounding the transition regime at 5fg and 10fg for these environments to our calculations of E_{abs} (Supplementary Table 3, data in brackets). This difference is not significant because the fraction of single particles affected by varying the threshold M_R is minor (1.5% for SF and 9.3% for BN). This indicates that though these large particles significantly contribute to total absorption, the hybrid model is relatively insensitive to the different transition regimes applied at different masses. In addition, the modelled E_{abs} is slightly higher than the observation which means a fraction of externally mixed BC may have not been fully captured by the model.

The global distribution of atmospheric aerosol was simulated using the 3D Global Model of Aerosol Processes (GLOMAP) [37], which is an extension to the TOMCAT chemical transport model, driven by analysed ECMWF meteorology. A horizontal resolution of 2.8°×2.8° and 31 vertical levels between the surface and 10 hPa for the year 2008 is used. GLOMAP simulates the influence of aerosol microphysical processes on the particle size distribution represented using seven log-normal modes: a soluble nucleation mode, and both soluble and insoluble modes for Aitken, accumulation and coarse size ranges. Insoluble modes are

assumed to be non-hygroscopic and not wet deposited via nucleation scavenging. Aerosol moves from insoluble to soluble modes through coagulation or after the condensation of ten monolayers of gas phase species (sulphuric acid and oxidised organics) [37]. Rate of ageing through condensation therefore depends on the aerosol size distribution as well as oxidant and precursor gas concentrations. The modal aerosol scheme used here is a simplified description of the aerosol distribution and by necessity includes a simplified representation of aerosol processes including ageing. In previous work we demonstrated that the modal aerosol scheme matches results from a more detailed sectional aerosol scheme[18], providing additional confidence in the results presented here.

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