SINGLE-PARTICLE CHARACTERISATION OF BLACK CARBON IN URBAN AND BIOMASS BURNING PLUMES AND IMPACTS ON OPTICAL PROPERTIES

A THESIS SUBMITTED TO THE UNIVERSITY OF MANCHESTER FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF ENGINEERING AND PHYSICAL SCIENCES

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Abstract

Black carbon (BC) is the light-absorbing component of soot, a combustion-generated aerosol that warms the climate by absorbing solar radiation. Its impacts on climate depend on its microphysical properties, which are modified by atmospheric processes including condensation, coagulation and wet removal. State of the art climate models consider soot in a concentric core/shell configuration, with a BC core coated by non-refractory material such as organics or sulphate. Within this model, thicker coatings enhance visible light absorption, but also wet removal efficiency, and these have opposing effects on the total amount of light absorbed over BC’s lifetime. How well the core/shell model can calculate Mass Absorption Coefficient (MAC, the ratio of absorption to BC mass) is uncertain, as real soot forms more complex (often fractal) shapes, and detailed optical models using these morphologies predict the core/shell model may under- or over-estimate MAC depending on the precise properties of the particles.

Few reliable measurements of variations in ambient MAC are available, as most older measurement techniques suffer from systematic uncertainties. In this work, a Single Particle Soot Photometer (SP2) and PhotoAcoustic Soot Spectrometer (PASS) were used to measure BC mass concentration and absorption, and these instruments do not suffer from such uncertainties. The SP2 was also used to report core size and coating thickness distributions that are required to test state of the art climate models.

Firstly, a method was developed to minimise bias in the measured coating thicknesses related to the limited detection range of the SP2. The sensitivity of this technique to the assumed density and refractive index of the BC core was also explored, and the most appropriate parameters to use with ambient measurements were determined.

Core and shell distributions were measured in Pasadena, California under a range of different photochemical ages. These were then used to calculate MAC, which was compared to that measured using the SP2 and PASS. The measured and modelled MAC agreed within 10% at 532 nm, though this was dependent on the assumed refractive index of the BC core. Overall MAC increased by 15–25% in around one third of a day of photochemical ageing. This is quite modest compared to some climate models, but not compared to the previous best estimate, which predicted MAC may increase by a factor of $\sim 1.5$ over BC’s lifetime.

Core and coating distributions were also measured in Canadian boreal biomass burning plumes. A case study was presented comparing the properties of BC in three plumes, one of which had passed through a precipitating cloud. It was demonstrated that larger and more coated BC-containing particles were removed more efficiently, in agreement with previous thermodynamic theory. By calculating MAC using the measured core/shell distributions and comparing to measured scattering, it was demonstrated that the MAC and single-scattering albedo in the plumes were likely not significantly affected by the wet removal, as greater differences were observed between the two plumes not affected by precipitation.
Layman’s abstract

This thesis focuses on measuring the properties of soot particles in the atmosphere. Soot absorbs the sun’s radiation and heats the air, and is the second strongest contributor to current global warming behind CO₂. Reducing soot emissions may delay the onset of warming, but in order to assess the impacts this could have, we need to measure the properties of soot and how they change with time.

Soot itself is made up of black carbon, which absorbs light, and other material that may reflect light but not strongly absorb it. The sizes of these two parts and the way they mix together is thought to affect how absorbing the black carbon is, by deflecting more or less light onto it. This also affects how soot interacts with water, which is important as the main way soot is removed from the atmosphere is by being taken up by clouds and rained out. Both of these processes depend on the properties of the soot, such as size, shape and what other components are mixed in with the absorbing black carbon.

The first part of this thesis focuses on improving a previous method to measure the size of soot particles and mixing between different components. This method was then used in different environments to explore the properties of soot under different conditions. In the Los Angeles area, the size and mixing of urban soot were measured as it ages. The amount of light absorbed increased with time, but to a lesser extent than might have been expected. In Canadian forest fire plumes, some of which passed through clouds, the measurements showed that larger particles were rained out more efficiently than others.

Studies like these will improve our understanding of the effects soot has on the climate, and help test and develop current and future climate models in order to better inform policymakers. To build upon this work, similar measurements should be made in different environments around the globe.
Declaration

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Jonathan William Taylor
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Acknowledgements

To the reader, the acknowledgements section in a typical thesis often follows a similar format. Thanks to the supervisors, friends, colleagues, family and partner, without whose support none of this would have been possible. To the reader, this may come across as a stale or overly-sentimental list of names, most of whom will never read the document in question.

As I come to the end of this journey, I now realise the true value of this section is to the writer. Trying to recall all those who have helped (to make sure no one has been missed out) leads one to reflect on the true contribution these people have made. Obviously, some have contributed directly to the body of work, but many have contributed to changes in life as a whole.

Professionally, the skills I have gained these past four years will stand me in good stead, whatever route my career will take. Personally, well, there’s nothing like a month on a ship with no internet to help you realise the important things in life. Admittedly, my social skills have taken a knock of late, but I think that’s quite common under the circumstances.

These changes didn’t happen on their own, and they are not just a result of travel to far-off lands, troubleshooting misbehaving instruments, or writing a function to average the average average. Most of these skills are gained by experience, though there is some element of trial and error (and trial by fire). But without someone to point you in the right direction when everything has hit a dead end, and someone to listen when you need to blow off steam, even the most gifted scientist would find this gargantuan task nigh on impossible. And so it is knowing all this that I now present to you, the reader, a list of names (which may come across as stale or overly-sentimental), most of whom will never read the document in question, but without whose support none of this would have been possible.

Firstly, I must acknowledge my funding in the form of a NERC PhD studentship, NERC project grants NE/F017391/1 and NE/H008136/1 and additional funding from NCAS for BORTAS. Without this there would have been no trips to California, no Finnish sauna adventures and I would remain ignorant of the virtues of Karlsruhe’s groundbreaking public transportation system.

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Finally, thanks to the people who have reminded me that there’s more to life than soot, and picked up the slack as this monstrous document tightened its grip on my life. Schadia, Harry, Dale, Mmmatt, Lisa, Phil, Laura, Beth, Ali, Rory, Sophie, Marcus, Miller and of course all my family. Thank you all.

It’s been stressful, its been a lot of hard work, but it’s been a lot of fun.
Chapter 1

Introduction

1.1 Motivation

While there is a clear scientific consensus (Cook et al., 2013) and a high level of scientific understanding (Forster et al., 2007) of the warming effects that anthropogenic Greenhouse Gases (GHGs) have on the climate, the nature and magnitude of the effects of atmospheric aerosols are much less certain. Aerosols are solid or liquid particles suspended in gas, and are formed both naturally and through anthropogenic activity (Seinfeld & Pandis, 1998). They come from many different sources—primary aerosols are directly emitted, such as soot from combustion and sea salt from sea spray. Inorganic salts such as nitrate and sulphate are formed through chemical reactions of atmospheric gases (which may be anthropogenic or natural), and Organic Aerosol (OA) has both primary and secondary sources.

Black Carbon (BC) is the light-absorbing component of soot, a combustion-generated aerosol ubiquitous throughout the lower levels of the atmosphere. Figure 1.1 presents the global distribution of BC emissions, and shows strong sources in industrialised regions (particularly China and South/Southeast Asia) and the biomass burning regions. In the year 2000, around 35% of global BC emissions were from fossil fuel combustion, a combination of diesel engines and industrial coal and coke burning (Lamarque et al., 2010; Bond et al., 2013). 22% of emissions were due to biofuel combustion, mostly for domestic heating and cooking. 42% were due to open biomass burning, a combination of natural fires and those used for land clearing and agricultural use.

Aerosols and GHGs cause perturbations in the Global Energy Budget (GEB), the balance between incoming shortwave radiation from the sun and outgoing radiation, a
Combination of reflected sunlight and longwave black-body emissions from the Earth and atmosphere (Boeker & van Grondelle, 2011). By absorbing and re-radiating outgoing longwave radiation, GHGs add energy to the Earth-atmosphere system, and conceptually this energy leads to an increase in temperature of the surface, oceans and atmosphere. The effects of aerosols on the GEB are more complex, due to the wide variety of physical and chemical properties of aerosols, and the opposing ways in which different types of aerosol interact with radiation and clouds.

Nonabsorbing (or weakly absorbing) aerosols, such as sulphate and sea salt, scatter visible light, which has a cooling effect by reducing the planetary albedo. In contrast, BC absorbs light and warms the surrounding atmosphere (Haywood & Shine, 1995). The optical properties of a mixed aerosol layer are dependent on the size, composition and mixing state of the particles, which vary with time due to processes such as condensation, evaporation and coagulation (Seinfeld & Pandis, 1998). Aerosols also affect the reflective properties of clouds, and interactions between aerosols and clouds are also size- and chemistry-dependent (Dusek et al., 2006b), and may have a net warming or cooling effect depending on the type of cloud and type of aerosol. The overall climatic impacts of aerosols are therefore a combination of opposing (and interacting) warming
1.1. MOTIVATION

and cooling terms. Overall, anthropogenic aerosols (including sulphate, nitrate, organics, fly ash, dust and soot) have a cooling effect on the climate (Forster et al., 2007), though the climatic effects vary between different aerosol sources and different regions of the globe.

Understanding the impact of aerosols on the GEB is important not only to assess the current effects of human emissions, but also to improve predictions of short- and long-term climate change. Thusfar, warming due to GHGs has been partially masked by the net cooling effect of aerosols (Andreae et al., 2005). Stronger current cooling by aerosols implies a stronger warming by CO₂, and consequently a greater effect on the climate as CO₂ levels increase in the future. As the dominant absorbing aerosol in the atmosphere, BC moderates the cooling effect of both anthropogenic and biomass burning aerosols, and recent estimates suggest its warming effect on global climate is second only to CO₂ (Chung et al., 2012b; Bond et al., 2013).

In recent years, reducing BC emissions has received much attention as a potential 'quick-fix' to dampen the effects of anthropogenic climate change (e.g. Jacobson, 2002; Bond & Sun, 2005; Grieshop et al., 2009). Over 80% of current global BC emissions are a direct result of human activities (Bond et al., 2013), meaning there is significant scope for emission reductions. Such strategies rely on the short lifetime of aerosols compared to GHGs: a reduction in global BC emissions would affect atmospheric concentrations within weeks, whereas similar reduction in CO₂ emissions would take decades to significantly affect atmospheric concentrations.

Despite legislation such as the Kyoto protocol, global CO₂ emissions continue to rise, particularly due to recent increases in emissions from Asia (Francey et al., 2013). While the original Kyoto protocol was due to expire at the end of 2012, this has been extended in the short-term, with a replacement to be agreed upon by 2015 and implemented by 2020 (UN Doha conference proceedings, 2013). Weaver (2011) suggested any replacement should include measures to reduce concentrations of short-term forcing agents such as BC, O₃ and CH₄. Technologies to achieve BC reductions (such as filters for diesel vehicles and clean-burning cooking stoves for use developing nations) are readily available, though not without cost, and have the added benefit of improving public health through reducing air pollution (Smith & Haigler, 2008).

The effects of BC mitigation on climate are complicated by the fact that any reduction in BC emissions may also be accompanied by a reduction in co-emitted nonabsorbing aerosols. Warming due to BC emitted by open biomass burning is thought to be entirely cancelled out by the cooling effects of co-emitted OA (Bond et al., 2013).
Kopp & Mauzerall (2010) highlighted diesel emissions and coal burning as targets for mitigation due to the lower amounts of co-emitted cooling species. Increased regulation of diesel vehicles has led to significant reductions of BC levels in California and Tokyo (Bahadur et al., 2011; Kondo et al., 2012), proving this can be an effective policy even in developed nations.

In order to improve our understanding of BC (and aerosols in general) in the climate system and to assess the impacts of any mitigation efforts on future climate change, there are several key problems that must be addressed. The following sections present an overview of BC’s life cycle and its role in the climate system, and identify the direct aerosol effect (scattering and absorption of light) as a significant source of uncertainty. Key observations are also identified to improve understanding of microphysical changes which take place during BC’s lifetime, in order to inform and test climate model parameterisations and constrain estimates of BC’s effects on the climate system.

1.2 The nature of BC and soot

Fresh soot takes the form of individual graphitic spherules bound together in a fractal structure, which may subsequently be mixed with nonabsorbing material such as sulphate or organics (Bond et al., 2013). Figure 1.2 shows example morphologies of soot particles in the atmosphere; fresh soot typically has a fractal morphology, but can become compacted and encapsulated by ageing and mixing with other aerosols (Shi et al., 2008; Zhang et al., 2008).

Although BC has been studied for many years, its definitions remain ambiguous due to the subtleties of the different measurement techniques used (Andreae & Gelencser, 2006; Petzold et al., 2013). The terms ‘black carbon’, ‘elemental carbon (EC)’ and ‘soot’ are often used interchangeably, even though they refer to different properties of a particle. The definitions of relevant terms are summarised in Table 1.1. ‘Soot’ is used a catch-all term for dark particles emitted by combustion. Historically, BC measurements focused on particles’ absorbing properties (i.e. blackness) whereas EC measurements characterised volatility, though the term is also used to refer to graphitic structures seen in Raman spectroscopy (e.g. Mertes et al., 2004) or pure-carbon fragments observed in mass spectrometry (e.g. Spencer & Prather, 2006). Many older techniques used to measure BC/EC suffer from interferences due to nonabsorbing material, and actually measure BC$_e$ or EC$_a$. Newer Light-Induced Incandescence (LII) techniques measure refractory BC (rBC) (see Chapter 3).
1.3. BC’S LIFE CYCLE

While the material forming the basis of such measurements is similar (there is clearly a large fraction of soot formed from elemental carbon that strongly absorbs light), the differences and uncertainties between different measurement techniques mean the derived concentrations and properties can show large variation (Schmid et al., 2001). Not all Light Absorbing Carbon (LAC) is black, as some organic species absorb, particularly at ultraviolet wavelengths (Kirchstetter et al., 2004). This is known as Brown Carbon (BrC). It is not clear where the boundary between black and brown carbon lies, and even within BC spherules there is a fraction of elements other than carbon (e.g. Fitzpatrick et al., 2008; Vander Wal et al., 2010). Likewise, not all EC is strongly absorbing; carbon in soot spherules from different sources show different levels of graphitization, which affects optical properties (Bond & Bergstrom, 2006). Most emission inventories use EC due to the abundance of measurements (Koch et al., 2009), however the ambiguous definition and differences between measurement techniques continues to pose a challenge when comparing measurements and estimating emissions (Bond et al., 2004).

1.3 BC’s life cycle

BC is formed by incomplete combustion. When burned in a high oxygen atmosphere, pure hydrocarbons undergo complete combustion, producing CO₂ and H₂O. Outside
Table 1.1: Summary of carbonaceous absorbing aerosol terminology, adapted from Andreae & Gelencser (2006), Bond & Bergstrom (2006), Schwartz et al. (2012) and Petzold et al. (2013).

<table>
<thead>
<tr>
<th>Term</th>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soot</td>
<td></td>
<td>A black or brown solid formed by incomplete combustion.</td>
</tr>
<tr>
<td>Soot carbon</td>
<td></td>
<td>Aggregates of spherules made of graphitic layers, consisting largely of elemental carbon, with minor amounts of bound heteroelements, especially hydrogen and oxygen.</td>
</tr>
<tr>
<td>Brown carbon</td>
<td>BrC</td>
<td>Light-absorbing organic matter (other than BC) in atmospheric aerosols of various origins. The brownish appearance is associated with a non-uniform absorption over the entire visible wavelength range</td>
</tr>
<tr>
<td>Light-absorbing carbon</td>
<td>LAC</td>
<td>General term for light-absorbing carbonaceous substances in atmospheric aerosol, BC + BrC.</td>
</tr>
<tr>
<td>Elemental carbon</td>
<td>EC</td>
<td>Conventionally used as a poorly-defined term for near-elemental soot carbon, often used interchangeably with black carbon or apparent elemental carbon.</td>
</tr>
<tr>
<td>Apparent elemental carbon</td>
<td>EC$_a$</td>
<td>Operationally defined as the fraction of carbon that is oxidized above a certain temperature threshold in the presence of an oxygen containing atmosphere.</td>
</tr>
<tr>
<td>Black carbon</td>
<td>BC</td>
<td>The most commonly used term, refers to material with optical properties and composition similar to soot carbon. Also used for the result of an LAC measurement by an optical absorption technique.</td>
</tr>
<tr>
<td>Equivalent black carbon</td>
<td>BC$_e$</td>
<td>Operationally defined as the amount of strongly light-absorbing carbon with the approximate optical properties of BC that would give the same signal in an optical instrument (e.g. the Aethalometer) as the sample.</td>
</tr>
<tr>
<td>Refractory black carbon</td>
<td>rBC</td>
<td>Used to refer to black carbon with vaporisation temperature high enough to reach incandescence.</td>
</tr>
</tbody>
</table>
of carefully controlled conditions, combustion is rarely complete due to reduced oxygen supply in parts of the flame. This causes incomplete combustion products such as soot and CO. Sooting tendency is highly dependent on fuel composition and the morphology of the combustion system (Seinfeld & Pandis, 1998). For example, with the air hole closed, a bunsen burner acts as a diffusion flame, with high sooting tendency due to a central region not in contact with the oxygen supply in surrounding air. With the air hole open, the fuel is pre-mixed and burns more efficiently. Fuels with lower H:C ratios also require more oxygen for complete combustion, due to the different number of oxygen molecules in CO\textsubscript{2} and H\textsubscript{2}O (Haynes & Wagner, 1981).

The precise mechanisms of soot formation remain difficult to characterise, though a generalised model has been developed (Smith, 1981; Moosmuller et al., 2009). First, the fuels are broken down by thermal degradation of long-chain aliphatic and aromatic molecules to form radical fragments. These are building blocks that form Polycyclic Aromatic Hydrocarbons (PAH), which are soot precursors. As more small fragments are produced, the PAH structures grow until they are large enough to act as particle nuclei. Condensation of gas-phase species then occurs, forming primary spherules of a graphitic material mixed with minor amounts of unburnt hydrogen, oxygen and impurities in the fuel. The diameter of these spherules varies depending on the combustion conditions, and is typically 5 – 40 nm (Seinfeld & Pandis, 1998; Wentzel et al., 2003). Collisions between the spherules results in agglomeration to form fractal soot chains, and upon cooling and exiting the flame particles may become mixed with other species such as primary organics.

Following emission, primary aerosols such as BC undergo mixing with other aerosol types by condensation and coagulation. Particles may change shape and become partially or wholly encapsulated by nonrefractory material. In typical ambient aerosol concentrations, condensation is the dominant process for coating growth (Pandis et al., 1995), and can occur through cooling of primary semi-volatile organic species immediately following emission, or through oxidation of gas-phase precursors of secondary species such as inorganic salts and Secondary Organic Aerosol (SOA). Coagulation-led particle growth does occur in some circumstances, such as highly polluted conditions (e.g. biomass burning plumes) or in the absence of condensable species (Riemer et al., 2010).

Highly fractal soot aggregates are restructured when mixed with other material, and this is thought to be driven by surface tension forces during coating condensation (Kutz
This restructuring has been seen in numerous laboratory studies, using $\text{H}_2\text{SO}_4$ (Zhang et al., 2008; Pagels et al., 2009) and various organics (Xue et al., 2009; Tritscher et al., 2011; Ghazi & Olfert, 2013) as the condensing species, and some experiments have also included humidification. Ghazi & Olfert (2013) demonstrated that larger amounts of condensed material led to increasingly spherical particles, however not all species appear to cause such restructuring. Despite similar composition and surface tension, Xue et al. (2009) found glutaric acid ($\text{C}_5\text{H}_8\text{O}_4$) effective at restructuring, particularly when humidified, however succinic acid ($\text{C}_4\text{H}_6\text{O}_4$) was not, which they suggested may be due to the higher melting point of succinic acid. Electron microscopy of ambient soot captured on filters generally shows a combination of fractal chains or compacted spheres (Shi et al., 2008; Adachi & Buseck, 2013), with variable mixing with other aerosol types, though electron microscopy measurements are not ideal for assessing mixing due to the evaporation of semi-volatiles between sampling and measurement (Adachi et al., 2010).

The restructuring and encapsulation of initially-hydrophobic BC by soluble material has two key effects. Firstly, the shift to more spherical morphology and coating by nonabsorbing material is thought to affect light absorption and scattering (Fuller et al., 1999; Schnaiter et al., 2005a). This is discussed further in Chapter 2. Secondly, the addition of soluble material means the BC increases in size and hydrophilicity, and may activate at lower water supersaturations (Khalizov et al., 2009; Liu et al., 2013). This is a key factor in moderating BC lifetime, as wet removal processes are the dominant removal mechanism (Jacobson, 2010). BC with soluble coatings can act as Cloud Condensation Nuclei (CCN) in liquid clouds, though this may inhibit BC’s Ice Nucleation (IN) potential (Koehler et al., 2009). Once inside cloud droplets or ice particles, BC is carried to the ground when these precipitate. Particles may also be deposited by impaction scavenging with pre-formed droplets (Seinfeld & Pandis, 1998).

### 1.4 BC in the climate system

The effects BC has on the climate system are wide ranging and vary over its lifetime. Such effects are summarised in Figure 1.3. The recent review by Bond et al. (2013) divides such effects into three main categories, which are summarised briefly in the following sections.
1.4. BC IN THE CLIMATE SYSTEM

Aerosols interact with radiation through scattering and absorption. The absolute and relative magnitudes of these two effects depend on many factors, such as particle size, shape, refractive index and the wavelength of radiation. Mie theory, which governs the interaction of radiation with spheres, predicts strong interactions at wavelengths similar to particle size (Bohren & Huffman, 1983), meaning both spectral and size distributions must be taken into account. The combination of scattering and absorption of solar radiation due to aerosols is known as the direct effect. While the atmospheric effects may be warming or cooling depending on aerosol composition, the surface is almost always cooled, as aerosol extinction reduces the flux of radiation to the ground.

The direct effect is dependent on the burden and optical properties of aerosol in the atmosphere, the cloud fraction and the albedo of the underlying surface (Haywood & Shine, 1995). As aerosol lifetimes are relatively short, they do not mix as fully as longer-lived species such as CO\textsubscript{2}. It is therefore a highly localised effect; areas with high aerosol emissions, such as the biomass burning regions and South Asia, have strong direct forcing (Bond et al., 2013). BC has a warming effect on the atmosphere,
but is co-emitted with species such as primary organics and secondary aerosol precursors, which lead to a cooling effect. The dependence on the albedo of the underlying surface means BC’s warming effect is large at high latitudes by lowering the planetary albedo. Similarly, BC above bright low-lying cloud also has a stronger warming effect, meaning the vertical profile of mass loadings is important (Samset et al., 2013). The combination of a cooler surface with warmer air aloft increases the stability of the atmosphere and inhibits convection. The reduction in surface flux reduces evapotranspiration, and the combined effect may be a ‘spin-down’ of the entire hydrological cycle (Liepert et al., 2004; Wild, 2009).

Estimates of the effect of BC on surface temperature vary between models, and this is less studied than the impacts on the GEB. Bond et al. (2013) summarised the impact of BC’s climatic effects on global mean surface temperature as between 0.1 –2.0 K, though not all of this has been realised due to cooling by co-emitted species. The effect of BC on surface temperature is also strongly dependent on altitude (Ban-Weiss et al., 2011), and high altitude BC has a cooling effect on surface temperatures.

While the overall direct effect due to BC and co-emitted species is very likely a warming effect (Ramanathan & Carmichael, 2008; Chung et al., 2012b; Bond et al., 2013), significant uncertainty remains regarding BC emissions, optical properties and lifetime. These lead to disagreements between models and observations that are not well understood. Such uncertainties are discussed further in Section 1.6.

1.4.2 Cloud effects

Aerosols may influence the radiative properties of the atmosphere by modifying the properties of clouds. Clouds are highly reflective, optically thick surfaces that reflect shortwave radiation, and to a lesser extent absorb and re-radiate longwave radiation. At any one time, ~60% of the Earth’s surface is covered with cloud (Lohmann & Feichter, 2005), and so changes in overall cloud cover could cause a significant perturbation in the GEB. Liquid cloud droplets form through heterogeneous nucleation, with water condensing onto a pre-existing particle (Seinfeld & Pandis, 1998). Higher CCN concentrations increase the number, but reduce the size of the cloud droplets formed. This increases the cloud albedo (Twomey, 1974) and cloud lifetime (Albrecht, 1989), both of which have a cooling effect. Diesel soot is hydrophobic upon emission, and may only act as a CCN if sufficiently mixed with soluble material (Andrews & Larson, 1993; Lammel & Novakov, 1995). Several laboratory studies have demonstrated this transformation (e.g. Dusek et al., 2006a; Khalizov et al., 2009; Koehler et al., 2009).
and although ambient measurements are limited, some recent studies have shown increased hygroscopicity by internally mixed BC (McMeeking et al., 2011; Liu et al., 2013).

At sub-zero temperatures BC may act as an IN, though internal mixing is thought to inhibit this (Koehler et al., 2009). In mixed-phase clouds, IN increase the rate of sedimentation, reducing cloudiness, however in ice clouds such as cirrus this effect is much more uncertain (Karcher et al., 2007). BC emission from aircraft may have a significant effect on ice number concentration (Hendricks et al., 2005), however Gettelman et al. (2012) estimated the climatic effect of BC as an IN may be small. Laboratory measurements of BC ice nucleation show wide variation in their results (Hoose & Möhler, 2012), though it is generally thought that BC is not as effective an IN as mineral dust.

Atmospheric heating of BC in or near cloud also affects cloud dynamics. The consequences of this are known as the semi-direct effects (Hansen et al., 1997). BC in cloud absorbs light and lowers cloud albedo. This heating may cause cloud droplets to evaporate, causing a net warming effect for low altitude clouds but cooling for clouds at high altitude. BC near cloud affects atmospheric dynamics- low altitude BC aids convection (and hence convective cloud formation), but high altitude BC increases stability (Koch & Del Genio, 2010). Such effects are closely linked to the direct effect, as the concentration and optical properties of BC determine how strongly it may affect atmospheric dynamics. Semi-direct effects may be considered a rapid adjustment to the direct heating of the atmosphere.

The hemispheric nature of BC emissions (weighted heavily towards the Northern Hemisphere) likely causes a northward shift of the inter-tropical convergence zone, a region of strong convective storms near the equator (Chung & Seinfeld, 2005). Many studies show that atmospheric heating by BC can reduce regional precipitation by up to 10%, but models differ on the locations of these effects. Due to the high aerosol loadings in the region, the monsoons of South and East Asia are particularly affected, but do not agree on the specific effects in these regions (Bond et al., 2013).

### 1.4.3 BC in the cryosphere

Surface warming occurs in the case of absorbing aerosol in/on snow and ice, which decreases albedo by darkening the surface. This is primarily the result of BC particles scavenged by clouds and precipitation, though there is also a small contribution by dry deposition. Hadley et al. (2010) observed below-cloud scavenging by snowfall as
an efficient removal process for atmospheric BC. Even relatively small concentrations of BC within snow can cause a 1% reduction in albedo (Jacobson, 2004), causing a warming of the surface and leading to an increased rate of ice-melting. This is a key climate feedback- the ice is more reflective than the surface underneath, whether land or open ocean, so if the surface warming is enough to fully melt the snow/ice, a large decrease in surface albedo occurs. Most studies focus on the globally-averaged impact of this effect on surface temperatures, which is typically $<0.2$ K. Warming of the arctic by BC could be up to several degrees K, though this varies with the seasonality of sunlight (Sand et al., 2013). Even when BC is mixed with large amounts of non-absorbing aerosols, such as in emissions from open biomass burning, the aerosols are still darker than ice, meaning weakly absorbing BrC is responsible for a large fraction of particulate light absorption (Bond et al., 2013). An improved understanding of the optical properties of BC and BrC would help to improve estimates of this effect.

1.5 Quantification of climate forcings

Perturbations to the Earth’s radiative budget are most often quantified using Radiative Forcing (RF). The Intergovernmental Panel on Climate Change (IPCC) defines RF as “...the change in net (down minus up) irradiance (solar plus longwave; in W m$^{-2}$) at the tropopause after allowing for stratospheric temperatures to readjust to radiative equilibrium, but with surface and tropospheric temperatures and state held fixed at the unperturbed value.” (Ramaswamy et al., 2001). The surface and tropospheric temperatures are fixed because otherwise the system would simply return to a new equilibrium; the increased energy flux would cause an increase in surface and tropospheric temperatures, which would increase the outgoing longwave flux. RF for aerosols is often calculated at the Top Of the Atmosphere (TOA), as there is little difference between calculating forcing here or at the tropopause (Forster et al., 2007). A linear relationship may be assumed between radiative forcing and the change in global surface temperatures (Forster et al., 2007):

$$\Delta T_S = \lambda RF,$$

where $\lambda$ is the climate sensitivity.

In the IPCC’s fourth assessment report, Forster et al. (2007) estimated globally-averaged RF by long-lived GHGs at $+2.63 \pm 0.26$ W m$^{-2}$ (90% confidence range). In comparison, they estimated RF by anthropogenic aerosol at $-0.5 \pm 0.4$ W m$^{-2}$ by direct interaction with sunlight and $-0.7^{+0.4}_{-1.1}$ W m$^{-2}$ by changing the properties
of clouds. The greater uncertainty reflects the lower level of scientific understanding compared to GHGs.

\( \lambda \) is often quantified by calculating the temperature change caused by a doubling of CO\(_2\) concentrations (compared to preindustrial levels) when models are run long enough to adjust to the new equilibrium. This is referred to as the equilibrium climate sensitivity (ECS), and recent estimates calculated in this way suggest ECS lies in the range 3.44 ± 0.84 K, for RF of 3.22 ± 1.32 W m\(^{-2}\) (90% uncertainties) (Forster et al., 2013). The corresponding values of \( \lambda \) are 0.96 ± 0.48 (90% uncertainty).

The RF-\( \lambda \) model was designed for use with GHGs, and is a simple way to explain how radiative forcing affects familiar quantities. However, nonradiative forcings such as variations in rainfall, biodiversity, and sea level changes are not described by this equation (Jacob et al., 2005). For absorbing aerosol, RF has limitations as many effects cancel out. Warming of the atmosphere is accompanied by surface cooling; this changes the distribution of energy within the column, but the TOA forcing may be small. In the case of the semi-direct effect, the temperature change at the surface may not even be the same sign as the RF (Cook & Highwood, 2004; Ban-Weiss et al., 2011), and \( \lambda \) shows much larger variations than when calculated for a doubling of CO\(_2\).

Several variations to the IPCC’s definition of RF have been proposed (e.g. Gregory et al., 2004; Hansen et al., 2005; Jacob et al., 2005). Recently, Bond et al. (2013) presented the global climate forcing for BC, which represents the sum of all known radiative forcings, as well as rapid adjustments of clouds and the snowpack. Their metric also takes into account the high efficacy (the fractional change in surface temperature, for a given agent’s forcing, relative to the same forcing of CO\(_2\)) of BC in and above snow and ice. Again, this globally-averaged metric does not explicitly quantify many of the impacts BC has on climate, or their localised nature, but is useful to compare the magnitude and uncertainties of different competing effects.

Figure 1.4 presents the most recent estimates of climate forcing by Industrial era BC and co-emitted species, calculated by Bond et al. (2013). Net forcing by BC alone is positive, and much of this is due to the direct effect. The net BC cloud effects are also positive, though in liquid clouds the net climate forcing is negative. All terms have large uncertainty, similar or larger in magnitude than the forcing estimates. This suggests all forcing terms would benefit from improved understanding.

The bottom line of Figure 1.4 shows the total estimated climate forcing by BC-rich sources (diesel engines, industrial coal, residential solid fuel and open biomass burning), which collectively co-emit large amounts of primary organics, secondary
organic precursors and SO$_2$. This net forcing is negative, though highly uncertain, suggesting any BC mitigation attempts should be carefully considered. However, Bond et al. (2013) also calculated that the net forcing by BC-rich sources excluding open biomass burning was $+0.22^{+1.06}_{-0.72}$ W m$^{-2}$, meaning mitigation of transportation-related, industrial and residential BC emissions is likely to be beneficial to climate.

While the direct effect has the highest level of scientific understanding, this is by far the biggest RF term. The 90% uncertainty is still $\sim$85% of the median, and this range is the largest in absolute terms of all the terms shown in Figure 1.4. Improved constraint on the BC direct effect is therefore an important research topic to quantify total BC climate forcing, and consequently net aerosol climate forcing. In the next section, the direct forcing is explored in more detail, to summarise the uncertainties and lines of investigation.

Figure 1.4: Globally averaged climate forcing estimates (in W m$^{-2}$) for industrial era (1750 – 2005) BC from Bond et al. (2013). Additional forcings by pre-industrial era emissions are shown by the white dashed boxes. Uncertainties represent the 90% confidence interval (i.e. 5 – 95%). The Level Of Scientific Understanding, (LOSU, similar to Forster et al. (2007)) of the different forcing terms is also listed.
1.6 Estimating direct aerosol forcing

The previous section highlighted the importance of the direct aerosol effect in determining BC’s impact on global and regional climate. This section details the ways in which direct forcing is calculated using two contrasting techniques: bottom-up approaches using climate models and top-down approaches using remote sensing data. There is often significant disagreement between the two approaches, and this highlights the need for further understanding of BC’s optical properties and transformation/removal processes. Several key variables are introduced that are required when considering aerosol optical properties. Further details of their calculation are discussed further in Chapter 2.

1.6.1 Optical properties of aerosols

The intensity of light transmitted \( I_T \) through a volume of homogeneous, monodisperse aerosol is governed by the Beer-Lambert law:

\[
I_T = I_0 e^{-C_{Ext} l N} = I_0 e^{-(C_{Sca} + C_{Abs}) l N},
\]

(1.2)

where \( I_0 \) is the incident light intensity, \( l \) is the path length, \( N \) is the concentration of particles per unit volume and \( C_{Ext} \), \( C_{Sca} \) and \( C_{Abs} \) are the per-particle extinction, scattering and absorption cross-sections. In real aerosol systems, \( C_{Sca} \) and \( C_{Abs} \) vary on a per-particle basis, as they are dependent on the size and physical properties of the particle. It is therefore necessary to consider the bulk extinction, scattering and absorption coefficients \( B_{Ext} \), \( B_{Sca} \) and \( B_{Abs} \), the sum of the cross-sections for all particles per unit volume in the system. It is often useful to normalise \( B_{Ext} \), \( B_{Sca} \) and \( B_{Abs} \) to the mass of optically active material, giving Mass Extinction Coefficient (MEC), Mass Scattering Coefficient (MSC) and Mass Absorption Coefficient (MAC) respectively, measured in \( \text{m}^2 \text{g}^{-1} \). Remote sensing techniques often derive the Aerosol Optical Depth (AOD) and Absorption Aerosol Optical Depth (AAOD), equivalent to \( B_{Ext} \) and \( B_{Abs} \) integrated over the atmospheric column.

The relative contributions of scattering and absorption are parameterised by the Single Scattering Albedo (SSA):

\[
\text{SSA} = \frac{B_{Sca}}{B_{Ext}} = \frac{B_{Sca}}{B_{Sca} + B_{Abs}}
\]

(1.3)
A layer of nonabsorbing (or very weakly absorbing) aerosol such as sulphate has SSA close to 1. BC scatters light but also absorbs a large fraction; nascent soot may have SSA as low as 0.15, but mixing with other aerosols components significantly increases this (Haywood & Shine, 1995).

### 1.6.2 Bottom-up estimates from climate models

Schulz et al. (2006) presented a simple diagnostic equation to highlight the factors affecting direct radiative forcing, adapted for BC \( \text{DRF}_{\text{BC}} \) by Bond et al. (2013):

\[
\text{DRF}_{\text{BC}} = \text{Emissions} \times \text{Lifetime} \times \text{MAC} \times \text{AFE},
\]

where AFE is the Absorption Forcing Efficiency (forcing per AAOD), which accounts for factors such as cloud fraction, surface albedo and scattering by non-BC aerosols. All quantities are global means.

Bond et al. (2013) compiled estimates of each of the factors in Equation 1.4, comparing global models used in the AeroCom (Aerosol Comparisons between Observations and Models) phase I model intercomparison (Schulz et al., 2006) and several others. Table 1.2 summarizes the range of values used/calculated in the various studies considered by Bond et al. (2013), and also includes data from the AeroCom phase II simulations (Myhre et al., 2013), though some BC properties are estimated rather than explicitly calculated. The standard deviations of each terms within each model comparison range from 20 – 55%, and this is similar to the variation in averaged terms between each study. It is useful to examine each term separately to identify key sources of uncertainty and highlight areas that may be better constrained by observations.

Emissions in Table 1.2 are ‘industrial era’ emissions (i.e. the difference between modern-day and pre-industrial emissions) (Bond et al., 2013). For comparison, Lamarque et al. (2010) recently estimated current total BC emissions at 7.7 Tg yr\(^{-1}\). These are the emissions for the IPCC’s 5th assessment report (AR5), due in late 2013. There are some differences between the different years the different models consider as modern-day (2000 or 2006) and pre-industrial (1750 or 1850). The AeroCom exercises mostly used harmonized emissions for each study, meaning it is difficult to assess the uncertainty in emission estimates. For the models not included in AeroCom, the diversity is large. Emission inventories are difficult to compile due to incomplete emissions data and uncertainty into the characteristics of certain emitters (Streets et al., 2006). Few studies report uncertainty in their emission estimates. Bond et al. (2004)
### 1.6. Estimating Direct Aerosol Forcing

Table 1.2: Estimates of the different parameters in Equation 1.4 to calculate \( \text{DRF}_{\text{BC}} \). Data are taken from global climate models included in AeroCom phases I & II and other models listed by Bond *et al.* (2013). The values shown are the mean and standard deviations of all the model estimates. Emissions are industrial era emissions, and those in the AeroCom phase I model intercomparison were standardised. During AeroCom phase II, most models used standardised emissions from Lamarque *et al.* (2010), though a few models used different years for modern-day and pre-industrial.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Emissions ( \text{Tg yr}^{-1} )</th>
<th>Lifetime days</th>
<th>( \text{MAC} ) 550 nm ( \text{m}^{-2} \text{g}^{-1} )</th>
<th>AFE ( \text{W m}^{-2} \text{AAOD}^{-1} )</th>
<th>( \text{DRF}_{\text{BC}} ) ( \text{W m}^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AeroCom I</td>
<td>6.3</td>
<td>6.8 ± 27%</td>
<td>7.7 ± 24%</td>
<td>168 ± 31%</td>
<td>0.27 ± 21%</td>
</tr>
<tr>
<td>AeroCom II</td>
<td>5.7</td>
<td>3.5 ± 45%\textsuperscript{a}</td>
<td>7.9 ± 37%\textsuperscript{b}</td>
<td>133 ± 28%</td>
<td>0.18 ± 39%</td>
</tr>
<tr>
<td>Other models\textsuperscript{c}</td>
<td>8.0 ± 54%</td>
<td>6.0 ± 31%</td>
<td>10.1 ± 29%</td>
<td>175 ± 21%</td>
<td>0.43 ± 53%</td>
</tr>
<tr>
<td>Schulz <em>et al.</em> (2006)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Myhre <em>et al.</em> (2013)</td>
<td></td>
<td></td>
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<tr>
<td>Bond <em>et al.</em> (2013)</td>
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</tr>
<tr>
<td>and references therein</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

* Calculated from atmospheric burden and total emissions
* Calculated from BC MEC assuming SSA of 0.25
* Excluding models that include total BC rather than industrial era BC

Considered the 95% uncertainty in BC emissions to be around a factor of 2, meaning that even within a single study, errors tend to be large. However, Granier *et al.* (2011) compared different emission inventories, and estimated the uncertainty in BC emissions as around 30% in 2005, though the uncertainty was greater for previous years, and much greater when considering regional emissions.

BC lifetime is largely determined by wet removal schemes as, like most submicron aerosol, this is the biggest sink (Jacobson, 2010). However, such processes are typically sub-grid scale in global models, and are therefore difficult to calculate (Textor *et al.*, 2007; Croft *et al.*, 2010). Accurate determination of lifetime is particularly important in determining vertical profiles and transport to remote transport regions such as the Arctic, which strongly affect radiative forcing (Lund & Berntsen, 2012; Samset *et al.*, 2013). Textor *et al.* (2007) showed differences in transport schemes were a source of model diversity, and BC lifetime is longer once it is lifted into the free troposphere. Some models do now include more realistic wet removal processes (e.g. Croft *et al.*, 2010), which have shown improved accuracy in predicted vertical profiles (Kipling *et al.*, 2013) and transport to the Arctic (Lund & Berntsen, 2012), however wet removal of BC is sensitive to the assumptions of size and mixing state. Observations, both of BC mixing state and of wet removal efficiency (e.g. Moteki *et al.*, 2012) are required to validate and improve such mixing state schemes.

Calculated MAC is dependent on assumptions of BC refractive index, mixing state and size distribution. Bond & Bergstrom (2006) averaged measurements of fresh MAC
to give $7.5 \pm 1.2 \text{ m}^2 \text{ g}^{-1}$ at 550 nm, and estimated that mixing with other aerosols may increase this by a factor of 1.5 over time, giving a range of $7.5 - 11.25 \text{ m}^2 \text{ g}^{-1}$. Most models listed by Bond et al. (2013) and Myhre et al. (2013) had average MAC within the range recommended by Bond & Bergstrom (2006), though some were above or below. The minimum and maximum values of MAC in the different models were 4.3 and 15.0 $\text{ m}^2 \text{ g}^{-1}$, which lie outside the recommended range.

Bond & Bergstrom (2006) recommended that models including internal mixing would be an improvement on those that did not. Péré et al. (2009) demonstrated that assuming a core/shell morphology improved agreement with remote sensing SSA in Europe, though this may not be the case in all regions. Ghan et al. (2012) assumed all BC was internally mixed, which resulted in the highest MAC of all the models. In terms of optics, this approach is no better than assuming all particles are externally mixed, as both assume a constant mixing state throughout particle lifetime, which observations have shown is not the case (Shiraiwa et al., 2007; Sahu et al., 2012). Around half of models listed by Bond et al. (2013) consider internal mixing and, on average, those that do have higher MAC. If only these models were considered, the average model estimate of DRF$_{BC}$ would increase (Myhre, 2009). However, the internal mixing schemes employed are often extremely simplistic (see Section 1.6.3). Additionally, despite observations of BC internal mixing, there remains uncertainty into the magnitude to which this affects optical properties. This is discussed further in Chapter 2.

1.6.3 BC parameterisations in climate models

The complexity of climate models varies depending on what is being investigated and the computing power available. Box models (e.g. Riemer et al., 2009; Oshima et al., 2009; Zaveri et al., 2010) may contain detailed time-dependent condensation and coagulation calculations and are useful for examining physical and chemical processes in ways that are too complex to run in a global model. 3-D (in terms of spatial dimensions) models (e.g. Jacobson, 2001, 2010; Matsui et al., 2013) can be used to examine processes and effects over regional or global scales. Models may consider particle composition in explicit size bins or in mode-based schemes which consider particle size in terms of parameters such as geometric mean diameter and geometric standard deviation (Mann et al., 2010; Ghan et al., 2012). Simpler schemes may consider all aerosols within a mode or size bin to be either entirely externally or internally mixed, in order to simplify calculations, but observations have repeatedly shown variable mixing between the two (Adachi et al., 2010; Liu et al., 2011; Laborde et al., 2013). Optical
properties of internally mixed particles are either calculated using core/shell Mie theory (e.g. Jacobson, 2001; Bauer et al., 2008; Matsui et al., 2013) or volume mixing rules (e.g. Mann et al., 2010; Zhang et al., 2012; Bellouin et al., 2013).

Jacobson (2010, 2012) presented the most complex global model, which includes mixing-state resolved size bins for many aerosol species and cloud droplets, and hygroscopic growth at high Relative Humidity (RH). Primary BC from fossil fuel and biofuel/biomass burning have different properties, and transfers to internally mixed BC with ageing. However, the values for MAC generated for the internally mixed particles are very high: MAC ranges between 14 – 18 m$^2$g$^{-1}$, with a global mean of 16.2 m$^2$g$^{-1}$, which is much higher than the range proposed by Bond & Bergstrom (2006). Similarly, core/shell absorption enhancements for these particles were 2 – 3. The premier instrument for determining BC mass concentration and mixing state is the Single Particle Soot Photometer (SP2), which can measure BC coatings on a single-particle basis (Gao et al., 2007; Moteki & Kondo, 2007). This method is discussed further in Chapters 3 and 4. Absorption enhancement calculated by Jacobson (2012) is significantly higher than that calculated using measured SP2 core/shell data (e.g. Schwarz et al., 2008a,b; Shiraiwa et al., 2008). Though Jacobson (2012) did not list size and coating thicknesses for the internally mixed BC, the high MAC and absorption enhancement suggests coatings were very thick.

Matsui et al. (2013) present a recently-developed mixing state scheme for WRF-Chem, a widely-used regional climate model. Unlike Jacobson (2010), this scheme is compared directly to observations of core and shell diameter from SP2 measurements in East Asia. The BC mixing state parameterization is based on Oshima et al. (2009), with a 2-D matrix of 12 size bins × 10 BC mass fraction bins, ranging from BC-free particles to externally mixed BC. Mean shell/core ratios were typically 1.1 – 1.6 for 200 nm BC cores, though coatings were thicker for smaller particles due to coagulation processes. Matsui et al. (2013) demonstrated that compared to their detailed calculations, a simpler scheme (using just one mixing state for each size bin) overestimated absorption by 40% as all particles were assumed to contain BC, and all BC was assumed to be coated. This demonstrates the importance of considering multiple BC mixing states within one parameterization, rather than assuming a single size distribution and determining shell/core ratios from mass ratios.

To date, several studies have reported average coating properties (e.g. Schwarz et al., 2008a,b; Kondo et al., 2011b; Sahu et al., 2012), but there are few studies that have reported the distributions of these properties that are required to test such models.
Shiraiwa et al. (2008) provided the shell/core ratios used to test (Matsui et al., 2013). Laborde et al. (2013) reported shell/core ratios in Paris under different meteorological conditions, and Schwarz et al. (2008b) reported a single absolute coating thickness distribution for each of the lower troposphere (1–5 km) and lower stratosphere near Costa Rica. Metcalf et al. (2012) reported 2-D distributions of BC core and coatings, but did not assess how efficiently the SP2 can report such parameters over the entire measured size range. Variability in this efficiency is likely to be large, as the SP2 does not efficiently measure smaller particles (Schwarz et al., 2010b; Kondo et al., 2011b).

1.6.4 Top-down estimates from remote sensing data

When emissions are normalised to ground surface area, the first two terms in Equation 1.4 multiply together to give the column burden of BC, while the first three give AAOD. These can both be quantified by observations, providing a means of model validation and testing. Long-term in-situ measurements of BC surface concentrations are available, though different monitoring methods cause uncertainty in the derived measurements (Quincey et al., 2009). Vertical profiles must be measured directly with in-situ measurements (e.g. Schwarz et al., 2010a). Satellite-based remote sensing techniques can derive AOD (Bellouin et al., 2005), but ground-based AERONET (AERosol RObotic NETwork) sun photometers or modelled aerosol properties must be used to infer AAOD (Myhre, 2009). Uncertainties remain in the conversion from AOD to AAOD, and the relative contributions of BC, BrC and mineral dust, which show strong spatial variation (Chung et al., 2012b). AERONET sites are also limited to land coverage, and can only provide measurements in clear conditions (Bond et al., 2013).

Table 1.2 shows model diversity for the factors in Equation 1.4, but does not show how accurate any modelled values are. Koch et al. (2009) compared AeroCom phase I model estimates to measurements of BC mass loadings and AAOD. In most regions, BC surface concentrations were overestimated in models, but AAOD or column BC burden were underestimated. In Asia, both were underestimated; BC surface concentrations by a factor of 2 and AOD by a factor of 1.5. BC in the upper troposphere was overestimated in the tropics and underestimated at higher latitudes. Koch et al. (2009) suggested improvements in modelled optical properties, scavenging schemes and vertical dispersion in order to improve the agreement between models and observations. Bond et al. (2013) refined Koch et al.’s analysis by separating AAOD into contributions by BC and dust, but still found a global mean underestimation in models of BC AAOD of a factor of 3. BC AAOD was underestimated in all regions, with
lesser-studied regions of South/Southeast Asia and the Pacific showing the greatest discrepancies. However, Schwarz et al. (2010a) compared modelled BC vertical profiles between 80°N – 67°S over the Pacific, and showed most models overestimated BC concentrations in the upper troposphere, particularly at tropical and midlatitudes. Jacobson (2012) presented the global model with the most sophisticated treatment of BC mixing state, which showed better agreement with the measurements in remote regions.

The final column in Table 1.2 lists the average DRF$_{BC}$ values calculated in each model intercomparison. It is important to note that as Equation 1.4 is a simplification of numerous non-linear processes, many of which may cancel out, the averages and spread of DRF$_{BC}$ do not scale linearly. The largest spread in DRF$_{BC}$ is from the studies without harmonised emissions, and the similar spread in emissions and DRF$_{BC}$ (∼54%) in these studies appears to suggest a strong link. However, the model diversity in the AeroCom phase II intercomparison was not much lower than that for the models without harmonised emissions, meaning processes within models are also a large source of diversity. Between AeroCom phase I and II model diversity in DRF$_{BC}$ increased; the corresponding increases in diversity in lifetime and MAC suggest this is likely due to differences in mixing state schemes.

The disagreement between modelled and observed BC concentrations and AAOD means that recent estimates of DRF$_{BC}$ have been constrained by observations. Ramathan & Carmichael (2008) combined modelled BC spatial distribution with measurements of AAOD to calculate estimated DRF$_{BC}$ of 0.9 W m$^{-2}$. Chung et al. (2012b) included BrC in their estimates, which reduced the direct forcing attributed to BC by 20%. Their estimate of DRF$_{BC}$ was 0.7 ± 0.1 W m$^{-2}$, however their AFE was only 97 W m$^{-2}$ AAOD$^{-1}$, which is significantly smaller than the average in Table 1.2. Recently, Bond et al. (2013) combined multiple models with remote sensing data to estimate DRF$_{BC}$ as 0.71$^{+0.27}_{-0.08}$ W m$^{-2}$ for industrial era BC (1750 – 2005) and 0.88$^{+0.48}_{-0.17}$ W m$^{-2}$ (90% uncertainty bounds) for all sources in 2005. Using the current model values for lifetime, MAC and AFE, this is equivalent to total emissions of 13.9 Tg yr$^{-1}$ and 17 Tg yr$^{-1}$ for industrial era and all-source BC respectively. Huneeus et al. (2012) used a similar technique and estimated total BC emissions of 15 Tg yr$^{-1}$, which demonstrates the consistency of this approach, though it does not guarantee emissions are this high in reality.

The discrepancy between high model bias of BC concentrations and low model bias of AAOD suggests underestimation of BC MAC. Such variations may account for
much of the model disagreement, but not all (Bond et al., 2013). Increased mixing with soluble material may enhance MAC but also decrease lifetime. On a global scale, such effects may cancel out, but lead to localised variations in forcing (Stier et al., 2006; Ghan et al., 2012). Until model estimates of BC concentration and AAOD are improved, scaling techniques such as those used in Bond et al. (2013) are probably the best method for estimating DRF$_{BC}$. But the discrepancy still warrants explanation. Improved agreement between models and measurements would provide validation to AAOD scaling techniques, and improve confidence of AFE values, which only models can provide. Observational constraint of optical properties, removal and transport processes are therefore critical to improve model parameterisations and provide additional constraint on DRF$_{BC}$. This will also improve our understanding of regional climate effects, such as the weakening of the Asian monsoon, which perhaps have a greater impact on human lives.

1.7 Summary

The previous sections have provided an overview of BC’s role in the climate system, and demonstrated that current knowledge of such effects is limited in many areas. Greater understanding is required to inform policy and improve predictions of the causes and effects of current and future climate change, both on regional and global scales. MAC is clearly an important parameter as not only is it needed to convert from mass to absorption, it also is a useful way to track changes in absorption over BC lifetime. While Equation 1.4 is clearly a gross simplification of numerous complex and competing effects, it is useful to highlight the different areas of uncertainty.

Lifetime, MAC and AFE are all strongly influenced by BC mixing state. The most sophisticated models use detailed parameterizations of mixing state at different sizes (Jacobson, 2010; Matsui et al., 2013), but there are few measurements available to constrain such schemes. Jacobson (2012) and Matsui et al. (2013) appear to have considerable differences in their coating thickness distributions, and only Matsui et al. (2013) used observations to test their scheme. Few observations of such distributions are available (Shiraiwa et al., 2008; Metcalf et al., 2012; Laborde et al., 2013), and there is evidence that averaged properties differ significantly between different environments (Schwarz et al., 2008b; Kondo et al., 2011b; Sahu et al., 2012). Several recent studies have shown the importance of mixing state on BC’s hydrophilicity (McMeeking et al., 2011; Liu et al., 2013; Laborde et al., 2013), so these parameters are important
to determine lifetime as well as optical properties.

1.8 Thesis overview

This thesis uses measurements to explore BC’s mixing state and optical properties, to improve understanding of how these may change over the lifetime of black carbon, and between different environments. Chapter 2 discusses in detail the issues related to the calculation of MAC using different optical models, bearing in mind the variation of BC size, shape and mixing state. While complex microphysical modelling studies predict that for individual particles, core/shell Mie theory may not generate accurate optical cross-sections, the discrepancies vary with size, morphology and mixing state, and between study to study. Bearing in mind the variation in shape, size and mixing state of ambient particles, there is little evidence that core/shell Mie calculations systematically over- or under-predict absorption in ambient environments.

This is partly due to previous difficulties in obtaining reliable measurements of optical properties, and these are explored in Chapter 3, as well as an overview of the instrumentation used in this thesis. Chapter 4 details the practical aspects of development of Mie core/shell code to generate single-particle mixing state data with the SP2, and the use of such data to calculate bulk optical properties.

Chapter 5 presents results from ambient measurements carried out as part of this thesis. Single-particle BC properties are reported from urban emissions in Pasadena, California as part of the CalNex project, and from biomass burning plumes over Canada as part of the BORTAS project. The effects of physical processes (photochemical ageing and wet removal) on these properties are explored, as are the resulting impacts on optical properties.
Chapter 2

Modelling particle absorption

The previous chapter highlighted the importance of optical properties in several aspects of BC’s climate forcing. MAC is a key variable, required to convert BC mass loading to absorption, and column burden to AAOD. MAC may change over a particle’s lifetime due to changes in morphology and mixing with other aerosol. Observations show aged BC is often internally-mixed with other material (Reid & Hobbs, 1998; Pósfai et al., 1999; Vester et al., 2007), but closer to source both internally- and externally-mixed BC are often present (Moffet & Prather, 2009; Adachi & Buseck, 2013). Initially fractal soot may be restructured to form compact spheroids, and partially or fully encapsulated by nonabsorbing or weakly absorbing material. The change in morphology causes difficulty in calculating optical properties, as micro-scale optical models are morphology-dependent. Such models are essentially different ways of solving Maxwell’s equations using boundary conditions that are determined by the size, shape and refractive index of the particle. Many climate models use Mie theory, which assumes a spherical geometry, as it is less computationally intensive than more complex models, and observations of particle morphology are limited. Some climate models use volume mixing approaches, where all components are assumed to be equally distributed within a particle, and the average refractive index is input into the Mie code. Such approaches are no longer recommended as they may overestimate absorption (Bond et al., 2006). However, even some recently-developed schemes adopt such an approach (e.g. Mann et al., 2010; Bellouin et al., 2013), as the calculations are much more computationally efficient than more complex optical models, and reliable observations of both MAC and mixing state (required to test such schemes) are limited.

Mie theory may be extended to include coated spheres in a concentric core/shell configuration (Bohren & Huffman, 1983). As BC is insoluble, this is a more physically
CHAPTER 2. MODELLING PARTICLE ABSorption

A reasonable representation of internally-mixed BC (Jacobson, 2001). Similar configurations are often observed in highly aged BC (Okada et al., 1992; Martins et al., 1998; Pósfai et al., 1999). The coating of a BC core enhances the amount of light absorbed. This is often thought of as a lensing effect (e.g. Lack & Cappa, 2010), though ray tracing studies suggest it is a consequence of internal reflections between the surfaces of core and shell (Lock et al., 1994; Takano & Liou, 2010). This absorption enhancement by coating has been observed in several lab studies (e.g. Schnaiter et al., 2005a; Mikhailov et al., 2006; Slowik et al., 2007; Zhang et al., 2008; Shiraiwa et al., 2010). Enhancements of over a factor of three were seen by Mikhailov et al. (2006), however for BC of the size typically seen in atmospheric BC, absorption is predicted to increase up to around a factor of two compared to an uncoated core (Bond et al., 2006).

2.1 Scattering and absorption of light by a sphere

As aerosol particles are typically found at diameters similar to the wavelength of light, scattering and absorption falls into the Mie regime (Mie, 1908). The intensity of light scattered \( I_s \) by a sphere of diameter \( D_p \) is the product of the incident light intensity, the scattering efficiency \( Q_{\text{Sca}} \) and the particle’s geometric cross-section \( \pi (D_p/2)^2 \). \( Q_{\text{Sca}} \) is calculated by Mie theory, and is a function of a particle’s refractive index and size parameter \( \chi_p \), defined as:

\[
\chi_p = \pi D_p / \lambda
\] (2.1)

The scattering and absorption cross-sections \( C_{\text{sca}} \) are formally defined as:

\[
C_{\text{Sca}}(\chi_p, n) = \pi (D_p/2)^2 Q_{\text{Sca}}(\chi_p, n) \] (2.2)
\[
C_{\text{Abs}}(\chi_p, n) = \pi (D_p/2)^2 Q_{\text{Abs}}(\chi_p, n). \] (2.3)

or for a two layered sphere:

\[
C_{\text{Sca}}(\chi_C, \chi_p, n_{\text{core}}, n_{\text{coat}}) = \pi (D_p/2)^2 Q_{\text{Sca}}(\chi_C, \chi_p, n_{\text{core}}, n_{\text{coat}}) \] (2.4)
\[
C_{\text{Abs}}(\chi_C, \chi_p, n_{\text{core}}, n_{\text{coat}}) = \pi (D_p/2)^2 Q_{\text{Abs}}(\chi_C, \chi_p, n_{\text{core}}, n_{\text{coat}}). \] (2.5)
where $\chi_C$ is the size parameter of the core and $n_{\text{core}}$ and $n_{\text{coat}}$ are the complex refractive indices of the core and coating.

Single-particle MAC is calculated simply by dividing the calculated $C_{\text{Abs}}$ by the mass of BC ($m_{\text{BC}}$):

$$\text{MAC} = \frac{C_{\text{Abs}}}{m_{\text{BC}}} = \frac{\pi (D_P/2)^2 Q_{\text{Abs}}}{\pi (D_C^3/6) \rho_C} = \frac{3}{2} \frac{Q_{\text{Abs}}}{\rho_C} \left( \frac{D_P}{D_C} \right)^2$$

(2.6)

where $D_C$ is the BC core diameter and $\rho_C$ is the core density.

$Q_{\text{Abs}}$ is a strong function of the size parameters $\chi_C$ and $\chi_P$, and MAC is highly dependent on the dimensions of the particle, as shown in Figure 2.1a. It is easiest to consider the effects of changing $D_C$ and $D_P$ separately.

For an uncoated core, $D_P = D_C$ so Equation 2.6 simplifies to:

$$\text{MAC} = \frac{3}{2} \frac{Q_{\text{Abs}}}{\rho_C} \frac{D_C}{D_P}$$

(2.7)

This dependence on BC core size is shown in Figure 2.1b and explained by Bond et al. (2006):

1. For very small particles, mass-normalized absorption cross section is constant because the entire particle mass participates in absorbing light.

2. For larger particles, absorption cross section decreases with the inverse of the diameter because only the surface of the particle participates in absorbing light.

3. The peak in absorption at intermediate sizes [...] occurs when the frequency of the forcing (incident radiation) is near a characteristic frequency of the system (governed by the size), so an engineer might think of this as resonance.

The dependence on coatings is shown in Figure 2.1c. As coatings increase, $Q_{\text{Abs}}$ decreases as less of the total particle is absorbing. Initially, MAC increases as the increase in $D_P$ focuses more light onto the absorbing core. However, at the thickest coatings a limit is reached where no more light can be focused, and the system oscillates normal modes of the sphere (Bohren & Huffman, 1983). However, the bulk of the BC mass distribution typically found in the atmosphere does not exhibit such thick coatings, and in ambient conditions the calculated absorption is generally enhanced by thicker coatings.
CHAPTER 2. MODELLING PARTICLE ABSORPTION

Figure 2.1: Modelled MAC for particles of different diameters and shell/core ratios, calculated using Mie theory. Part (a) shows MAC at typical BC core size and shell/core ratios seen in the atmosphere. MAC (solid lines) and $Q_{Abs}$ (dashed lines) are shown as a function of (b) core diameter for fixed shell/core ratios and (c) as a function of shell/core ratio for fixed core diameter. All the calculations were performed using $n_{core} = (1.85 - 0.71i)$ and $n_{coat} = (1.5 - 0i)$. 
2.2 Optical properties of nonspherical particles

Optical properties of fractal aggregates may be modelled using the Rayleigh-Debye-Gans (RDG) approximation. Scattering and absorption by particles small compared to the wavelength of light are calculated by (Bohren & Huffman, 1983):

\[
\text{MAC} = \frac{6\pi}{\rho \lambda} \text{Im} \left[ \frac{(n^2 - 1)}{(n^2 + 2)} \right] \quad (2.8)
\]

\[
\text{MSC} = \frac{4\pi^4 d^3}{\rho \lambda^4} \left| \frac{(n^2 - 1)}{(n^2 + 2)} \right|^2 \quad (2.9)
\]

where \( \rho \) is the density of the BC, \( \lambda \) is the wavelength of light and \( n \) is the complex refractive index.

Under the RDG approximation, for a fractal aggregate composed of \( N \) spherules the cross-sections are those of the individual spherules scaled by \( N \) for absorption and \( N^2 \) for scattering. RDG therefore explicitly excludes the effects of multiple scattering within the aggregate. There are several mathematical approaches that do include multiple scattering between spherules, such as the Discrete Dipole Approximation (DDA) (Draine & Flatau, 1994), Superposition T-Matrix (STM) (Mackowski, 1994; Liu et al., 2008) and Generalised Multiparticle Mie (GMM) (Xu, 1995, 1997; Chung et al., 2012a). These are all computationally intensive and require precise knowledge of the morphology of the particles in terms of the size of the spherules and their locations relative to each other.

Several studies have considered the effects of multiple scattering on absorption, and estimated enhanced absorption due to aggregation between 0 – 50\%, depending on the size and number of spherules (Iskander et al., 1991; Fuller, 1995; Liu & Mishchenko, 2005). Fuller et al. (1999) showed that this enhanced absorption by aggregation was extinguished when the particle became encapsulated by nonabsorbing material. Bond & Bergstrom (2006) reviewed measurements of the MAC of fresh BC, and found these generally lay in the range 7.5 ± 1.2 m² g⁻¹ at 550 nm. They also suggested a range of \( n \) appropriate for BC, and showed that MAC calculated using the RDG approximation underpredicts this range by ~30\%, even when using the value for \( n \) that resulted in the strongest absorption. They therefore proposed that the source of this discrepancy may be multiple scattering by the spherules.

More recent studies considering the optics of fractal soot have presented mixed results. Many optical models struggle to calculate values of MAC that are physically reasonable (Kahnert, 2010b), and \( C_{Abs} \) is often reported instead. Adachi et al. (2010)
and Chung et al. (2012a) studied a limited number of morphologies and calculated that absorption by fractal aggregates would show minimal variation when the particles collapsed, however Liu et al. (2008) and Kahnert (2010a) predicted absorption may increase or decrease when aggregates collapse, depending on the size, refractive index and number of the spherules. Some studies report results that are directly contradictory- Chung et al. (2012a) highlighted the strong dependence of absorption on the size of the primary spherules, but Kahnert (2010b) demonstrated little dependence as particles are close to the Rayleigh limit. The modelling techniques used in the two studies (GMM and STM respectively) are both supposedly exact solutions to Maxwell’s equations. Evidence of a change in absorption due to aggregate collapse is extremely limited; Mikhailov et al. (2006) collapsed aggregates coated with a thin monolayer of soluble glutaric acid, but the ratio of $B_{Abs}$ to particle number concentration showed very little variation. Lewis et al. (2009) exposed biomass burning soot to high RH to collapse the fractal structure, and reported a decrease in absorption of 10 – 20%, but they suggested this was likely due to evaporation of the condensed water decreasing the photoacoustic signal.

For internally mixed particles, there is a similarly complex picture. Adachi et al. (2010) examined the sensitivity of absorption to soot volume fraction, fractal dimension and relative position (centre vs off-centre) in mixed particles, and calculated that any deviation from a concentric core/shell morphology would reduce absorption. However, they did not consider variation in total particle size. Kahnert et al. (2012) calculated the absorption of a fractal core partially encapsulated by sulphate; for particles small compared to the wavelength of light, there was little difference between DDA and volume-equivalent core/shell Mie absorption, but for larger particles the Mie absorption was lower as the core centre was shielded by the core edge.

Numerous laboratory studies have demonstrated absorption enhancement due to coatings (e.g. Schnaiter et al., 2005a; Slowik et al., 2007; Shiraiwa et al., 2010), though some have presented mixed results. Bueno et al. (2011) coated flame soot with dibutyl phthalate, and calculated absorption enhancement as the ratio of absorption by a coated sphere (using Mie theory) to that of an aggregate (using RDG). Their calculations agreed well with the measured absorption enhancement for 150 nm and 200 nm cores, but not for 100 nm. Slowik et al. (2007) observed absorption enhancement by a 60 nm coating of anthracene, but not by a 50 nm coating of oleic acid. Schnaiter et al. (2005a) coated diesel soot with biogenic SOA, and Shiraiwa et al. (2010) coated graphite particles with oleic acid and glycerol; both observed absorption enhancement in excellent
agreement with core/shell Mie calculations.

Detailed optical models present a confused picture due to the complexity of BC shape, size and mixing state. The optical properties of externally mixed soot may depend on the size and number of spherules and their position relative to each other. For internally mixed BC, the amount and relative location of non-BC material adds further complexity. The wavelength of light and refractive indices of the different components (some of which may be wavelength-dependent) add further variables, which strengthen or weaken the different, often competing effects. More realistically-shaped soot particles may be more or less absorbing than spherical, whether coated or not, depending on the precise morphology and properties of the particle. There is undoubtedly question regarding how accurately the core/shell model may be used to reproduce optical properties. However, more advanced optical models are difficult to test even under laboratory conditions, and there is currently little evidence that agreement between measured and modelled optical properties is systematically improved when using other optical models. The next section discusses observations of MAC and the need for measurements, using modern techniques, in ambient environments.

2.3 Linking microphysical models to observations

Bond & Bergstrom (2006) considered both possible sources of absorption enhancement (due to multiple scattering within an aggregate and coatings on a core/shell particle) and proposed that the absorption of BC over its lifetime may increase by a factor of $\sim 1.5$. Their reasoning was that if nonabsorbing material filled in spaces between spherules, the multiple scattering enhancement would be inhibited (Fuller et al., 1999), reducing absorption by up to 30%, but the coating would enhance absorption by up to 100%. Combined with their estimate for fresh BC, Bond & Bergstrom (2006) suggest a range of MAC between $7.5 - 11.25 \, \text{m}^2 \, \text{g}^{-1}$ at 550 nm. MAC derived from AERONET retrievals falls into the range $7.7 - 12.5 \, \text{m}^2 \, \text{g}^{-1}$ (Schuster, 2005), but this study did not consider the contribution of BrC to absorption. Comparison to in-situ measurements can be difficult, as many older techniques suffer from artefacts related to mixing with nonabsorbing aerosol (Lack et al., 2008). These issues are discussed further in Chapter 3. Some techniques are considered to be more reliable- the SP2 and PhotoAcoustic (Soot) Spectrometer (PAS/PASS) measure BC mass loading and $B_{Abs}$ respectively, and do not suffer from artefacts related to mixing with nonabsorbing aerosol. These instruments are also discussed in Chapter 3.
There are, however, very few studies that have combined such techniques to measure changes in MAC in ambient environments. Cappa et al. (2012) compared MAC against a measure of photochemical age, but presented mixed results—off the Californian coast, ambient MAC remained close to Bond & Bergstrom’s values for fresh BC, but in an urban centre were up to 40% higher at 532 nm. Lan et al. (2013) showed MAC between 5 – 8.5 m² g⁻¹ in a mega-city in South China, though they considered only a qualitative measure of particle mixing state. Knox et al. (2009) measured ambient MACs of ~9.5 m² g⁻¹ in different conditions, which they termed ‘fresh’, ‘semi-aged’ and ‘aged’ based on the size distributions. Some studies have used thermodenuders to measure absorption enhancement; Cappa et al. (2012) found limited absorption enhancement in urban pollution, whereas Lack et al. (2012a) found a factor of 1.4 in biomass burning emissions at 532 nm. Knox et al. (2009) observed 2 – 42% enhancement in urban measurements in downtown Toronto, which varied depending on the age of the airmass, but suffered from limited statistical significance in this result. However, thermodenuders do not always fully remove coatings from particles, and may therefore give mixed and/or misleading results (Knox et al., 2009; Fuentes & McFiggans, 2012; Cappa et al., 2013). Both Cappa et al. (2012) and Knox et al. (2009) found disagreement between estimates of absorption enhancement using thermodenuders and by comparing to Bond & Bergstrom’s values for fresh BC. Such differences may be explained either by calibration errors, nonvolatile coatings, or a combination of the two.

In particles with morphologies other than core/shell, changes in absorption may be limited, as the effect of mixing with nonrefractory material is reduced (Adachi et al., 2010). Sedlacek et al. (2012) used the SP2 to show evidence of BC on a particle’s surface in biomass burning emissions. Adachi et al. (2010) and Adachi & Buseck (2013) found a variety of soot morphologies in urban areas, many of which were not core/shell, however their electron microscopy technique removes any semi-volatile material from the particles before they are sampled, and thus underestimates mixing. Adachi & Buseck (2013) reported compacted BC in Los Angeles with no coatings, which they stated may be due to evaporation of volatile coatings before sampling. This seems likely, as soot is thought to be compacted by condensation. Modelling work by Adachi et al. (2010) and Adachi & Buseck (2013) suggests the core/shell model may overestimate absorption by up to 20% compared to BC on the edge of particles.

Observations of MAC using reliable techniques are very limited, and only Cappa et al. (2012) compared MAC to a measure of airmass age, however their mixed results
between the different environments studied did not present a clear picture. Further measurements are required in different environments to assess how much variation there may be in MAC over the lifetime of BC. The contribution of brown carbon is also still a large source of uncertainty—while BrC absorption is strong in the ultraviolet (Kirchstetter et al., 2004; Zhang et al., 2011), its relative contribution to total absorption over the entire solar spectrum is much less clear. This is discussed in the next section.

### 2.4 Brown carbon absorption

The wavelength-dependence of absorption is commonly characterised by calculating the Absorption Ångström Exponent (AAE):

\[
\frac{B_{\text{Abs}}(\lambda_1)}{B_{\text{Abs}}(\lambda_2)} = \left(\frac{\lambda_1}{\lambda_2}\right)^{-\text{AAE}}
\] (2.10)

Under the RDG approximation, AAE = 1; in urban pollution, AAE is typically close to this value (Kirchstetter et al., 2004; Bergstrom et al., 2007; Lack et al., 2008). In biomass burning emissions AAE exponent may be between 2 – 7, though is typically towards the lower end of this range (Andreae & Gelencser, 2006; Rizzo et al., 2011; Corr et al., 2012; Kirchstetter & Thatcher, 2012). Determination of AAE is dependent on which wavelengths are used for comparison, as AAE for brown carbon is higher at UV wavelengths. Chung et al. (2012b) used multiple-wavelength AERONET AAOD data to estimate global direct radiative forcing of BrC as 20% of the total by carbonaceous aerosols, however their method required prescribed “best guess” estimates of the AAE of BC and BrC. The AAE of BC may vary due to internal mixing (Lack & Cappa, 2010) and AAE of BrC due to different composition of OA, meaning the use of such techniques to assign absorption to either BC or BrC may have large errors (Lack & Langridge, 2013). In-situ measurements by Lack et al. (2012a) showed that BC coatings can enhance absorption by lensing, but measured additional absorption by BrC at 405 nm.

While there is increasing evidence of the ubiquity of brown carbon in biomass burning aerosols (e.g. Gadhavi & Jayaraman, 2010; Chakrabarty et al., 2010; Chen & Bond, 2010), the abundance and strength of absorption is still subject to much uncertainty. Variations in combustion conditions yield differences in the relative abundances of black and brown carbon, which in turn affects absorption. It is also thought that there
may be an absorbing component of SOA, biogenic and marine aerosols (Andreae & Gelencser, 2006; Moosmuller et al., 2009), and Chen & Bond (2010) measured weak absorption in the soluble components of diesel emissions, but noted that unless atmospheric organic carbon absorbs much more strongly, this would have little effect on global clear-sky forcing. Conversely, Park et al. (2010) modelled brown carbon in Asian outflow, and predicted brown carbon contributes 15% of RF due to absorbing aerosols. When considering BC absorption measurements, the presence of BrC may give the appearance of absorption enhancement even if the particles are externally mixed. It is therefore important to consider such effects when measuring optical properties in ambient environments.

2.5 Summary

There is significant uncertainty in the evolution of BC optical properties over its lifetime, and between different environments. While the core/shell model has limitations there is little evidence to suggest that core/shell schemes, when constrained by observational data (e.g. Matsui et al., 2013) are appropriate or inappropriate to use for bulk optical property calculations. Section 2.2 summarised the confused picture provided by different studies modelling BC optics with more complex morphologies. Many studies choose only a few ‘representative’ geometries or sizes, but real particles show a wide variety of shapes, sizes and mixing states (Pósfai et al., 1999; Adachi et al., 2010). The relative importance of brown carbon absorption in different environments is also poorly constrained, and is thought to vary between different emission sources (Cappa et al., 2012; Lack et al., 2012a). Few studies have measured variations in MAC using reliable techniques, and those that have present mixed results (Cappa et al., 2012, 2013; Lan et al., 2013). Measurements of MAC in different environments, and under different conditions, are required to test the accuracy of core/shell schemes if they are to be used to examine BC’s effect on climate. The reasons for the disagreement between models and measurements of BC mass concentration and AAOD is still an unsolved and troubling issue. Observational constraint of key parameters such as mixing state and MAC will help to improve model parameterizations to better represent BC in climate models, and to better understand BC’s overall impact on the climate system.
Chapter 3

Instrumentation

This chapter provides a summary of the key instrumentation used in Chapter 5. Historically, soot measurement techniques consisted of capturing particles on a filter and measuring their properties, and these are discussed further in the next section. Not only are such approaches limited to bulk measurements, the techniques can suffer severe uncertainties due to ambiguities in the measurement method, interferences due to non-BC particles in the filter and from the filter matrix itself (Moosmuller et al., 2009; Baumgardner et al., 2012).

In the past decade, large advances have been made in BC mass quantification, particularly with the emergence of the SP2 (Stephens et al., 2003). BC mass and mixing state can now be measured in-situ on a single-particle basis, providing a tool to characterise mass concentrations, size distributions and coating properties. Through the use of Mie modelling, this provides a basis for prediction of optical properties, discussed in Chapter 4. MAC can be calculated by combining BC mass concentration with absorption measurements, giving a means to constrain changes in BC optical properties in ambient conditions. In this thesis the SP2 is used with a photoacoustic soot spectrometer to directly measure MAC, and to monitor changes with photochemical processing. These data are also compared to Mie calculations using SP2 core/shell data from the same conditions.

3.1 Filter-based measurements

Many previous measurements of BC/EC concentration and optical properties rely on filter-based measurements, and combinations of such techniques may in theory be used to calculate MAC. However, the range of values this type of analysis has yielded
(3.8 – 58 m² g⁻¹ (Cappa et al., 2012, and references therein)) extends beyond that which is physically plausible based on multiple optical models. Systematic errors inherent in these methods are large enough to render any such calculations unreliable.

### 3.1.1 Thermal optical analysis

Thermal optical analysis is a technique for measuring the Total Carbon (TC) collected on a filter and dividing into Organic Carbon (OC) and EC fractions (ECa in Table 1.1). Particle-laden filters are heated in a controlled atmosphere, which is stepped through increasing temperatures and different mixes of helium, air and/or oxygen. The amount of carbon released at different temperatures (measured as CO₂ or reduced to CH₄) yields the concentrations of OC and EC and an optical measure (transmission through or reflectance from the filter) is used to correct for charring (Birch & Cary, 1996; Cavalli et al., 2010).

This method suffers interferences due to the uncertain divide between OC and EC, and different temperature protocols and optical measures yield different derived EC concentrations (Chow et al., 2001; Schauer et al., 2003; Chow et al., 2004). Further interferences are possible due to carbonate carbon (Robles et al., 2011) and low-volatility organics (Piazzalunga et al., 2011). Not only are there inherent uncertainties due to the specific method used, ambiguity over the OC/EC split means these are composition-dependent, and hence render such techniques unreliable for assessing changes in MAC.

### 3.1.2 Filter-based absorption measurements

The most widely available instruments for absorption measurement are the Aethalometer (Magee Scientific, Berkeley, California, USA) and Particle Soot Absorption Photometer (PSAP) (Radiance Research, Seattle, Washington, USA) which both operate on a similar principle. The transmission of light through a piece of filter tape is measured at periodic intervals while sample air is drawn through the tape. Particles are deposited on the filter and absorbing aerosols decrease the transmission, reducing the flux of light detected. Attenuation through the filter, ATN, is therefore defined as:

\[
ATN = \ln \left( \frac{I_0}{I} \right),
\]

where \( I \) is the intensity of light detected through the filter and \( I_0 \) is the intensity through a pristine section of filter.
3.1. FILTER-BASED MEASUREMENTS

$B_{\text{Abs}}$ is then determined by comparing $\Delta ATN$, the change in $ATN$ during time $\Delta t$. The $n$th measure of $B_{\text{abs}}$ at wavelength $\lambda$ is given by (Coen et al., 2010):

$$B_{\text{abs},n}(\lambda) = \frac{\Delta ATN(\lambda)}{\Delta t} \cdot \frac{A}{V},$$

(3.2)

where $A$ is the area of the sample on the filter tape and $V$ is the volumetric flow rate through the filter.

While they are relatively cheap and easy to run, filter-based absorption measurements have some severe drawbacks which can significantly affect their measurements. They suffer from measurement artefacts due to scattering aerosols embedded in the filter, multiple scattering from filter fibers and accumulation of material in the filter reducing the optical path (Bond et al., 1999; Coen et al., 2010). There is also evidence of size-dependent sensitivity, probably due to the different backscatter fraction and penetration depths of different-sized particles (Lack et al., 2009; Moteki et al., 2010b). Significantly, the measurement biases are dependent on the properties of the aerosol sampled, and are therefore different in different environments. Lack et al. (2009) observed agreement between PSAP and PAS within 12% in a remote environment, but suggested the overestimation of absorption in PSAP measurements may be $> 100\%$ in heavily polluted conditions.

Several empirically-derived correction algorithms have been published (e.g. Bond et al., 1999; Schmid et al., 2006; Coen et al., 2010); the two instruments require different corrections due to the different filter tapes, as the PSAP uses glass fiber tape while the Aethalometer uses quartz fibers. The PSAP also uses a reference filter to account for non-particulate interference such as changes in humidity. Even when corrections are applied, if any differences in MAC are observed it is difficult, if not impossible, to determine how much is real variation and how much is artefact. Müller et al. (2011) compared numerous filter-based absorption instruments, and concluded that current correction algorithms were inadequate. Even using corrected data, the uncertainty and ambiguity involved in such measurements means it is difficult, if not impossible, to investigate sensitivities to model/measurement agreement (e.g. Highwood et al., 2012).

In the past decade there have been some improvements in filter-based absorption. The Multi-Angle Absorption Photometer (MAAP) (Petzold & Schonlinner, 2004) is a modification of the PSAP that attempts to remedy some of these issues. Concurrent measurement of backscattered light at several angles removes some of the external correction required, and generally reduces the overestimation of absorption (Petzold et al.,
2005). This is not to say that the MAAP is without artefacts; Slowik et al. (2007) compared a MAAP to a photoacoustic spectrometer and showed that the ratio of the two differed between different soot samples. The COntinuous Soot MOntoring System (COSMOS) (Miyazaki et al., 2008) utilizes a heated inlet to evaporate nonabsorbing particles and reduce scattering artefacts. The instrument compares well to the SP2 for measuring BC mass concentration (Kondo et al., 2011a), but the heated inlet strips off coatings and there is no way of assessing difference in absorption of coated particles.

While filter-based absorption measurements are generally cheap and easy to use, they are more appropriate for use in air quality studies and long-term monitoring. Most importantly, their artefacts vary with changes in the mixing state and optical properties of particles, meaning they are not reliable for investigation of these effects.

### 3.1.3 Difference method

When scattering and extinction measurements are performed on the same volume of air, the difference between the two may be used to calculate absorption. This is referred to as the difference method.

Cavity Ring-Down (CRD) spectrometers provide a robust measure of extinction, utilising either continuous or pulsed lasers (Strawa et al., 2003; Pettersson et al., 2004). The technique relies only on the change in laser power as a beam of light passes through a volume of aerosol and, as long as the laser power meter responds linearly, no calibration is needed. Massoli et al. (2010) also demonstrated the use of a Cavity-Attenuated Phase Shift (CAPS) technique, calculating extinction based on the phase shift of modulated LED light as it passes through a volume of aerosol.

The main limitation in the difference method lies in the scattering measurement used. Older-style nephelometers measure light scattering either by illuminating a volume of aerosol with a cosine-law diffuse light source and standard detector, or a parallel light source and cosine-law detector (Mulholland & Bryner, 1994; Anderson & Ogren, 1998). Newer designs may use integrating spheres to gather light from many angles reflected towards a detector (e.g. Varma et al., 2003; Thompson et al., 2008). All nephelometers require truncation corrections to account for light scattered that falls on areas such as the aerosol inlet/exhaust or reflects back to the light source, and is therefore not detected. Such corrections may be empirical or theoretical (e.g. Anderson & Ogren, 1998; Qian et al., 2012), however these are approximations at best, as the angular distribution of scattered light depends on the wavelength of light and the size, shape and refractive index of the particles (Bohren & Huffman, 1983).
Comparisons between the difference method and more absolute measurements of absorption have shown mixed results depending on the properties of the particles and the concentrations involved. Sheridan et al. (2005) compared CRD/nephelometer absorption to a PAS using several different artificial soot sources. They found good agreement when comparing all their data, but noted the high signal points dominated the fit. With these points removed the agreement was reduced, and although overall this was still within 10%, some runs with lower signals disagreed by over 50%. Schnaiter et al. (2005b) showed general good agreement under laboratory conditions between a custom-built extinction cell/nephelometer and a PAS, but the difference between the two varied between different soot sources. Thompson et al. (2012) ran their CRD/integrating sphere albedometer in ambient conditions and noted the derived absorption compared well to a co-located PASS at some times, and poorly at others. In typical ambient conditions (where SSA is relatively high and concentrations are low compared to laboratory conditions), calculating small differences between much larger quantities can yield high errors in the derived absorption.

One strength of the difference method is that it is currently the only method that can be used to measure absorption at high humidities (e.g. Mikhailov et al., 2006; Wei et al., 2013). The main limitations for the purposes of investigating the effects of mixing state on BC absorption are that the inferred absorption is not only sensitive to the truncation (assumed and real) of the light scattered by BC-containing particles (which may vary over particles’ lifetime and between different sources), it also depends on the scattering properties of any LSP also in the sampling volume. In typical ambient conditions this method can also yield large errors, and is most often used in the laboratory or in high ambient concentrations.

3.2 The Single Particle Soot Photometer (SP2)

The following section refers to the 4-channel SP2, which was used for the experimental work discussed in Chapter 5.

3.2.1 Operating Principle

The single particle soot photometer (Droplet Measurement Technologies, Boulder, Colorado, USA), shown in Figure 3.1, measures accumulation mode black carbon using the principle of light-induced incandescence. Particles are drawn through a
1064nm Nd:YAG laser cavity, and scattered light is measured by 2 Avalanche Photo-Diode (APD) detectors. Absorbing particles vaporise when passing through the beam, and black carbon heats to incandescence. The incandescent light is detected with 2 PhotoMultiplier Tubes (PMTs), which respond linearly with BC mass, regardless of BC coatings (Slowik et al., 2007; Moteki & Kondo, 2007).

An example of a single particle detection is shown in Figure 3.2. As the particle enters the laser, the two APDs measure scattered light. The high gain scattering detector is a Twin-Element APD (TEAPD), and its signal is initially inverted, before becoming positive. This is to measure the position of the particle, and is discussed further in Section 3.2.3. For a Light Scattering Particle (LSP, a particle which contains no BC and therefore does not incandesce in the SP2), the APDs record Gaussian signals, as the particle passes through the Gaussian laser beam. For a BC particle, the scattering degrades as the particle evaporates in the laser. There is a time delay between the onsets of scattering and incandescence detected by the PMTs, due to the latent cooling as any nonrefractory material evaporates and the BC core takes time to heat to incandescence.

The two PMTs are set to different gains, allowing a greater range of particle mass to be detected, and they are restricted to different wavelength ranges through the use of optical filters. One APD measures broadband incandescent light between 350–750 nm, while the other is filtered to 630–750 nm. This allows measurement of the incandescent temperature, as the ratio of blue/red light is dependent on the black body emission spectrum. Assuming the SP2 has sufficient laser power, all BC particles incandesce at roughly 4300 K (Schwarz et al., 2010b). The peak emission wavelength is inversely proportional to temperature, and using Wien’s law (Young et al., 2004) is $\sim 675$ nm for incandescence at this temperature.

### 3.2.2 SP2 Calibration procedures

The SP2’s APDs are calibrated using polystyrene latex spheres (PSLs), which are spheres of known size and refractive index. The PSLs are nebulised from suspension, dried, then size-selected by a Differential Mobility Analyser (DMA) to minimise any interference from polydisperse background aerosol, and finally sampled by the SP2. Day-to-day, such calibrations are useful for ensuring the SP2 is properly aligned, but they are also used to calibrate the SP2’s scattering response. This is discussed further in Section 4.2.2.

Best practice for calibrating the SP2’s incandescence channels has undergone significant improvement in the past few years. As the SP2 PMTs respond linearly to particle
3.2. THE SINGLE PARTICLE SOOT PHOTOMETER (SP2)

Figure 3.1: Schematic of the SP2. The aerosol jet is drawn through the laser cavity, and confined by sheath air to ensure all particles pass through the laser beam. The sample line and exhaust flow are drawn on the page for simplicity; they are actually located vertically into and out of the page. The sample flow (typically $120 \text{ cm}^3 \text{ min}^{-1}$) is confined by a filtered dried sheath flow of $1 \text{ l min}^{-1}$, and a purge flow of $300 \text{ cm}^3 \text{ min}^{-1}$ keeps particles away from the optical detectors. The two-element detector (the TEAPD) measures the position of the particle in the beam. The cavity leakage detector measures the laser power in arbitrary units. *Aerosol Science & Technology*: The Detection Efficiency of the Single Particle Soot Photometer, 44: 612 – 628. Copyright 2010. Mount Laurel, NJ. Reprinted with permission.
Figure 3.2: Example of SP2 raw data for (a) an LSP and (b) a soot particle.
mass, ideally a mass selector would be used, such as Aerosol Particle Mass analyser (APM) (Ehara *et al.*, 1996) or Centrifugal Particle Mass Analyser (CPMA) (Olfert & Collings, 2005). As these are expensive, DMAs are more common, but these measure mobility diameter ($D_{mob}$) rather than mass-equivalent diameter ($D_m$), and so there are two key technical challenges to this approach:

1. Fractal soot surrogates are oversized by DMAs ($D_{mob} > D_m$), meaning the mass-mobility relationship of the calibrant must be known

2. Different soot surrogates produce different incandescent signals, even for particles of the same mass

Several polydisperse soot surrogates are available, each of different composition, shape and density. Fullerene soot is the most representative of ambient Tokyo soot in terms of mass-mobility relationship and SP2 response (Moteki & Kondo, 2010), however it shows batch-to-batch variations (Laborde *et al.*, 2012a). The manufacturer originally recommended using Aquadag, a colloidal graphite suspension used for coating cathode ray tubes, and all SP2 users therefore have Aquadag available. By comparing 6 SP2s, Laborde *et al.* (2012b) showed the relative response of the broadband PMT to Aquadag and fullerene soot is stable for 8.95 fg particles (300 nm mobility diameter). The recommended SP2 calibration is therefore to measure the response to 300nm Aquadag and correct the slope by a factor of 0.75 to account for the difference (Baumgardner *et al.*, 2012; Laborde *et al.*, 2012b).

During the BORTAS project (see Section 5.3), the SP2 was calibrated using this approach. The calibration curves for the two detectors are shown in Figure 3.3. As Laborde *et al.* (2012b) only showed the difference between Aquadag and fullerene soot for the broadband detector, the narrowband detector was cross-calibrated using particles measured in biomass burning plumes. The two slopes in Figure 3.3a represent fits either using all data points (using the mass-mobility relationship reported by Gysel *et al.* (2011)) and only the 300 nm point. The two slopes agreed to within 2%, which adds additional validations to the single-point calibration.

During CalNex, the SP2 was calibrated using glassy carbon spheres, as there was no consensus at the time on which calibrant was best to use. Figure 3.4 shows the calibration curves, using a power law fit to glassy carbon diameter as a function of detector signal. Ambient particle diameter was then calculated using these curves, but corrected for the difference in density between glassy carbon and ambient soot.

To validate this approach, Figure 3.5 shows BC core size distributions, using the
Figure 3.3: Calibration curves for the SP2’s (a) broadband and (b) narrowband incandescence detectors using during BORTAS.
3.2. THE SINGLE PARTICLE SOOT PHOTOMETER (SP2)

The SP2’s incandescence detectors using glassy carbon.

same raw data, generated using the two calibrations. While the calibrations were carried out a year apart, the SP2’s PMTs are stable as long as the detector gains are not adjusted. The two distributions in Figure 3.5 are near-identical, and the total mass calculated using each calibration differ by < 0.4%. This means that although the approaches used were different, the results of each calibration were extremely similar. During CalNex, an intercomparison with NOAA’s SP2, which was calibrated using fullerene soot, showed agreement in mass to within 10% (Anne Perring, private communication), which provides additional validation to this calibration.

3.2.3 Leading edge only fitting

The SP2’s scattering detectors measure the time-dependent scattering as each particle passes through the laser. As the laser has a Gaussian profile, the SP2 records a Gaussian signal when an LSP is measured, shown as the low-gain scatter in Figure 3.6a. When a BC-containing particle passes through the laser it vaporizes, losing mass and hence lowering its scattering cross-section. This is shown as the low-gain scatter trace in Figure 3.6b, which decays as the particle evaporates. In order to calculate a particle’s optical size, it is necessary to measure a particle’s scattering cross-section before it begins to evaporate. Leading edge only (LEO) fitting (Gao et al., 2007) is used for this purpose. A Gaussian profile is fit only to the leading edge of the measured scattering,
Figure 3.5: Example BC size distributions, using the same raw data, to compare the two calibration methods. Part (a) shows the BC number distribution, and part (b) shows the mass distribution.
before the particle started to evaporate, to infer what the peak scattering would have been. In the example shown in Figure 3.6, the leading edge is defined as the first 5% of laser intensity.

The high-gain scatter traces in Figure 3.6 show the signal recorded by the TEAPD, which utilises two separate detection elements (though four are available, only two are used). One element is electronically inverted, and both element’s signals are added together. The particle initially passes over the inverted element, so the signal starts with a negative Gaussian shape. As the particle passes the boundary between the two elements, the signal switches to positive, shown as the split position in Figure 3.6. The SP2 triggers a particle when either the scattering or incandescence signals pass above a pre-defined threshold. This may occur at different points in a particle’s path through the laser as larger particles scatter more light. As the split is fixed in space, this provides a reference point for each particle as it passes through the laser. The laser width and the position of the split relative to the peak laser intensity (shown as the “notch position” in Figure 3.6) are fixed in space, and are therefore near-constant for LSP in the SP2. There is some variation, as not all particles pass directly through the centre of the laser, but the particle jet is narrower than the laser width, so such variations are relatively small as long as the instrument is well aligned (Schwarz et al., 2006).

The utility of measuring the laser beam width and notch position is that when they are known, they can be used to constrain the LEO fit. The equation of a Gaussian function is shown defined as:

\[
I(t) = \frac{A}{\sigma \sqrt{2\pi}} \exp\left(-\frac{(t-\mu)^2}{2\sigma^2}\right),
\]

where \(I\) is the measured signal as a function of time \(t\), \(A\) is the peak height, \(\sigma\) is a measure of width and \(\mu\) is the fit centre. \(\mu\) is the (split position + notch position), and \(\sigma\) is the Gaussian width, related to the Full Width at Half Maximum (FWHM) by \(\sigma = \text{FWHM} / 2\sqrt{2\ln 2}\).

Once the baseline has been subtracted from each particle, this leaves \(A\) as the only parameter left to fit, and this greatly reduces the uncertainty in the derived peak height. Figure 3.6b shows an example LEO fit for a BC particle measured during BORTAS, which was fit using the measured notch position and FWHM from Figure 3.6a. LEO fitting is performed by the SP2 LabView code (Liu, 2009), which processes the raw signals. For each fit, the modal notch position and FWHM of the previous 200 LSP are
used for the calculation.

3.2.3.1 Defining the leading edge

A successful leading-edge fit must accurately represent the properties of the particle before it began to evaporate in the laser. Moteki & Kondo (2008) and Kondo et al. (2011a) described a method to measure the scattering cross-section of a particle as it passes through the laser beam, which was later refined by Laborde et al. (2012a). This is calculated simply by dividing the measured scattering by the profile of laser intensity (calculated using the parameters $\mu$ and the FWHM described in Section 3.2.3).

Figure 3.7 shows examples of measured BC scattering signal and scattering cross-section from Laborde et al. (2012a) using this technique. The scattering cross-section begins with a noisy region, when the measured signal is too low to be reliable. As the signal increases, a flat region emerges as the coated particle has not yet begun to evaporate. As the coating evaporates, the cross-section decreases, before flattening again as the uncoated core is exposed but is yet to start evaporating. The cross-section then drops to zero as the core evaporates.

Figure 3.8 shows example scattering cross-sections measured with the Manchester SP2 during BORTAS. An example LSP is shown, and this has a flat profile, as it does not evaporate as it passes through the laser. Initially the BC profiles are similar to those presented by Laborde et al. (2012a), with a noisy section when the signal is low and a flat section for the coated particle. There is some variation in how flat these sections are, probably due to variations in the path of particles through the laser (relative to the split and the peak laser power), which cause small differences between the average laser profile and that seen by an individual particle. There is also some variation in how long the flat sections last before the coated particles start to evaporate. The ideal leading-edge would need to be after the noisy section but before any particles start to evaporate. In Figure 3.8, defining the leading-edge as from the baseline up to 5% of peak laser power fits these criteria.

The flat section for a bare BC core, evident in Figure 3.7, does not appear in the data shown in Figure 3.8, and it is not immediately clear why. Possible explanations are that the laser power was too high (so the bare BC core did not have a chance to remain stable before evaporating) or differences related to the size and morphology of the individual particle. Larger BC-containing particles saturated both the Manchester SP2’s scatter detectors, and these may behave differently to those shown in Figure 3.8.
3.2. THE SINGLE PARTICLE SOOT PHOTOMETER (SP2)

Figure 3.6: Example baseline-subtracted scattering signals for (a) an LSP and (b) a BC-containing particle. Also shown are the split position, peak centre, notch position and FWHM, and the position of 5% laser intensity. The measured parameters from part (a) are used in part (b) to calculate the LEO fit, which was fit to the first 5% of laser intensity.
Figure 3.7: Idealised BC particle in the SP2 showing (a) the raw scattering data showing distinct peaks for the coated particle and the bare core, and (b) the corresponding scattering cross-section as the particle passes through the laser. Image adapted from Laborde et al. (2012a).

Figure 3.8: Calculated scattering cross-sections across the laser profile for several particles measured during BORTAS. Negative data and data when the ch0 detector was saturated are not shown.
3.2.3.2 Quality assuring LEO fits

A poor LEO fit will produce inaccurate derived coating properties, and such particles should not be used when performing calculations. The main reasons for poor fits are either when the measured scattering signal is too small or too large, or the split position is not measured. The LabView code does produce LEO fits equal to zero for particles where the scattering signal is too small, but in practice it is extremely rare for this size of particle to measure a valid split position. In practice, the majority of poor LEO fits are due to the particle evaporating before the split is seen and, rather than the high-gain scatter signal flipping from negative to positive (as shown in Figure 3.6b) the signal merely returns to the baseline. However, due to random noise in the signal the signal at some point passes above the baseline, which would wrongly be interpreted as the split position. The split was therefore re-defined as the point where the signal reaches 20 units above the baseline. While this has little effect on particles with detectable split, it provides an effective means of filtering particles where the notch is not seen. When this is the case, the reported fit centre is at the end of the array for a particle, and hence these particles can be easily filtered out.

3.3 The Aerosol Mass Spectrometer (AMS) and Soot-Particle Aerosol Mass Spectrometer (SP-AMS)

The Aerosol Mass Spectrometer (AMS, Aerodyne Research Inc., Billerica, Massachusetts, USA) is currently a widely-used instrument for online measurement of atmospheric aerosol composition (Canagaratna et al., 2007). It provides quantitative, size-resolved composition data for non-refractory accumulation-mode aerosols. In order to sample particles, the AMS vaporizes them on a tungsten heater set to 600 °C, meaning the AMS cannot measure refractory species such as BC, though it can be used to study the nonrefractory elements of soot (Slowik et al., 2004). The Soot-Particle AMS (SP-AMS, (Onasch et al., 2012)) is a modification of the original design, replacing the tungsten vaporizer with an Nd:YAG laser of the same type used in the SP2. This selectively vaporizes particles that absorb light at 1064 nm, and can therefore measure the bulk composition of BC-containing particles, including both the core and coating.
3.3.1 Operating principle of the standard AMS

The AMS can be divided into 3 main sections, as described by Canagaratna et al. (2007) and shown in Figure 3.9. The particle beam generation region contains the inlet and aerodynamic lens; a critical orifice controls the flow into the inlet (Jayne et al., 2000). The aerodynamic lens consists of a series of cylindrical orifices with decreasing radius that serve to collimate the particle beam. During passage through the final orifice, the gas-particle suspension undergoes supersonic expansion, and the gas beam is highly divergent whilst the particle beam remains collimated. Particle velocities are determined by their size, with smaller particles travelling faster (Jayne et al., 2000; Zhang et al., 2002). This allows particles to be size-stratified by the time they take to pass through the next region, the Particle Time-of-Flight (PToF) region.

Once through the PToF region, particles impact upon a tungsten plate heated to $600^\circ\text{C}$ and nonrefractory material is vaporized. Some larger molecules can undergo pyrolysis on the vaporizer and are fragmented into simpler ones such as $\text{CO}_2$ and $\text{H}_2\text{O}$ (Allan et al., 2004). Molecules are further fragmented during electron ionisation, after which a pulsed electric field accelerates them into the mass spectrometer. Initially the AMS used a quadrupole mass spectrometer (Jayne et al., 2000), but most current instruments now use Compact Time-of-Flight (C-ToF) or High-Resolution Time-of-Flight (HR-ToF) designs (Drewnick et al., 2005; DeCarlo et al., 2006). These systems have the advantage of improved resolution and the ability to measure single-particle mass spectra at low number concentrations, though this is typically only used for calibration purposes.

3.3.2 Calibration and mass quantification

The standard AMS is calibrated with $\text{NH}_4\text{NO}_3$, which is nebulised and size-selected in the same manner as described in Section 3.2.2. The ion rate for a known mass of $\text{NO}_3$ is measured either by comparing the detected ion signal with the particle concentration or selectively detecting single particles by triggering on simultaneous detections of $\text{NH}_4$ and $\text{NO}_3$ ions. This allows calculation of the ionisation efficiency of $\text{NO}_3$ ($IE_{\text{NO}_3}$), the fraction of nitrate molecules that are ionised and detected, as the particles are of a known mass. The ratio of other species’ ionisation efficiencies to $IE_{\text{NO}_3}$, their Relative Ionisation Efficiencies ($RIE$), have been measured experimentally and so the performance of the instrument for all species is calibrated with a single calibration.

The mass concentration of a species ($C_s$) measured by the AMS is calculated by
3.3. THE AMS AND SP-AMS

Figure 3.9: Schematic of a standard HR-ToF-AMS. The chamber is held at vacuum to reduce background in the detector, and pressure in the detection region reaches $10^{-9}$Torr. Particles are sampled through an aerodynamic lens to collimate them into a narrow beam. They then pass through the chopper, a rotating disc that modulates the particle beam to determine particle size, and are vaporized on a tungsten plate held at 600°C. Vapour molecules undergo electron-ionisation and are detected in the mass spectrometer. Reprinted with permission from DeCarlo et al. (2006). Copyright 2006 American Chemical Society.
(Canagaratna et al., 2007):

\[ C_s = \frac{10^{12}}{CE} \frac{MW_{NO_3}}{RIE_s I_{E_{NO_3}} Q N_A} \sum I_{s,i}, \quad (3.4) \]

where \( MW_{NO_3} \) is the molecular weight of nitrate in g mol\(^{-1}\), \( CE \) is the Collection Efficiency (the fraction of molecules that are vaporised), \( RIE_s \) is the relative ionisation efficiency of the species, \( Q \) is the volumetric flow rate in cm\(^3\) s\(^{-1}\), \( N_A \) is Avogadro’s number and \( I_{s,i} \) is the detected ion rate for an ion \( i \) that the species fragments into.

The key unknown terms for determining the mass concentration of a particular species are \( CE \), \( RIE_s \) and \( i \) (i.e. which ions to sum over). In order to highlight the challenges of mass quantification in the SP-AMS, it is useful to consider these terms separately.

### 3.3.2.1 Ion selection

Calculation of mass concentration requires a summation of all the ions a species fragments into. The fragmentation patterns of inorganic species are well characterised in the AMS (Allan et al., 2004), for example nitrate has major ions of \( m/z=30 \) (NO\(^+\)) and \( m/z=46 \) (NO\(_2^+\)), and sulphate at \( m/z=48 \) (SO\(^+\)) and \( m/z=64 \) (SO\(_2^+\)). Organics have major fragments such as \( m/z=43 \) (H\(_3\)C\(_2\)O\(^+\)) and \( m/z=44 \) (CO\(_2^+\)), but due to their complex nature a large number of organic fragments may be measured, and any ion with \( m/z \) not of a known species (air, water, inorganics) is classified as organic.

In the SP-AMS, black carbon typically fragments into C\(_x^+\) ions, clusters of carbon atoms spaced 12 m/z apart. Figure 3.10 shows an example mass spectrum of thermodeposited flame soot. The ratios of the different C\(_x^+\) fragments vary between ambient and calibration soot, and can extend to several hundred m/z for the larger carbon clusters. In ambient measurements, the majority of BC mass is in the clusters C\(_1\)–C\(_5\), with C\(_3\) the largest peak (Massoli et al., 2012; Onasch et al., 2012).

Fragmentation of inorganics in the SP-AMS is typically very similar to the AMS, as it occurs during the ionisation stage which is unchanged. In the standard AMS, organics may pyrolyse on the heater, and break into smaller fragments. As the SP-AMS uses a different ionisation step, the fragmentation patterns are modified, and so individual organic species may have different mass spectra in the SP-AMS. In ambient measurements however, the main difference between organic mass spectra between the AMS and SP-AMS is the different organic composition between BC coatings and LSP, which may be from non-combustion sources (Massoli et al., 2012).
There is some outstanding uncertainty regarding the fragmentation of BC into non-C\(_x^+\) ions. Regal black is a form of carbon black, which typically contains > 97% elemental carbon, with C:H ratios >20:1 (Watson & Valberg, 2001). This is purer than is typical for BC spherules, which may contain C:H \(\sim\) 8:1 (Cain et al., 2010) and up to 10% oxygen by weight due to the presence of functional oxygen groups, particularly on the surface (Fitzpatrick et al., 2008; Vander Wal et al., 2010). In the SP-AMS such groups would be interpreted as organic coatings. Onasch et al. (2012) ran an SP-AMS with both laser and tungsten vaporizers on and, by turning the laser on and off, highlighted a CO\(_2^+\) peak associated with BC from a propane burner, which formed the majority of what was interpreted as organics (i.e. OA + the non-C\(_x^+\) fragments of BC). CH\(^+\) ions are not detected in SP-AMS mass spectra, suggesting any hydrogen in BC may fragment into H\(^+\) which is ignored in the mass spectrum as it is difficult to quantify. To date this issue has not been resolved, as it is difficult to distinguish between non-C\(_x^+\) fragments of BC and fragments due to coatings. The net result is an overestimates of the organic/BC ratio, as some fraction of BC is misinterpreted as organic.

![Figure 3.10: Example mass spectrum of thermodenuded flame soot measured by the SP-AMS.](image)
3.3.2.2 Relative ionisation efficiency

The relative ionisation efficiency is a measure of what fraction of vaporized molecules are detected in the mass spectrometer, normalised to that of NO$_3$. Onasch et al. (2012) utilised the dual-vaporizer SP-AMS by performing several calibrations using NH$_4$NO$_3$ and regal black, comparing the ion signals to particle concentration. The particle beam for regal black is $\sim$0.4 mm, narrower than the 1 mm laser, meaning the CE term in Equation 3.4 is unity. They calculated $RIE_{BC}$ of $0.2 \pm 0.1$ (2σ uncertainty), though further measurements using BC of different composition may yield different values. More measurements of this quantity, particularly from different types of soot, would provide greater confidence of this value, but this is made difficult by ambiguities in the collection efficiency.

3.3.2.3 Collection efficiency

The collection efficiency, the fraction of particles sampled that are detected, presents the greatest source of uncertainty in mass quantification in the SP-AMS. In the AMS the CE is governed by the fraction of particles that bounce off the vaporizer (typically $\sim$ 50%) (Canagaratna et al., 2007). The vaporizer is around $\sim$3.8 mm in diameter, which is typically much wider than the particle beam (Huffman et al., 2005). Fractal particles produce a more divergent beam when they pass through the aerodynamic lens, and around 5% of the Gaussian beam profile of fractal flame soot misses the vaporizer (Huffman et al., 2005).

In the SP-AMS, assuming sufficient laser power is achieved, 100% of particles that pass through the laser are vaporized (Onasch et al., 2012), however the fraction of particles that miss the beam may be large due to its narrow width. Onasch et al. (2012) observed systematic differences in CE when comparing soot sources of different shape. By comparing BC mass concentrations with a MAAP (see Section 3.1.2) in an urban area, Massoli et al. (2012) calculated $CE = 0.19$ in the SP-AMS, meaning over 80% of BC mass missed the laser.

As BC particles become larger and are restructured by condensation of coatings, their particle beam becomes more collimated, increasing CE. The detection efficiency of the SP-AMS is therefore strongly dependent on soot size and mixing state, and changes in these properties pose a large challenge to mass quantification (e.g. Onasch, 2012, Section 5.2). While relative properties of particles are measurable, these are biased towards the largest, most spherical (and therefore most coated) BC particles.
Such particles may not necessarily need a large amount of BC in them to be detected. The extent to which this affects derived data has not yet been properly characterised, and remains a barrier to mass quantification in the SP-AMS.

### 3.4 The PhotoAcoustic Soot Spectrometer (PASS)

#### 3.4.1 Operating principle

Absorption can be measured in-situ by use of the photoacoustic effect (Bell, 1880), shown in Figure 3.11. Adams et al. (1989) first applied this technique to atmospheric absorption, and Arnott et al. (1999) described the prototype of the current instrument, the PhotoAcoustic Soot Spectrometer (Droplet Measurement Technologies, Boulder, Colorado, USA). Particles are irradiated with a pulsed laser, heating the particles and hence the air around them. The heated air expands, creating a pressure wave that travels through the instrument cavity. The laser is pulsed at the resonant frequency of the cavity, creating a standing sound wave, which is measured with a microphone. The microphone signal \( P_{\text{mic}} \) is directly proportional to \( B_{\text{Abs}} \), (Arnott et al., 1999):

\[
B_{\text{Abs}} = \frac{P_{\text{mic}} A_{\text{res}} \pi^2 f_{\text{res}}}{P_L (\gamma - 1) Q}
\]  

(3.5)

where \( A_{\text{res}} \) is the cross-sectional area of the resonator, \( f_{\text{res}} \) is the resonant frequency (calculated from temperature, pressure and RH), \( P_L \) is the laser power, \( \gamma \) is ratio of isobaric and isochoric specific heat (1.4 for air) and \( Q \) is the resonator quality factor. Laser power is measured continuously, and the acoustic properties \( f_{\text{res}} \) and \( Q \) are calibrated regularly when the instrument performs an acoustic calibration and self-zero.

Evaporation of semi-volatile species such as water vapour can cool the particles through uptake of latent heat, inhibiting their photoacoustic response. It is therefore necessary to dry air before sampling with a PASS; for particles with a high water content this raises uncertainty regarding absorption in humid ambient conditions (Moosmuller et al., 2009). The PASS is considered to be the most reliable absorption measurement in general use (Baumgardner et al., 2012), and high-precision instruments are used as the standard against which the artefacts of filter-based instruments are measured (e.g. Lack et al., 2008; Cappa et al., 2008). Multiple-wavelength versions have measured AAE and been used to show evidence of the presence of brown carbon (Lewis et al., 2008; Gyawali et al., 2009; Lack et al., 2012a).
Photoacoustic systems respond linearly to the amount of radiation absorbed, regardless of the nature of the absorbing species. Absorbing gases such as O₃ or NO₂ are often used (e.g. Lack et al., 2006; Flowers et al., 2010) as they have well-defined absorption spectra and provide an unambiguous absolute absorption standard, provided the spectral profile of the light source is well characterised. Absorbing particle standards are less well characterised, and there is currently no recommended reference material (Baumgardner et al., 2012). Arnott et al. (2000) demonstrated linear relationships with monodisperse kerosene flame soot concentration, but this is not a practical solution for use in the field. Lack et al. (2006) showed similar results with nebulised nigrosin dye, but as this is not standardised for this for this purpose there is no guarantee its optical properties do not vary between batches. (Lack et al., 2009) measured absorption cross-sections at 532 nm for several sizes of monodisperse Absorbing PolyStyrene Spheres (APSS) using a photoacoustic instrument calibrated with O₃. The advantage of APSS is that they are easy to use, have a standardised manufacturing process and give reproducible calibrations within a given batch (Lack et al., 2009, 2012b).
During CalNex (see Chapter 5) the PASS was calibrated using two sizes of monodisperse APSS (327nm and 378nm) which were nebulised, drawn through a diffusion drier and size-selected by DMA before being sampled by the PASS and SP2. Once a steady concentration had been reached from the nebuliser, a zero filter and acoustic calibration was performed on the PASS. As the APSS do not incandesce, the SP2 detects them as LSP and this measurement was used to count the number concentration, and multiplied by the absorption cross-sections reported by Lack et al. (2009) to calculate $B_{Abs}$. The resultant calibration slope is shown in Figure 3.12a, and slopes are shown with a free fit offset and zero offset. As the instrument was zeroed before each data point, there should not be an offset. Both slopes were similar, and the offset was small in the fit not through zero.

In order to validate this calibration, after the campaign the PASS was cross-calibrated with NO$_2$. The experimental setup of this calibration is shown in Figure 3.13. A cylinder containing a mix of 5ppm NO$_2$ carried in synthetic air was connected to the PASS and a TeCo 42i NO$_x$ analyser, which was calibrated with NO. To vary the concentration, the NO$_2$ flow was diluted with compressed air which was passed through a scrubber to remove background NO$_x$. The 405nm laser was turned off to avoid photolytic conversion. A minor modification to the PASS flow system was required in order to replace the silicone tubing with stainless steel and Teflon lines, as the silicone reacts with NO$_2$. This meant the sample chamber had to be disconnected from the T&RH sensor, so this had to connected separately for the PASS to perform an accurate acoustic calibration.

The calibration slope for the NO$_2$ calibration is shown in Figure 3.12b. The x-axis was calculated using the NO$_2$ concentration measured by the NO$_x$ analyser, and using absorption cross-section data from Schneider et al. (1987). Before each data point, the PASS was zeroed using purely the dilution flow, so the fit through zero should be the most appropriate; however, the fit with a free offset had a slope closer to the APSS calibration, though the error on this fit parameter was larger.

While there was not absolute agreement within the fit errors between the APSS and NO$_2$ calibrations for all slopes, the spread between all the slopes was less than 20%. A number of issues may be the cause of this difference, including the flow calibration of the SP2, the calibration of the NO$_x$ analyser, uncertainties in the absorption cross-sections and the laser bandwidth and line losses during either calibration. It is clear that between the two calibrations, the slope was consistent to within 20%, and the instrument responded linearly to both calibrants. In Chapter 5 the PASS is largely
used to monitor relative changes, and so this calibration was adequate for the purposes of the experiments carried out.
3.4. THE PHOTOACOUSTIC SOOT SPECTROMETER (PASS)

Figure 3.12: Calibration slopes for the PASS, using (a) APSS and (b) NO$_2$ as the calibrant. Statistical errors were calculated but are too small to be seen. Orthogonal distance regression fits to measured data are also shown, both fit through zero and allowing an offset.
CHAPTER 3. INSTRUMENTATION

Figure 3.13: Schematic of the instrumental setup for calibrating the PASS with NO\textsubscript{2}.
Chapter 4

Development of SP2 Mie core/shell code

This chapter covers a brief overview of core/shell Mie theory, and details the necessary optics for calculating coating properties in the SP2, as well as their practical implementation. Many of the terms are described more fully, and in wider applications, in Bohren & Huffman (1983).

4.1 Using the SP2 to determine coating thickness

The morphology of black carbon varies during its lifetime, changing from initially fractal towards idealised core/shell spherical shapes. This may cause differences in the scattering and absorption behaviour of individual BC particles (Fuller et al., 1999; Liu et al., 2008). However, the SP2 has no measurement of either particle size or orientation as they pass through the laser. Moteki et al. (2010a) demonstrated that for several calibration standards, and ambient Tokyo soot, particles below $10^{-20}$ m$^3$ in volume (equivalent to a sphere $\sim 270$ nm in diameter) are in the Rayleigh regime when using a wavelength of 1064 nm, meaning scattering is independent of particle shape. It is also demonstrated in Chapter 5 that scattering by thermodenuded BC particles in the size range 135 – 200 nm can be approximated well by assuming spherical, uncoated particles.
4.1.1 Light scattering in the SP2

The APDs in the SP2 cover a finite solid angle, so it is also necessary to consider the differential cross-section, defined as:

\[ \frac{dC_{\text{Sca}}}{d\Omega} = \frac{r_{\text{det}}^2 I_S(\theta, \phi)}{I_i}, \]

(4.1)

where \( r_{\text{det}} \) is the distance to the detector and \( \theta \) and \( \phi \) are co-ordinates defined in Figure 4.1. The scattering signal detected by the SP2 is therefore equal to the differential cross-section at \( \lambda = 1064\text{nm} \) multiplied by the angular weighting function of the detectors \( (W_D(\theta, \phi)) \), integrated over the surface of a sphere:

\[ C_{SP2} = \alpha_{\text{cal}} \int_0^{2\pi} \int_0^{\pi} \frac{dC_{\text{Sca}}(\theta, \phi)}{d\Omega} W_D(\theta, \phi) \sin(\theta) \, d\theta \, d\phi, \]

(4.2)

where \( \alpha_{\text{cal}} \) is a calibration factor. As the incident light comes from both directions, each detector receives a fraction of forward scatter and backscattered light. The angular widths of the APDs in \( \theta \) are \( 15^\circ \leq \theta \leq 75^\circ \) and \( 105^\circ \leq \theta \leq 165^\circ \) (Moteki & Kondo, 2007). When the scattering plane is defined horizontally, as in Figure 4.1, the detector weighting function can be expressed in terms of the angular width of the APD \( \Delta\phi \) as a function of \( \theta \) (Martin Gysel, personal communication):

\[ W_D(\theta) = 2 \Delta\phi(\theta) = 2 \left( \Delta\phi_{\text{fwd}}(\theta) + \Delta\phi_{\text{back}}(\theta) \right) \]

(4.3)

where

\[ \Delta\phi_{\text{fwd}}(\theta) = \arctan \left( \frac{\sqrt{1 - p_{\text{fwd}}^2 - \cos^2(\theta)}}{p_{\text{fwd}}} \right) \]

\[ \Delta\phi_{\text{back}}(\theta) = \arctan \left( \frac{\sqrt{1 - p_{\text{back}}^2 - \cos^2(\theta)}}{p_{\text{back}}} \right) \]
4.2. IMPLEMENTATION OF SP2 MIE CODE

4.2.1 Scattnlay

Scattnlay (Pena & Pal, 2009) is a set of Mie code written in C, and available for download at http://www.scattport.org/index.php/programs-menu/mie-type-codes-menu/390-scattnlay. It implements algorithms developed by Yang (2003) to calculate absorption and scattering by a multi-layered sphere using a different set of base functions to previous version of Mie code (e.g. Bohren & Huffman, 1983). Yang (2003) describes calculations (such as strongly absorbing spheres with very large size parameters) whereby these algorithms are an improvement to previous Mie code. For the purposes of processing SP2 data these are irrelevant; in this case the
main advantage was that code in C could be incorporated into Igor Pro, and this was kindly carried out by Dr Jonathan Crosier.

The resultant function calculates $Q_{\text{Ext}}, Q_{\text{Sca}}$, and $Q_{\text{Abs}}$ for a sphere of multiple layers, and also outputs $S_1(\theta)$ and $S_2(\theta)$, elements of the angular scattering matrix (Bohren & Huffman, 1983). As the SP2’s laser is unpolarised (Schwarz et al., 2010b), these are used to calculate the differential cross-section (Bohren & Huffman, 1983):

$$\frac{dC_{\text{Sca}}}{d\Omega}(\theta) \propto \left[ |S_2(\theta)|^2 + |S_1(\theta)|^2 \right]. \quad (4.4)$$

The efficiency and differential cross-section outputs from Scattnlay were compared to the examples listed in the appendices to Bohren & Huffman (1983) for a homogeneous sphere and a coated sphere, and the results were numerically identical. By inputting Equations 4.3 and 4.4 into Equation 4.2, it was possible to calculate the signal detected by the SP2 for different sizes of PSL (shown in Figure 4.2), though these required normalising to the units measured by the SP2’s low-gain APD. This comparison showed excellent agreement, meaning Equation 4.2 accurately describes the amount of scattered light detected by the SP2. Figure 4.2 also shows a comparison to NOAA’s Mie calculations (Shuka Schwartz, private communication). These also show excellent agreement, though there is a small deviation for the largest diameters. This may be as the assumed detection angles were $13^\circ \leq \theta \leq 77^\circ$ and $103^\circ \leq \theta \leq 167^\circ$ (Gao et al., 2007), which are slightly wider than the angles measured by Moteki & Kondo (2007). However the difference between the two calculations is smaller than the typical spread on the measured signals of monodisperse PSLs, and therefore this is only a minor source of uncertainty.

### 4.2.2 Generation of Mie lookup-tables for determining coating properties

In practice it is too CPU-intensive to perform Mie calculations for each particle (for example, during CalNex ~300 million particles were recorded). Instead, a series of lookup tables were generated containing $C_{\text{SP2}}$ for a range of core and coated diameters for $80 \leq D_C \leq 600$ nm and $100 \leq D_P \leq 600$ nm. This range covers the vast majority of BC-containing mass detected in the atmosphere, and also the range at which the SP2 can detect calibration particles. An example table is shown in Figure 4.3. One table was required for each combination of $n_{\text{core}}$ and $n_{\text{coat}}$, and in order to be used with SP2 data they must be normalised to take into account $\alpha_{\text{cal}}$. The tables were
4.2. IMPLEMENTATION OF SP2 MIE CODE

Figure 4.2: Comparison of measured PSL scattering signals and Mie calculations. Measured signals are taken from Schwarz et al. (2010b) and error bars are typical widths of Gaussian fits to PSL data to show the spread of the data.

normalised to the measured scattering signal of 200 nm PSLs, but any particle of a known size and refractive index may be used. For this purpose, the first row of each table corresponds to $D_C = 0$, an LSP with diameter $D_P$ and refractive index $n_{coat}$. In future, this may be used to calculate properties of measured LSPs, but this is not currently implemented. For each particle, the row corresponding to the closest $D_C$ is extracted and the scattering signal is interpolated to find the corresponding $D_P$. This is shown schematically in Figure 4.4.

4.2.3 Quality assuring coating calculations

There are a number of reasons why $D_P$ may not be able to be calculated using the lookup table. A function was developed that reports either $D_P$ or a code for why $D_P$ cannot be reported, based on the key in Table 4.1. For particles with bad LEO fits,
Figure 4.3: Example Mie lookup table for determining BC coated diameter for a given core diameter and measured scattering signal.

Figure 4.4: Schematic overview of the method to calculate BC coating thickness using a lookup table.
nothing is known about their coated diameter. As the split detector was poorly aligned, these represented the majority of particles during CalNex. This is discussed more fully in Section 5.1. For some particles, the measured scattering is smaller than that which is calculated for their bare core. This is expected due to random noise in the scattering data. The implication however is that for these particles, \( D_p < D_C \). As such a situation is nonphysical, for these particles it is assumed that \( D_p = D_C \).

The fraction of particles in each category in Table 4.1 have a strong dependence on BC core size. For the smallest cores, only the most coated particles scatter enough light for a good LEO fit. Considering coating properties in this range of \( D_C \) would therefore be heavily biased towards the most coated particles. Similarly, at the largest core sizes a high fraction of particles either saturate the scatter detectors or are too large for the Mie table. Unbiased coating properties are therefore only available in a range of core diameters, rather than across the whole distribution. Section 5.1 outlines a method to determine where this range lies.

<table>
<thead>
<tr>
<th>Number reported</th>
<th>Conditions</th>
<th>% during CalNex</th>
<th>% during BORTAS</th>
<th>Assumed properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 0</td>
<td>( D_p ) OK</td>
<td>12.8</td>
<td>68.5</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>Bad LEO fit</td>
<td>79.8</td>
<td>21.3</td>
<td>Cannot use ( D_p )</td>
</tr>
<tr>
<td>-1</td>
<td>LEO OK, ( D_C &lt; 80 ) nm</td>
<td>2.4</td>
<td>5.5</td>
<td>Cannot use ( D_p )</td>
</tr>
<tr>
<td>-2</td>
<td>( D_C &gt; 600 ) nm</td>
<td>0</td>
<td>0</td>
<td>( D_p = D_C = 600 ) nm</td>
</tr>
<tr>
<td>-3</td>
<td>( D_p &lt; D_C )</td>
<td>4.8</td>
<td>1.3</td>
<td>( D_p = D_C )</td>
</tr>
<tr>
<td>-4</td>
<td>( D_p &gt; 600 ) nm</td>
<td>0.2</td>
<td>3.4</td>
<td>( D_p = 600 ) nm</td>
</tr>
</tbody>
</table>

### 4.2.4 Calculating bulk optical properties at visible wavelengths

While the SP2 lookup tables were generated at 1064 nm, it is of more general interest to consider bulk optical properties at visible wavelengths. Additional lookup tables were generated to calculate the properties of BC particles once their core and coated diameters were known, shown schematically in Figure 4.5. When combined with BC core and coating distributions, these can be used to calculate bulk aerosol properties such as \( B_{Abs} \) and MAC. In practice, measurement of coating distributions unbiased by the issues listed in Table 4.1 is only possible for a narrow range of core diameters. As optical properties have such a strong dependence on BC core diameter, simply
calculating them over this narrow size range may result in biased results. It is therefore necessary to assume that the distribution of coating thickness measured in this size range is representative of the distribution across the entire range of BC core diameter, and to integrate over this distribution.

This calculation is simplified if the Mie tables use the same size bins as the distributions of $D_C$ and $D_p$, so the new tables were generated with matching bins. Different tables were required depending on whether the coating distributions were in the form of absolute coating thicknesses ($C_T = (D_p - D_C)/2$) or relative thicknesses ($C_S = D_T/D_C$), and again one table was needed for each combination of $n_{\text{core}}$ and $n_{\text{coat}}$. The calculation is then performed by matrix multiplication; 1D matrices consisting of Probability Density Functions (PDFs) of BC mass distribution ($D$) and either $C_T$ or $C_S$ ($C$) were generated by normalising the measured distributions, and mean MAC was calculated by matrix multiplying these with a 2D MAC matrix ($M_{2D}$), shown schematically in Figure 4.6:

\[
M_{1D} = M_{2D} \times C = M_{2D} \times (dM/d\log D_C \cdot d\log D_C)_{\text{norm}} \\
\text{MAC} = M_{1D}^\top \times D = M_{1D}^\top \times (dN/dC_S \cdot d\log C_S)_{\text{norm}}
\]

where $M_{1D}$ is a 1D matrix of MAC in $D_C$ space, incorporating the coating distribution across all diameters.
Figure 4.5: Schematic of the use of a second lookup table to calculate optical properties at visible wavelengths.
Figure 4.6: Conceptual schematic of the calculation to integrate average MAC over the entire BC core size and coating distributions.
Chapter 5

Papers

This chapter presents the experimental work carried out as part of this thesis, divided into three papers suitable for submission to journals for publication. The common motivation for the three works is in reporting core and shell parameters to test climate models, investigating processes that affect such properties, and the consequences of these on optical properties.

Sections 5.1 and 5.2 present results from the CalNex (California Research at the Nexus of Air Quality and Climate Change) study (Ryerson et al., 2013) which took place in Pasadena, California in May – June 2010. Firstly, Section 5.1 uses the code described in Chapter 4 to generate core/shell properties, and details a method to properly quality assure the input data in order to produce results that are not biased by the limited detection range of the instrument. Then the sensitivity of this technique to the assumed properties (density and refractive index) of BC input into the model is explored, and the most appropriate parameters to use with ambient data are determined. In Section 5.2 these core/shell distributions are then used to calculate MAC, and compared to measured values which were generated by combining measurements of BC mass concentration and $B_{Abs}$ measured with the SP2 and PASS. It is demonstrated that, when integrated over the entire ambient BC size distribution, the use of the core/shell model can produce values of MAC that agree well with measured values.

Section 5.3 presents a case study of BC wet removal in Canadian boreal biomass burning plumes sampled during BORTAS (Quantifying the impact of BORreal forest fires on Tropospheric oxidants over the Atlantic using Aircraft and Satellites) in July 2011. By examining size and coating properites of three individual plumes, one of which had passed through a precipitating cloud, it is demonstrated that larger, more thickly coated BC particles were scavenged more efficiently. The removal of the largest
BC cores and most thickly coated particles had opposing effects on calculated MAC, and consequently the wet removal process had little effect on the calculated MAC of the remaining BC. By comparing measured scattering and calculated absorption, it is also predicted that the wet removal had less effect on bulk SSA than the variations between different emission conditions.
5.1 Paper A: “Assessment of the sensitivity of core/shell parameters derived using the single-particle soot photometer to density and refractive index”

To be submitted to Atmospheric Measurement Techniques

Authors: Jonathan W. Taylor, James D. Allan, Dantong Liu, Michael Flynn, Rodney Weber, Xiaolu Zhang, Barry L. Lefer, Nicole Grossberg, James Flynn, Hugh Coe

Contributions from co-authors: James Allan helped run the field instruments, generated a time series of SP-AMS data and assisted with the preparation of the manuscript. Dantong Liu helped develop the code for the LEO fitting. Michael Flynn helped prepare the instrumentation for the field. Rodney Weber and Xiaolu Zhang provided the Sunset EC data. Barry Lefer, Nicole Grossberg and James Flynn provided the NO, NO$_2$ and NO$_Y$ data. Hugh Coe assisted with the preparation of the manuscript.
Assessment of the sensitivity of core/shell parameters derived using the single-particle soot photometer to density and refractive index

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Abstract

Black carbon (BC) is the dominant absorbing aerosol in the atmosphere, and plays an important role in climate and human health. The optical properties and cloud condensation nuclei (CCN) activity of soot depend on the amounts (both relative and absolute) of BC and nonrefractory material in the particles. Mixing between these two components is often considered using a core/shell coated sphere morphology. The Single Particle Soot Photometer (SP2) is the premier instrument for reporting distributions of both core size and coating thickness. Most studies combine the SP2’s incandescence and scattering data to report coating properties, but there is variation in the assumed density and refractive index of the core that are used in these calculations.

In this study we explore the sensitivity of the reported coatings to these parameters. An assessment of the coating properties of freshly-emitted, thermodenuded ambient particles demonstrated that a core density of 1.8 g cm\(^{-3}\) and refractive index \(n = (2.26 - 1.26i)\) were the most appropriate to use with ambient soot in the Los Angeles area. Using these parameters generated a distribution of shell/core ratio of 1.04±0.21, corresponding to an absolute coating thickness distribution of 1.7±17.5 nm. This demonstrates that using this technique the SP2 can accurately determine the mixing state (externally or internally mixed) of ambient soot, but with limited precision. Using other core parameters resulted in an offset in the coating distribution, but similar precision. For comparison, using the core parameters that resulted in the thickest coatings (on the same particles as before) generated a distribution of shell/core ratio of 1.40±0.19, corresponding to an absolute coating thickness distribution of 30.3±14.9 nm. Relative changes in coatings associated with secondary aerosol condensation were captured regardless of the assumed core parameters. These results must be taken into account when comparing BC coatings.
measured using this technique, or if using these data for optical or CCN activity calculations.
1. Introduction

Black carbon (BC) is a combustion-generated aerosol ubiquitous throughout the lower levels of the atmosphere. It is damaging to human health (Janssen et al., 2012) and has a warming effect on climate (Bond et al., 2013). Due to its strong absorption of visible light, BC has important effects on regional climate and meteorology near where it is emitted (Ramanathan and Carmichael, 2008), and reducing BC emissions could help to mitigate climate change and improve public health (Jacobson, 2002, 2010; Bond and Sun, 2005).

BC is co-emitted with primary organic aerosol and secondary aerosol precursors such as organic gases and NOx which, through coagulation and condensation, form an internal mixture that increases BC’s cloud nucleation activity (Khalizov et al., 2009) and can amplify light absorption (Schnaiter et al., 2005). The concentric core/shell model is often used to represent the mixing state of BC due to its computational simplicity, and the limited quantitative measurements of particle shape. Within this model, coatings can act as a lens, focusing light onto the absorbing core. This effect has been observed in numerous laboratory studies (Schnaiter et al., 2005; Zhang et al., 2008; Cross et al., 2010; Shiraiwa et al., 2010), but ambient measurements have shown mixed results. Lack et al. (2012) observed a mean enhancement of ~40% in biomass burning emissions, but Cappa et al. (2012) (and subsequently Cappa et al. (2013)) observed much smaller enhancements off the Californian coast. Measurements like these rely on the use of thermodenuders to remove all non-BC material, however these instruments are unable to remove refractory coatings such as salts, metals or some organics (Cappa et al., 2013), and nonrefractory aerosol may recondense after the heated section (Fuentes and McFiggans, 2012).
Even when taking into account the limitations of thermodenuders, Cappa et al.’s calculated absorption enhancements exceeded their measurements. Comparisons to detailed optical models (which use more complex soot morphologies) show that the concentric core/shell model overestimates the absorption enhancement due to coatings (Adachi et al., 2010). However, these models also often show that the absorption of the core is underestimated when assumed to be spherical, as the core’s centre is shielded by its edge (Liu et al., 2008; Kahnert et al., 2012). Absorption of a spherical core is also strongly sensitive to the core size distribution, which varies significantly between different BC sources (Huang et al., 2011; Kondo et al., 2011a; Sahu et al., 2012). Finally, absorption of BC in any morphology also depends on the assumed refractive index (Bond and Bergstrom, 2006). When taking into account all these effects, some of which oppose each other, there is little experimental evidence that the concentric core/shell model systematically over- or under-estimates absorption compared to more complex models, as the comparison depends on the properties (either measured or assumed) of the particles in question.

State of the art climate models (e.g. Matsui et al., 2013) use 2-dimensional matrices of particle diameter and BC mass fraction to represent the wide variety of sizes and mixing states of ambient particles. Within the core/shell model, these are analogous to distributions of core size and coating thickness. The Single Particle Soot Photometer (SP2, Droplet Measurement Technologies, Boulder, CO, USA) has emerged as a technique for measuring the distributions of both cores and coatings. The SP2 quantifies refractory black carbon (rBC) mass on a single-particle basis, irrespective of coatings (Moteki and Kondo, 2007; Slowik et al., 2007). This data can then be used to generate distributions of rBC core diameter ($D_C$). The SP2 is also capable of measuring the scattering cross section of BC-containing particles before they evaporate in the laser beam.
which, when combined with a Mie core/shell scattering model, can be used to calculate the spherical-equivalent diameter of the whole particle ($D_P$) (Gao et al., 2007; Moteki and Kondo, 2008). This can then be used to calculate optical properties (Gao et al., 2008; Schwarz et al., 2008b; Shiraiwa et al., 2008). Moteki et al. (2008) (and subsequently Kondo et al. (2011b)) described a technique where coating properties were determined by comparing light scattering of the coated particle to that of the core, though this is not used here. Here, we consider the more widely-used technique where coating properties are calculated using the scattering of the coated particle and the incandescence of the core (Gao et al., 2007). In literature, a range of different assumed rBC densities ($\rho_C$) and refractive indices ($n_C$) have been used with this technique.

In this paper, we quantitatively evaluate the capability of the SP2 to determine mixing state using the incandescence/scattering technique, providing a sensitivity analysis of the derived coatings to the assumed density and refractive index of the core. We do not assess the ability of the core/shell model to accurately predict optical properties when using the derived core and coating distributions, as this will be discussed in a future manuscript (Taylor et al., 2013).

2. Experimental setup

2.1. The Pasadena supersite

CalNex-LA, part of the wider CalNex project, took place from 15 May – 15 June 2010. The Pasadena supersite has previously been described in detail (Washenfelder et al., 2011; Hayes et al., 2013). Briefly, a wide array of aerosol and gas-phase instrumentation was deployed on the Caltech campus, Pasadena, CA. Atmospheric composition at the site showed a strong weekday diurnal cycle. During the afternoon, an advected plume from
the source-rich western LA basin reached the site after around 3 hours processing (Washenfelder et al., 2011). At other times, composition at the site was generally representative of fresher, more local emissions, which are found throughout the basin (Metcalf et al., 2012). Non-refractory aerosol composition was typical of a polluted, oxidizing urban environment, with secondary organics dominating during daylight hours, and strong nocturnal ammonium nitrate formation (Hayes et al., 2013). The main source of BC in the region is thought to be diesel emissions, and biomass burning did not strongly influence the site during the measurement period (Bahreini et al., 2012; Hayes et al., 2013).

The site was periodically impacted by emissions from a nearby loading area, specifically those from a large, diesel-powered forklift truck. This was manifested as short but strong spikes in the SP2 time series and, as these were not deemed representative of the ambient aerosol, these were removed from the dataset.

2.2. Overview of sampling system

The BC instruments consisted of an SP2, 3-wavelength PhotoAcoustic Soot Spectrometer (PASS-3, Droplet Measurement Technologies), Aethalometer and a Soot-Particle Aerosol Mass Spectrometer (SP-AMS, Aerodyne Research Inc., Billerica, MA, USA), though only the SP2 and SP-AMS data are considered here. Figure 1 shows the sampling system used by these instruments during CalNex. A shared 10.1cm inner-diameter NOAA common inlet, of PVC and aluminium construction, was used to sample from 6.9 m above ground level. A model 8450 air velocity transducer (TSI Incorporated, Shoreview, MN, USA) in the main inlet ensured flow remained laminar.

Air from the stack was sub-sampled 5.6 m down, perpendicular to the main inlet flow, and dried to 35% relative humidity using a Nafion drier (Perma Pure, Toms River, New
Jersey, USA). The counterflow was provided by a compressor connected to a Hankison membrane drier. Super-micron particles were removed using an inline PM$_1$ cyclone (URG Corporation, Chapel Hill, North Carolina, USA), through a 3 m long copper tube. The SP2, PASS, SP-AMS and Aethalometer were connected to the cyclone output by approximately 5m of copper tube, as shown in Figure 1. From 18 May 2010, the SP2, PASS and SP-AMS sampled through a line, alternating every 10 minutes between an ambient inlet and a line drawn through a thermodenuder (Huffman et al., 2008).

2.3. The single particle soot photometer

The SP2 (Stephens et al., 2003; Schwarz et al., 2010) measures rBC using the principle of light-induced incandescence. Particles are drawn through a high intensity intra-cavity 1064 nm Nd:YAG laser; rBC-containing particles absorb the infrared laser radiation and are heated to incandescence, emitting visible light. This light is detected on a particle-by-particle basis by two photomultiplier tubes (PMTs) which are optimized to different wavelength ranges (broadband and narrowband) to give an indication of the incandescence temperature (Schwarz et al., 2010). The amount of light detected is linearly proportional to the mass of black carbon in a particle, regardless of particle coatings or morphology (Moteki and Kondo, 2007; Slowik et al., 2007). The incandescence channels of the SP2 were calibrated using glassy carbon spheres (Type II, Alfa Aesar, Ward Hill, MA, USA) in the manner described by Liu et al. (2010) and McMeeking et al. (2010). Comparison to NOAA’s SP2, calibrated with fullerene soot, showed agreement to within 10%. The SP2 also has two avalanche photodiode (APD) scattering detectors which were calibrated with polystyrene latex spheres (PSLs; Duke Scientific, now Thermo Fisher Scientific, Waltham, MA, USA). Further details of SP2 calibrations are provided in supplementary Sect. A1.
During CalNex, the high-gain broadband detector measured between 0.2 – 27 fg (67-305 nm mass-equivalent diameter at core density $\rho_c=1.8$ g cm$^{-3}$) and the low-gain narrowband 0.6 – 130 fg (84 – 520 nm). The rBC mass concentration was corrected for particles outside the SP2’s detection range. Further details are provided in Sect. A2 of the supporting material. A comparison to a co-located Sunset OC/EC instrument is also presented in Sect. A3 of the supporting material. The SP2 showed excellent correlation ($R^2 = 0.94$) with the optical EC channel, and good correlation ($R^2 = 0.58$) with the more common thermal EC channel.

2.4. The Soot Particle – Aerosol Mass Spectrometer

The SP-AMS is a modified version of the HR-ToF Aerosol Mass Spectrometer (AMS; Aerodyne Research Inc., Billerica, Massachusetts, USA). The standard AMS utilizes a tungsten vaporizer heated to 600 °C, and hence cannot measure refractory species which remain solid at this temperature. The SP-AMS uses the same kind of 1064nm Nd:YAG laser as in the SP2 to selectively vaporize BC-containing particles and measure the composition of core and coating (Onasch et al., 2012). During CalNex, the tungsten vaporizer was removed and only BC-containing particles were vaporized. Note here that we are using the convention of referring to the BC material detected by the SP-AMS as rBC as recommended by Petzold et al. (2013), though it is not possible to unambiguously determine whether this is equivalent to the material detected by the SP2.

Mass concentrations were calculated using the standard fragmentation table technique (Allan et al., 2004), modified to account for rBC peaks at the m/z channels at multiples of 12, using a rBC relative ionization efficiency of 0.2 (Onasch et al., 2012). Where there was a conflict with other anticipated fragments (e.g. C$_3^+$ and HCl$^+$ at m/z=36 and C$_4^+$ and SO$^+$ at m/z=48), high resolution analysis (DeCarlo et al., 2006) was employed to
determine the fraction as a function of time. While there were theoretically many contributions possible, the high resolution analysis showed that the overwhelming majority of ambient rBC mass was accounted for by the C$_1$-C$_4$ fragments.

When attempting to quantify overall mass loadings, poor correlations were found when comparing the SP-AMS with the SP2 and Sunset instrument, in contrast to the measurements of Cappa et al. (2012). Upon investigation, it was found that the quantitative sensitivity of the SP-AMS to rBC was not independent of the other components. A greater fraction of the rBC was detected during periods of high concentrations of inorganics, which is speculatively linked to an improvement of the focusing of the particle beam with larger particles. This comparison is presented in Sect. A3.3 of the supplementary material.

Because of this issue, it is not possible to treat the mass concentrations generated by the SP-AMS as absolute, however the relative concentrations reported should be accurate for those particles detected. This is not necessarily representative of the BC-containing particles overall, as the smaller particles that escape detection are likely to have a higher rBC to coating mass ratio. The concentrations of coating materials relative to each other is likely to be more accurate, but it is likely to biased slightly towards secondary rather than primary coatings, as the latter will again be prevalent on the missed particles and be almost purely organic as opposed to mixed organic and inorganic. For the purposes of estimating the shell refractive index ($n_S$), the reported mass fractions are used. While it is recognised that this is more likely to be representative of the accumulation mode particles, there is no way of resolving this bias with these data.
2.5. Thermodenuder and data averaging

Semi-volatile aerosol was removed from the sample using a thermodenuder (Aerodyne Research Inc.) (Huffman et al., 2008). Particles were drawn through a heated tube, and vapors were adsorbed onto a charcoal trap. The temperature was cycled on a sawtooth profile, heating from 56 – 230 °C over 2 hours, with a 35 minute cool-down period. Temperature was measured using three temperature probes; data were excluded when the standard deviation of the three measurements was >4 °C, to reduce ambiguity in the internal temperature.

The SP2, PASS and SP-AMS were switched between the thermodenuder and ambient inlet every 10 minutes, with a bypass flow running through the unused line in order to maintain the temperature profile in the denuder and remove the need to flush out stagnant air after changes. The SP2 data were averaged to a 5-minute time basis. Using the 1-second data, a 20s delay time was observed between the valves switching and the sample line flushing through. Hence, data from the first 20s of each 5-minute period were excluded.

Losses through the thermodenuder were characterized by comparing the ratio of SP2 rBC mass and number concentrations to the average of the adjacent undenuded data points. Transmission of particles through the denuder exhibited a linear relationship with the thermodenuder temperature, parameterized by

\[
\text{Transmission} = 0.728 - 0.0006 \times T_{TD}
\]

where \(T_{TD}\) is the average of the thermodenuder’s three temperature probes, measured in °C.

Though the slope is similar to that found by Huffman et al. (2008), the intercept is much less than 1, which is likely to be due to the use of a longer charcoal trap after the denuder.
Number and mass losses measured by the SP2 were identical within 2% across the whole temperature range, suggesting any size-dependence was negligible.

rBC and coating composition through the thermodenuder is presented in supplementary Sect. A4. Though there were still some residual coatings, and the variable collection efficiency of the SP-AMS complicated factors, the majority of coating mass was removed when the thermodenuder was at its highest temperatures.

2.6. Co-located NO, NO₂ and NOₓ

NO, NO₂ and NOₓ were measured by chemiluminescence using Model 42C-TL detectors (Thermo Fisher Scientific) for NO and NOₓ, and model 42i-TL for NO₂. The NO₂ instrument was modified to use a blue LED instead of a molybdenum catalyst to convert NO₂ to NO, to exclude conversion of HNO₃ and PANs (Lefer et al., 2010). The NOₓ instrument was used as described by Luke et al. (2010), except the molybdenum catalyst was only heated to 320°C to reduce possible interference from NH₃ conversion. Data were reported as 1-minute averages, and NO₂ data were only available after 17:15 on 27th May. NOₓ is calculated as the sum of NO and NO₂. We calculate −log(NOₓ/NOₓ) as a qualitative measure of photochemical age (Kleinman et al., 2007), the method also used by Cappa et al. (2012). Data are only considered from periods when all three measurements (NO, NO₂ and NOₓ) were available.

3. Calculating rBC coating thickness

In the following section, we describe the data analysis routines and techniques required to use raw SP2 data to calculate coating and optical properties. Whilst the basic technique has been used before (Gao et al., 2007), here we explore the sensitivities of the Mie model to assumptions of density and refractive index, and describe data quality assurance
techniques that are necessary for comparison with measured optical properties. The data presented here were taken after 26 May 2010, when the SP2’s detectors were re-aligned.

3.1. The use of the core/shell model
Fresh soot particles often assume the form of fractal aggregates of BC spherules. Over time, mixing with other material by condensation and coagulation causes voids within the aggregates to be filled and the fractal shape to collapse to form a quasi-spherical particle (Zhang et al., 2008; Ghazi and Olfert, 2013). Given the variations in soot morphology, there is question as to the representativeness of the core/shell model, and to the use of scattering to derive coating properties.

Adachi et al. (2013) measured the shapes of soot particles in Pasadena during the same measurement period as this study. While they observed a variety of morphologies and with variable mixing of material, heavily compacted (but uncoated) BC was seen in period of high CO\textsubscript{2} concentrations, which correspond with the processed Western-LA plume reaching the site (Hayes et al., 2013). The dominant aerosol in these plumes was semi-volatile SOA, which Adachi et al. (2013) note they would be unable to detect as it would evaporate before or during the measurement process. Surface tension forces during condensation of coating material is thought to be the process by which fractal soot is compacted, so it therefore seems likely that these particles were coated by SOA that Adachi et al. were unable to detect.

How appropriate the use of light scattering is to derive coating properties depends on the particles in question. Particles small compared to the wavelength of light lie in the Rayleigh regime, where light scattering is independent of particle morphology. For a wavelength of 1064 nm used in the SP2, this regime is appropriate for externally-mixed BC (i.e. with a single refractive index) <10^{-20} m^{3} in volume (equivalent to 267 nm diameter) (Moteki et al., 2010).
For thickly coated particles (which are quasi-spherical in shape due to compaction of the primary BC and filling in voids between spherules), laboratory measurements have shown this method may be used to accurately determine the size of the coated particle (Shiraiwa et al., 2010). Laborde et al. (2013) also verified accurate sizing using this method for ambient particles with <35% rBC volume fraction when compared to particle mobility diameter.

For intermediate coatings, which may not exhibit a core shell morphology, the derived coating thickness is a useful qualitative indicator of mixing state that is widely used. Consideration of the scattering enhancement (compared to an uncoated particle) in any way more complex than a simple coating thickness would require detailed knowledge of particle morphology, measurements of which are extremely limited in terms of time resolution and their ability to measure semi-volatile coatings. Where soot of variable morphology is present (as is almost always the case in ambient environments), particle morphology would also need to be known on a single-particle basis as the particles were measured in the SP2.

Coating thicknesses derived using this technique are therefore considered semi-quantitative in ambient environments. However, in order to be able to interpret these measurements, one needs to be able to accurately predict the amount of light scattered by externally-mixed rBC. Any enhancement of this would then indicate particles are mixed with some amount of nonrefractory material. When using the SP2’s incandescence measurement to calculate the core size, the amount of light scattered then depends on the assumed refractive index and density of the core, as well as the calibration of the incandescence detectors. One must also carefully consider the limited detection range of the instrument (both its scattering and incandescence measurements) to avoid bias.
3.2. Overview of technique
For each particle, the incandescence signals are used to calculate the rBC mass, and the scattering signals provide the scattering cross section of the coated particle at 1064 nm, using the signals collected during the period between the particle beginning to interact with the laser beam and the point at which the particle starts to evaporate in the laser.

In order to calculate core and shell diameters, a number of parameters are required. The refractive index of the coating was calculated using the chemical composition of the coating material measured by the SP-AMS and allowed to vary during the course of the campaign. A number of lookup tables were generated for a range of different core and coating refractive indices, and thermally denuded data was used to constrain the most appropriate core density and refractive index, such that the measured scattering matched the modelled scattering if the cores were assumed to be uncoated. Size-dependent factors, such as small signals below detection limit or large signals saturating the detectors, could cause some of the scattering data to be considered unreliable. By examining the size dependence of these factors, a range of core diameters for which the scattering data was considered reliable was identified. Particles from this range were then used to calculate coating thicknesses.

3.3. Determination of optical particle size using the SP2
The SP2 uses two light scattering channels for optical sizing. When the laser and detectors are properly aligned, each purely-scattering particle records a Gaussian profile as it crosses the laser, with magnitude proportional to the laser intensity and scattering cross-section of the particle. For BC-containing particles, material evaporates as they pass through the laser, causing the scattering cross-section to decrease to zero. In order to properly size these particles, leading-edge only (LEO) fitting is used (Gao et al., 2007);
the signal as the particles enter the edge of the laser, before material has evaporated, is used to reconstruct the Gaussian profile of the original particle, had it not evaporated. A twin-element avalanche photodiode (TEAPD) was used to constrain the fits, such that the scattered light of the particle moves from one element of the detector to the other as it passes through the laser. The signal on one side is inverted, producing a clear notch as the particle passes the center of the detector and the signal switches from negative to positive. The difference in position between the notch and the peak laser power is fixed during measurements, meaning the position of a BC-containing particle within the beam profile can be inferred to constrain the Gaussian fit as the Gaussian response of non-absorbing particles is directly measured. For further explanation, the reader should refer to Laborde et al. (2012), where this scheme is presented graphically.

For each LEO fit, the baseline is calculated using the mean of the first six data points (1.2 µs). This is subtracted from the data, and a Gaussian function is then fit to the leading edge data. The modal notch position and width of the previous 200 unsaturated purely-scattering particles are used to constrain the fit, leaving the fit amplitude as the only free parameter. We define the leading edge as all data from the baseline-subtracted zero up to 5% of the maximum laser intensity, with the x position calculated using the fit position and width assuming a Gaussian laser profile. This was determined by examining the time-dependent scattering cross section for incandescent particles (Moteki and Kondo, 2008; Laborde et al., 2012).

A large fraction of particles evaporated before the notch position could be properly determined. Rather than rising above the baseline as the particle passes across the split in the TEAPD, these particles’ signals merely fell back to the baseline, giving no indication of position within the laser. To remove this ambiguity, in this dataset we redefine the notch position based on the point where the scattering signal crosses 20×2.44 mV units...
above the baseline rather than the baseline itself, such that particles that evaporate before the split are not counted for the purposes of particle size measurements. Note that the incandescence signal is still reported for these particles, so this does not affect the rBC mass concentrations reported.

Gao et al. (2007) identified particles with scattering signals too small to reliably size, as they generate noisy fits, and those with large signals that saturated the scatter detector within the leading edge, as unreliable fits. Schwarz et al. (2008b) explored the effect of assuming the thinnest and thickest possible coatings for these particles, and reported coating properties as the average of these two extremes. In this analysis we avoid this issue by choosing the core diameter range in which particle coatings are considered such that these particles only make up a small fraction of particles, and do not affect derived coating properties. This is discussed more fully in the next section. A series of filters was also used to identify and discard LEO fits that were poor due to electronic noise or coincident particles, though this affected <0.01% of incandescence triggers.

3.4. Determining a core size range for unbiased coating analysis

In order to minimize bias in the results, it is necessary to examine the distribution of detectable notch position and good LEO fits versus an independent variable, in this case core diameter. The range of these parameters varies depending on the instrumental setup of the SP2.

Figure 2a shows the fraction of particles with detectable notch position ($F_{\text{Notch}}$) as a function of $D_c$. The smallest cores, $D_c < 100$ nm, show approximately 10% detectable notch position, as most particles in this size range do not scatter enough light to be detected on either scatter detector. The ambient particles show a higher $F_{\text{Notch}}$ than the
denuded, as the ambient particles are, on average, more coated, and so a greater fraction of the smaller particles can be detected.

Figure 2b-e examine the probability distribution function of $E_{Sc}$, the ratio of a particle’s measured scattering cross section divided by that of its uncoated core predicted by Mie theory, integrated over the detection angles of the SP2. Figure 2b shows how $dP/d \log(E_{Sc})$ varies with core diameter for the cases most influenced by fresh emissions. These are defined as particles which have passed through the thermodenuder set at a temperature of greater than 220 °C, during periods when ambient $-\log(NO_x/NO_y)$ was lowest (defined as being less than 0.08, the 10th percentile). These particles are the least chemically aged, and have had almost all of their coatings removed by the thermodenuder. Such particles with a $D_C$ less than 100 nm show $E_{Sc}$ values greater than one, as only the most coated particles are detected. Using data from this range of core diameter would result in a bias towards thickly coated particles.

At core diameters 100 – 135 nm, $F_{Notch}$ increases and the distribution of $E_{Sc}$ shifts closer to one as the bulk of BC-containing particles become detectable in both scatter detectors. At $D_C = 135$ nm the two traces on Fig. 2a converge, and therefore $F_{Notch}$ is independent of coatings. This is also the point where $F_{Notch}$ reaches 50%. We choose this as the lower bound of the region in which to consider LEO fitting.

Figure 2c shows $dP/d \log(E_{Sc})$ versus core diameter of particles sampled under the most processed conditions. Such conditions are defined as being when particles are sampled through the ambient inlet and the ambient $-\log(NO_x/NO_y)$ was greater than 0.34 (the 90th percentile). The upper edge of the $E_{Sc}$ distribution is limited by saturation of the low-gain scatter detector. It is clear that for large core sizes, a significant fraction of the most coated particles are limited by saturation. We choose $D_C = 200$ nm as the upper
bound of the region in which coatings are considered, in order to limit this bias affecting the data.

Figure 2d and 2e show \(dP/d\log(E_{\text{Sc}})\) for \(135 \leq D_C \leq 200\) nm for the least coated and most coated particles respectively. Whilst this does not cover the entire rBC mass distribution, it is likely representative of the majority of ambient absorbing aerosol. For our choice of density and refractive index (discussed in Sect. 3.6) the least coated particles show \(E_{\text{Sc}}\) has a modal value close to 1, signifying uncoated particles, and for the most coated particles there is a clear shift towards larger \(E_{\text{Sc}}\).

To summarize, scattering measurements on particles with the smallest core size detected by the SP2 are biased towards the most coated particles, whilst particles with the largest cores are biased towards the least coated. These are due to scattering signals being below the detection limit, or above the saturation level, of the scattering detectors. This section has outlined a method to choose a range of core diameters that are least affected by these problems, to gain the most representative results possible.

3.5. The Mie model

A scattering model is used to relate the measured scattering signal to particle diameter (Gao et al., 2007). For BC-containing particles, we assume a concentric sphere core-shell configuration, and use Mie theory to calculate the scattering cross-sections. We used Scattnlay Mie code (Pena and Pal, 2009), which uses the same equations developed by Yang (2003) but runs in C. For ease of use and computational efficiency, this was compiled as an external operation (XOP) for Igor Pro (Wavemetrics, Portland, OR, USA).

A series of 2-dimensional lookup tables were produced containing scattering cross-sections for \(\lambda=1064\) nm, integrated over the angles of the SP2’s APDs (Moteki and Kondo, 2007), for core diameter \(80 \leq D_C \leq 600\) nm and coated diameter \(100 \leq D_P \leq 600\)
nm, with 1 nm resolution. 600 nm is considered the upper limit, as we were unable to reliably sample calibration particles larger than this size. Different tables must be used for different core and shell refractive indices. For each particle, $D_C$ is calculated using the incandescence data as described in Sect. 2.3 and $D_P$ is then interpolated using the selected look-up table, normalized to the measured scattering signal of a 200 nm PSL. The most basic product of Mie theory in the context of the SP2 is $E_{\text{Sc}}$, the enhancement in a particle’s scattering cross section (integrated over the angles of the SP2’s scatter detectors) compared to that of its uncoated core. To calculate this, only the rBC core density and refractive index are necessary, whereas calculating a coating thickness also requires the refractive index of the coating. Some particles recorded $E_{\text{Sc}} < 1$, such that the LEO scattering signal is smaller than Mie theory predicts for an uncoated core. This is equivalent to a negative coating thickness, which is nonphysical. These measurements are partly a consequence of random errors associated with the LEO fitting, but their likelihood is also strongly affected by the core density and refractive index used (this is discussed in the next section). In order to include these particles in coating calculations, they are assigned a coating thickness of zero. This approach does not affect the median shell/core ratio, though it may slightly bias any calculated bulk optical properties towards more coated particles. Discarding these particles would bias the data even further, as only the thickest coatings would be counted.

3.6. Sensitivity to density and refractive index

As noted in the previous section, calculation of $E_{\text{Sc}}$ requires prior knowledge of the density and complex refractive index of the rBC core. Using a higher refractive (real and imaginary) index increases the scattering efficiency of the rBC core, and consequently reduces the calculated $E_{\text{Sc}}$. Conversely, the scattering cross section of a particle of given
mass scales approximately with $\rho_C^{2/3}$, so increasing density increases $E_{\text{Sc}}$. These two parameters have been the subject of a large body of previous research, extensively reviewed by Bond and Bergstrom (2006). They recommended densities between $1.7 \leq \rho_C \leq 1.9$ g cm$^{-3}$ and refractive indices in the range $(1.75-0.63i) \leq n_C \leq (1.95-0.79i)$, noting the higher refractive (real and imaginary) indices looked the most promising. More recently, Moteki et al. (2010) used SP2 LEO measurements to infer $n_C = (2.26-1.26i)$ for denuded ambient soot in Tokyo, assuming a density $\rho_C = 1.8$ g cm$^{-3}$. These parameters were recently used by Laborde et al. (2013) to explore the properties of rBC in Paris. A variety of other parameters have been used in previous publications. These are discussed in Sect. A5 of the supplementary material, and summarized in Table 1.

Figure 3 demonstrates the sensitivity of calculated scattering cross section of uncoated rBC cores to density and refractive index, using the parameters in Table 1. While there appears to be a central group of similar cross sections, the difference between the highest and the lowest is a factor of 3. This equates to a difference in a factor of 3 when calculating $E_{\text{Sc}}$, and hence a significant change in calculated coating thickness. The effect this has on the measured distribution of $E_{\text{Sc}}$ is shown in Figure 4a for particles measured during the same least-processed conditions as presented in Fig. 2. The spread in the data is due to a combination of random error in the LEO fits, particles passing through different parts of the laser, and some remaining coatings on the particles at 220 °C. Ideally the distribution should be centred around 1 for uncoated particles. The fraction of particles with $E_{\text{Sc}}<1$ is strongly dependent on the core refractive index and density used, as would be the bias associated with discarding these particles for coating calculations.

It is encouraging that the density and refractive index recommended by Moteki et al. (2010), measured by a similar technique, result in a distribution centred close to 1. Moteki
et al. (2010) conducted their measurements at 1064 nm, whereas the others were either for visible wavelengths or broadband spectra. We therefore consider the parameters derived by Moteki et al. (2010) the most appropriate to use for this dataset, and likely other SP2 measurements where diesel engines are the dominant source of black carbon. Under the assumption that they represent the closest estimate to the physical properties of the measured rBC, all other parameters lead to an overestimation of \( E_{\text{Sca}} \), and further analysis would therefore overestimate coating thickness and absorption enhancement, for a given coating refractive index.

Figure 4b and 4c explore the sensitivity of the \( E_{\text{Sca}} \) distribution to density and refractive index separately. It is clear that within the range of parameters used, there is greater sensitivity to refractive index than density.

3.7. Calculating the coating refractive index using the SP-AMS

In order to convert \( E_{\text{Sca}} \) into a physical coating thickness, as described in Sect. 3.4, a coating refractive index must be assumed, in addition to the core density and refractive index. Previous studies have assumed a constant value, generally close to 1.5. We instead used the relative contributions of organics, nitrate, and sulphate measured by the SP-AMS to calculate a time-dependent refractive index using volume mixing rules (Stelson, 1990). Nitrate and sulphate were assumed to be associated with ammonium cations as the aerosol in Pasadena was for the most part neutralized (Hayes et al., 2013). Inorganic densities were taken from Weast (1977), and the density of organics was assumed to be 1.2 g cm\(^{-3}\), as suggested by Stelson (1990). This yields a refractive index of organics of 1.46, which is in the range typically assumed for organics, though it has been shown that oxidation of organics can increase both density (Kroll et al., 2009) and refractive index (Cappa et al., 2011), with opposing effects on scattering calculations. The mean refractive
index for the ambient data calculated with this approach is 1.48 ± 0.01 (one standard deviation). This number is dominated by organics, which form the bulk of the coating (we discuss this further in Taylor et al. (2013)). Changes were due to variation in the organic/inorganic fractions in ambient aerosol, and clear differences were observed when switching to the thermodenuder.

3.8. Sources of uncertainty
Uncertainties associated with the derivation of coating thicknesses have been discussed previously (Gao et al., 2007; Schwarz et al., 2008b). Some sources are relatively simple to quantify. The main source of statistical uncertainty is the position of a particle in the laser beam, which affects the amount of scattered light as well as the FWHM and notch position (while the notch position measures a particle’s passage through the laser in terms of time it does not measure how close a particle passes to the laser’s peak intensity at the centre of the beam). Calibrations with 200 nm PSLs showed the error on the full Gaussian fit was ~30%, but increased to 50% when using LEO fits (up to 5% of peak laser power) due to the decreased signal. For comparability, the amount of light scattered by a 200 nm PSL is similar to that scattered by a 149 nm rBC core when using a refractive index of $n_c = (2.26 - 1.26i)$. After the TEAPD was realigned on 26 May, the modal signal of 200 nm PSL calibrations throughout the campaign were all within 3%, demonstrating the stability of the laser power and scattering detectors. As discussed in supplementary Sect. A1, the single-particle statistical uncertainty in incandescence signal is ~30%, but overall accuracy in $D_c$ is ~3%.

Some uncertainties are difficult to investigate, but thought to be relatively small. The FWHM and notch position are constant for small particles, but for larger ones show some variation as these particles take longer to traverse the laser beam. However, 200 nm and 300 nm PSLs show similar distributions of FWHM and notch position, meaning for
particles <300 nm in total diameter (which represent the vast majority of rBC number) this sensitivity is small. The fraction of peak laser power used to generate the LEO fits could be a sensitivity, however Laborde et al. (2012) demonstrated the scattering cross-section of coated particles is stable before they start to evaporate in the laser. As discussed in Sect. 3.3, inspection of single particles showed that 5% of the peak laser power was within this plateau.

As discussed in Sect. 3.1, scattering at 1064 nm is not thought to be sensitive to particle shape for the sizes of externally-mixed particles considered here. For coated rBC shape may affect scattered light but, as we have already discussed, when soot is not in a core/shell configuration the derived coating thicknesses are only a qualitative indicator of mixing state.

For the purposes of this work it is most important to work out the overall uncertainty, not diagnose different sources of it. For the distributions of $E_{\text{Sca}}$ shown in Figure 4, the spread of the distribution is ~85%. Each of these distributions represents the average of ~15000 particles. The precision of the derived coating thicknesses is discussed in the next section.

4. The effect of core density and refractive index on derived coating thickness and absorption enhancement

Using the coating refractive index calculated from the SP-AMS, the absolute and relative coating thicknesses of BC-containing particles were calculated for particles with rBC core diameter in the range discussed previously. Figure 5 shows the distributions of coating thickness under the same conditions as Figure 4, using the combinations of core density and refractive index that resulted in the smallest and largest $E_{\text{Sca}}$. Gaussian fits to the distributions yield the accuracy and precision of using this technique to determine whether BC-containing particles are externally mixed. Using a core density $\rho_C = 1.8$ g cm$^{-3}$
and refractive index $n_c = (2.26 - 1.26i)$ generates a distribution of shell/core ratio of $1.04 \pm 0.21$, corresponding to an absolute coating thickness distribution of $1.7 \pm 17.5$ nm. For comparison, a density $\rho_C = 2 \text{ g cm}^{-3}$ and refractive index $n_c = (1.76 - 0.44i)$ generates a distribution of shell/core ratio of $1.40 \pm 0.19$, corresponding to an absolute coating thickness distribution of $30.3 \pm 14.9$ nm.

This demonstrates that when using the right parameters, this technique can accurately determine the mixing state (externally vs internally mixed) of ambient BC-containing particles, but with limited precision. We note however that the precision will depend on the specific setup of the instrument (e.g. alignment, detector gain settings). If used with different parameters, the precision is similar but accuracy is not guaranteed with ambient soot.

Figure 6 shows the effect these systematic offsets have on the measured shell/core ratios over the whole campaign. Using the density and refractive index recommended by Moteki et al. (2010), and shown in Sect. 3.6 to be the most appropriate for this dataset, results in the lowest coating thicknesses. A hypothetical comparison between parallel analyses using these parameters, and any one of the others used, could result in the conclusion that one set of particles were significantly more coated than the other, when in fact they were identical. This must therefore be considered when comparing datasets using this technique.

While the use of different core density and refractive index may artificially cause a systematic offset in reported coating parameters, there is also variation due to real changes in the ambient particles. Figure 7 compares changes in the median shell/core ratio, again using the refractive index and density combinations that result in the thickest and thinnest coatings, as a function of photochemical ageing. Changes in coatings are
captured regardless of the parameters used, but there is a significant offset between the
data using the different sets of density and refractive index of the rBC core. The range of
coating thicknesses reported does have a dependence on these parameters, but this is
small compared to the difference in the absolute values.

Coatings were thickest in the most processed airmasses, similar to results reported from
urban plumes in the Western Pacific, (Moteki et al., 2007; Shiraiwa et al., 2007) and in
California, including some in the Los Angeles area (Sahu et al., 2012). It is difficult to
directly compare coating thicknesses between these studies, due to the different coating
metrics and rBC core size ranges used, and the differences shown in Figure 4. What is
consistent between these studies is that, in regions where secondary aerosols also
constitute a large fraction of submicron particulate matter, condensation of secondary
material increases BC coatings with age. Even using the core parameters that result in the
thinnest coatings, the freshest ambient BC-containing particles were also associated with
some coating material.

Coatings measured through the thermodenuder were thinner than ambient coatings,
though this difference was smallest in the least processed airmasses as the ambient
particles were less coated. When using the core parameters that result in the thickest
coatings, even the thermodenuded particles appear to have significant coating material.
Taking these data in isolation could therefore lead to misleading conclusions about BC’s
optical properties and cloud condensation nuclei (CCN) activity. This must be considered
if SP2 coating data generated in this way are to be used quantitatively.

5. Conclusions
We have demonstrated that optical properties derived by core/shell modelling of SP2 data
show a strong sensitivity to assumed rBC core refractive index and density. For a given
measured scattering signal and core mass, a larger refractive index (real and imaginary) and smaller core density result in a larger scattering cross section due to the core, meaning less is attributed to a coating. This results in thinner calculated coating thicknesses for the same measured data.

An assessment of the coating properties of freshly-emitted, thermodenuded ambient particles demonstrated that, when using the appropriate core density and refractive index, the SP2 incandescence/scattering technique can accurately determine the mixing state (externally or internally mixed) of ambient rBC. Using a core density $\rho_c = 1.8 \text{ g cm}^{-3}$ (Bond and Bergstrom, 2006) and refractive index $n_c = (2.26 - 1.26i)$ (Moteki et al., 2010) generated a distribution of shell/core ratio of $1.04 \pm 0.21$, corresponding to an absolute coating thickness distribution of $1.7 \pm 17.5 \text{ nm}$.

When other core parameters were used, this caused a systematic offset in the reported coating data. Using the core parameters that resulted in the thickest coatings (on the same particles as before) generated a distribution of shell/core ratio of $1.40 \pm 0.19$, corresponding to an absolute coating thickness distribution of $30.3 \pm 14.9 \text{ nm}$. The precision of these measurements will depend on the instrumental setup of the SP2, and the new 8-channel instrument may represent an improvement on these values.

Temporal changes in coating thickness were also measured, and coatings were thickest in the most processed airmasses. This is similar to previous results from California and the Western Pacific, where a large fraction of submicron aerosol is also secondary, and suggests a consistent picture of increase coating by condensation of secondary aerosol. While these changes in coating thickness were captured well regardless of the density and refractive input into the Mie model, the sensitivity to assumed core properties must be taken into account when comparing different datasets, or using SP2 coating data to feed
into climate models. Omitting this information could lead to misleading conclusions regarding BC’s optical properties and CCN activity.

It was not in the scope of this manuscript to assess the appropriateness of the concentric core/shell model to predict bulk optical properties, which detailed optical models report may (or may not) under- or over-predict absorption depending on the particles in question and the wavelength. Comparison of optical properties using this technique will be presented in a future manuscript (Taylor et al., 2013).

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Table 1- summary of core densities and refractive indicies used in previous SP2 core/shell calculations

<table>
<thead>
<tr>
<th>Core density ($\rho_c$, g cm$^{-3}$)</th>
<th>Reference</th>
<th>Core refractive index $n_C$</th>
<th>Reference</th>
<th>Studies used</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>(Bond and Bergstrom, 2006)</td>
<td>(2.26$-1.26i$)</td>
<td>(Moteki et al., 2010)</td>
<td>This study (Laborde et al., 2013)</td>
</tr>
<tr>
<td>1.8</td>
<td>(Bond and Bergstrom, 2006)</td>
<td>(1.95$-0.79i$)</td>
<td>(Bond and Bergstrom, 2006)</td>
<td>(Langridge et al., 2012) (Metcalf et al., 2012)</td>
</tr>
<tr>
<td>1.9</td>
<td>(Bond and Bergstrom, 2006)</td>
<td>(1.95$-0.79i$)</td>
<td>(Bond and Bergstrom, 2006)</td>
<td>(Subramanian et al., 2010)</td>
</tr>
<tr>
<td>1.77</td>
<td>(Park et al., 2004)</td>
<td>(1.87$-0.56i$)</td>
<td>(Marley et al., 2001)</td>
<td>(Shiraiwa et al., 2008)</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>(2$-i$)</td>
<td>(Schnaiter et al., 2005)</td>
<td>(Schwarz et al., 2008a) (Schwarz et al., 2008b) (Schwarz et al., 2009)</td>
</tr>
<tr>
<td>2</td>
<td>(Hess et al., 1998)</td>
<td>(1.76$-0.44i$)</td>
<td>(Hess et al., 1998)</td>
<td>(Kondo et al., 2011a)$^a$ (Moteki et al., 2012)$^a$ (Sahu et al., 2012)$^a$</td>
</tr>
</tbody>
</table>

$^a$ These studies used the scattering-only technique to derive coating thickness, but the values are included here for comparison.
Figure 1: Schematic of the sampling system used for the University of Manchester BC instruments during CalNex, showing the instruments’ sample flows. Stainless steel Y-pieces were used when splitting flows. Before the thermodenuder and bypass flow were setup, the Aethalometer flow rate was 5.4 lmin⁻¹ to ensure sufficient flow through the cyclone.
Figure 2 – Diagnostics for determining the range of rBC core diameter used for Mie modelling. Figure 2a shows the fraction of BC-containing particles with detectable notch
positions, averaged over the whole campaign, as a function of $D_C$. Figures 2b and 2c show probability density functions, $dP/d \log(E_{\text{sc}})$ for each core diameter bin, under the least processed (particles drawn through the thermodenuder >220°C and $-\log(\text{NO}_X/\text{NO}_Y) < 10^{\text{th}}$ percentile) and most processed (direct inlet and $-\log(\text{NO}_X/\text{NO}_Y) > 90^{\text{th}}$ percentile) conditions respectively. The thick dashed black lines represent the calculated saturation of the scattering detector at 5% of maximum laser intensity. Figures 2d and 2e are $dP/d \log(E_{\text{sc}})$ distributions for particles in the range $0.135 \leq D_C < 0.2 \ \mu m$, bordered by the vertical dashed lines. The horizontal dashed lines show a core scatter ratio of 1. Figures 2b and 2c are scaled in arbitrary units, and are normalized such that each column, sums to 1. Figures 2d and 2e are also normalized to sum to 1, though they are distributions over the range $0.135 \leq D_C < 0.2 \ \mu m$, rather than averages of 2b and 2c, and are thus weighted more heavily towards the smaller particles within the range. Figures 2b, 2c, 2d and 2e were calculated assuming $\rho_C = 1.8 \ \text{gcm}^{-3}$ and $n_c = (2.26 - 1.26i)$. 
Figure 3 - Calculated scattering cross section, integrated over the angles of the SP2’s scatter detectors, for the different combinations of density and refractive index used in previous SP2 ambient core/shell modelling. Densities are in units of g cm$^{-3}$. The vertical dashed lines bound the range of core diameter used for coating calculations in this study.
Figure 4 – Normalized $E_{sca}$ distribution for the least coated particles (thermodenuder $>220$ °C and $-\log(NO_X/NO_Y) < 10$th percentile) for different rBC core densities and refractive indices. Figure 4a shows data for density (in units of g cm$^{-3}$) and refractive index combinations used in previous SP2 core/shell modelling, whilst 4b and 4c illustrate the sensitivity to core density and refractive index respectively.
Figure 5 - Distributions of (a) relative and (b) absolute coating thickness, measured under the same conditions as Figure 4. The dashed grey lines are Gaussian fits to the distributions, and fit parameters are listed in the legend. The first bin represents all particles with \( E_{\text{Sca}} \leq 1 \), and this bin was not used in the Gaussian fits. The vertical dashed lines are the median values, also listed in the legend. These are often used to compare changes in coatings and are only biased by particles with \( E_{\text{Sca}} < 1 \) if the median value falls in this range.
Figure 6 - Sensitivity of the median shell/core ratio to rBC core refractive index and density, listed in units of g cm$^{-3}$. Data shown are the medians of each 5-minute period throughout the campaign, with error bars for the 25$^{th}$ and 75$^{th}$ percentiles.
Figure 7 - Median shell/core ratio for particles with $135 \leq D_C \leq 200$ nm plotted versus ambient $-\log(\text{NO}_x/\text{NO}_y)$. Data are plotted for the sets of core refractive index and density that result in the thickest and thinnest coatings. Both ambient and thermodenuded ($>220 \, ^\circ\text{C}$) data are shown. The straight lines are linear orthogonal distance regression fits to the data. By definition, the minimum measurable shell/core ratio is 1.
Supporting material for:

Assessment of the sensitivity of core/shell parameters derived using the single-particle soot photometer to density and refractive index

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A1. SP2 calibrations

Glassy carbon spheres were nebulised, drawn through a diffusion drier and size-selected using a differential mobility analyser (DMA). Monodisperse sizes between 80-500 nm mobility diameter spanned the dynamic range of the instrument. A power law fit was used to relate glassy carbon diameter to SP2 detector response, and particle mass was calculated using an assumed density of glassy carbon of 1.42 g cm\(^{-3}\) (Slowik et al., 2007). Ambient particle mass-equivalent diameter was calculated assuming a core density, \(\rho_C\), of 1.8 g cm\(^{-3}\) (Bond and Bergstrom, 2006). The exponents of the power law fit were 0.34 and 0.36 for the broadband and narrowband detectors. An exponent of 1/3 corresponds to a linear fit vs particle mass; the small deviation from this is likely due to the nonlinearity of the SP2 for large masses (Moteki and Kondo, 2010). The response of the incandescence channels was stable to within 4% during the course of the experiment.

The per-particle uncertainty in mass measurement is 30% (Schwarz et al., 2008a; Shiraiwa et al., 2008). The statistical uncertainty in rBC mass concentration for each 5-minute averaging period was \(\sim 2.5\%\). There is also likely a systematic error in bulk rBC mass concentration due to the test aerosol used (Laborde et al., 2012a). To assess the impact of this, Manchester’s SP2 was compared to the NOAA SP2 (Perring et al., 2011), which was calibrated using fullerene soot. Both instruments sampled from three Teflon bags containing different sizes of monodisperse fullerene soot, in the same intercomparison described by Metcalf et al. (2012). rBC modal mass measured by Manchester’s SP2 was approximately 10% higher than that reported by the NOAA instrument [Anne Perring, private communication, 2012]. Convolving this with the 10% uncertainty due to the SP2’s response to fullerene soot relative to diesel (Laborde et al., 2012a) gives a systematic uncertainty estimate of 14%, assuming any error due to flow calibration is negligible. This corresponds to a difference in derived core diameter of \(\sim 2.5\%\).

The SP2 also uses avalanche photodiodes (APDs) to measure light scattered by particles as they pass through the beam. One APD is position-sensitive, allowing measurement of the position of a particle as it passes through the laser (Gao et al., 2007). This is necessary for calculating the size of a coated BC-containing particle before it begins to vaporise. Calibrations of the scattering channels were performed periodically with polystyrene latex spheres (PSLs; Thermo Fisher Scientific, Waltham, MA, USA) 90-500 nm in diameter, and showed the response was stable to within 3% throughout the experiment. No systematic time or temperature dependence in the scattering response was observed. PSLs were also used to ensure proper alignment of the particle jet with the laser beam [SP2 operator manual, 2007].

Prior to 2150 UTC on 18 May, the SP2’s laser power was deemed insufficient to fully quantify the rBC mass concentration, based on a careful analysis of initial calibration data. The laser power was increased and data obtained using the lower laser power were discarded. The higher laser intensity was deemed high enough to properly detect rBC mass using the colour ratio method described by (Schwarz et al., 2010).
The SP2 only records a particle when either the scattering or broadband incandescence detector voltages increase above a certain threshold, and cannot record another until it drops back below. The SP2 data acquisition software used at the time (version 2.9.4) calculated the threshold using a user-defined level above the baseline. During some periods the scattering threshold would be set too low or high, rendering the instrument unable to record particles, and causing the recorded concentrations to be artificially low. These data were filtered on a 10-second time basis by removing extreme outliers, defined as periods where the rBC number concentration was less than three interquartile ranges below the lower quartile for each 10-minute sampling period. This filtered out 0.8% of the 10s data when the auto-thresholding was used. After 21:50 on 19 May, the auto-thresholding was disabled and the trigger threshold held constant. No time-dependent variations in the broadband incandescence threshold were observed, so this did not affect the measured rBC concentration.
A2. rBC core size distribution

The average volume-equivalent rBC core diameter ($D_C$) distribution is shown in Figure A1. While the distribution showed some variation throughout the campaign, this was relatively minor (this is discussed further in Taylor et al. (2013)). The average distribution was nearly identical through the thermodenuder. The peak position at 130 nm is close to that reported by Metcalf et al. (2012) in the LA basin during May 2010, and other previous measurements of fresh diesel emissions (McMeeking et al., 2010; Laborde et al., 2012b). Liggio et al. (2012) reported a mass mode of 145 nm during relatively high-HDDV period in Toronto, though they calibrated their instrument with Aquadag. Accounting for the 40% difference in instrument response between Aquadag and ambient soot (Laborde et al., 2012a) gives excellent agreement between the peak positions.

Liggio et al. (2012) also observed the tail of a distribution that peaked at $D_C < 75$ nm, which they attributed to gasoline emissions, which was not seen in Pasadena. This provides further evidence that diesel emissions are responsible for the majority of black carbon measured during CalNex.

A smaller secondary mode, with peak at 450 nm, is also evident, however using the Gaussian fits this mode was calculated to contain only 5% of rBC mass. This second mode may be due to local emissions, coagulated diesel recirculated within the LA basin, or long-range transport.

The fraction of rBC mass outside the detection range of the SP2 was estimated as 4.6% of the total. rBC mass concentration measured by the SP2 was corrected for this.
Figure A1 - Average rBC mass-equivalent core diameter mass and number distributions measured by the SP2 during CalNex. A normal distribution was fit in log space to the dark grey region. This was then subtracted from the data, and a second normal distribution was fit to the residual data in the light grey region. The discontinuity around 330 nm is due to the switch in detectors as the narrowband detector reached saturation. The fit modes (translated to diameter-space) and standard deviations are 130nm ± 23% and 426nm ± 41%.
A3. Black/Elemental carbon instrument comparison

A3.1. Sunset OC/EC analyser

The Sunset OC/EC analyser (Birch and Cary, 1996) is widely used for measuring Elemental Carbon (EC). The specific instrumental setup during CalNex was described by Zhang et al. (2011). Data were reported on an hourly basis, representing the average of the first 44 minutes of each hour.

The instrument reports two separate calculations of EC, one based on the NIOSH 5040 thermal protocol (Birch, 2002) (which we refer to as $EC_{Sun}$) and the other referred to as “optical EC” (Jeong et al., 2004). Laser attenuation through a filter is defined as $ATN = \ln\left(\frac{I_{\text{Loaded}}}{I_{\text{Blank}}}\right)$, where $I_{\text{Loaded}}$ and $I_{\text{Blank}}$ are the measured laser powers through a loaded and blank filter respectively.

The concentration of elemental carbon embedded per unit area ($[EC]$, $\mu$gcm$^{-2}$), is then calculated by $[EC] = ATN/\sigma$, where $\sigma$ is the attenuation coefficient. This is a function of the aerosol embedded on the filter, due to filter loading and scattering artefacts, similar to those in other filter-based absorption measurements (e.g. Cappa et al., 2008; Lack et al., 2008; Coen et al., 2010). Rather than explicitly correcting for these artefacts individually, $\sigma$ is calculated by the empirically-derived relationship [David Smith, Sunset Laboratories, Private communication, 2012] $\sigma = (0.75 \times ATN + 2.25)^{-1}$. $[EC]$ is then divided by the total flow through the filter during each sampling period, corrected for difference in units, to yield the mass concentration in $\mu$gm$^{-3}$. Due to the optical nature of the measurement, Jeong et al. (2004) considered this as a measure of black, rather than elemental, carbon and we adopt their notation in referring to the “optical EC” mass concentration as $BC_{Sun}$.

Total carbon concentration ($TC$) is only measured by the thermal method.

For most of the experiment, the OC/EC analyser was sampling through a PM$_{2.5}$ cyclone. During several periods during 12$^{th}$-15$^{th}$ June, the instrument switched periodically between a PM$_{2.5}$ and PM$_{1}$ cyclone. Based on this comparison, it is estimated around 7% of the $BC_{Sun}$ mass was contained in particles greater than 1µm in diameter.

A3.2. SP2/Sunset comparison

Figure A2a shows an excellent correlation between rBC mass concentration measured by the SP2 and $BC_{Sun}$, indicating both are measuring the same quantity. This is an important distinction, as rBC, $BC_{Sun}$ and $EC_{Sun}$ are all operationally defined, and may be similar but fundamentally different quantities on a physical and chemical level (Andreae and Gelencser, 2006). The ratio between the two shows agreement within 20%, though the Sunset instrument was measuring on a PM$_{2.5}$ inlet, which accounts for some of this difference. Accounting for the 7% fraction of supermicron $BC_{Sun}$ during CalNex leaves a difference of 14% (Hayes et al., 2013). Whilst this may indicate greater losses in the SP2 sampling system, this does not affect calculation comparison of the BC instruments which used the same inlet. Other explanations are also possible, such as the calibration of either instrument. Nevertheless, the excellent correlation between rBC and $BC_{Sun}$ warrants further study to see if this is consistent in different environments.
Figure A2b shows the correlation between rBC and $EC_{\text{Sun}}$, which is weaker than that with $BC_{\text{Sun}}$. This suggests that while the two are clearly from the same source, the relationship between the two shows more variation. Multiple factors are likely involved. Errors in measurement of blank filters affect both Sunset measurements, and increased organic loadings cause interference, for $BC_{\text{Sun}}$ due to increased scattering artefacts, and for $EC_{\text{Sun}}$ due to changes in thermogram properties.
Figure A2 – Comparison between the SP2 and Sunset instruments. Figures A2a and A2b show the correlation between rBC and Sunset $BC_{\text{Sun}}$ and $EC_{\text{Sun}}$ respectively. The black lines are orthogonal distance regression fits to the data.
A3.3. SP2/SP-AMS comparison

The sensitivity of the SP-AMS rBC collection efficiency to SP-AMS inorganic mass concentration is presented in Figure A3. When inorganics were higher, the ratio of SP-AMS rBC to SP2 rBC was also higher. As the SP2 rBC measurement is insensitive to nonrefractory species (Moteki and Kondo, 2007), this behaviour must be due to the SP-AMS.

An explanation for this behaviour is that the SP-AMS was not detecting the smaller, fresher particles through them not efficiently hitting the laser beam. The SP-AMS particle time-of-flight size distributions, shown in Figure A4, demonstrate that inorganics were indicative of a shift in rBC particle diameter to larger particles. The difference between Figures A4 and A1 is that the SP-AMS measures coated particle diameter, rather than core diameter. The rBC size distribution shown in Figure A4 is therefore dependent not only on the amount of rBC per particle, but also on the amount of coating.

Unlike the standard AMS, the particle beam of the SP-AMS has a much smaller target to hit to become detected (a <1 mm laser as opposed to a 3 mm vaporiser) (Onasch et al., 2012). As such, this makes the SP-AMS much more sensitive to the width of the particle beam (Huffman et al., 2005) and smaller, particles may not be sufficiently focused to be detected efficiently. Note that because of signal-to-noise considerations, the lens alignment is normally performed with larger (~300nm) particles.

Another possible sensitivity is to particle shape, as more fractal particles are focused less efficiently through the aerodynamic lens (Huffman et al., 2005). If condensation of secondary inorganics caused a collapse of fractal soot structure, and this was determining the collection efficiency, similar results would be seen for the ambient and thermodenuded data. However, the thermodenuded data in Figure A3 only a weak dependence on ambient inorganics, meaning overall particle size was more important.

Compared to Cappa et al.(2012), there will have been a generally greater fraction of fresher particles in Pasadena, however the apparent discrepancy in performance may also be due to physical differences between the instruments. The AMS chamber used here was the longer 255 type (395 mm between nozzle and ioniser) as opposed to the 215 type used by Cappa et al. (2012) (295 mm), which would enhance any focusing problems. However, it is also possible that the aerodynamic lens was under-performing, for example due to loose or misaligned internal components, which can cause particle of different sizes to focus in different directions.
Figure A3 – Comparison of the SP-AMS and SP2 rBC mass concentrations, for ambient (black) and thermodenuned (red) rBC data, compared to the ambient inorganic concentration measured by the SP-AMS. The y-axis is normalized to the average ambient ratio, as only the relative changes are meaningful.
Figure A4 – Size distribution of coated particles’ vacuum aerodynamic diameter measured by the SP-AMS. The most aged particles are defined as those measured when \(-\log(\text{NOx}/\text{NOy})\) was >90\(^{\text{th}}\) percentile (0.34), and the most fresh when \(-\log(\text{NOx}/\text{NOy})\) was < 10\(^{\text{th}}\) percentile (0.08). rBC and organics showed a bimodal distribution, suggesting smaller primary particles and secondary coating growth. Inorganics were present only in larger particles, and rBC was contained in larger particles when they were present.
A4. Thermodenuded composition
A thermogram of the different species measured by the SP-AMS is presented in Figure A5. The volatility of species is similar to those in Riverside, CA (Huffman et al., 2009), though we did not see the apparent enhancement in SO\textsubscript{4} at 80-140 °C that they observed. This was thought to be due to a phase change in the sulphate causing increased collection efficiency in the heater. As the SP-AMS does not have a heater, this result may support their hypothesis; SO\textsubscript{4} was however enhanced compared to SP-AMS rBC.

As all the data are normalised to the SP2 rBC mass fraction remaining, which we consider to be reliable, it is not immediately clear why the SP-AMS rBC mass fraction decreases with temperature, and is <1. This may be due to the removal of semi-volatile material causing a change in particle size and shape, which affected the transmission of particles through the aerodynamic lens, and hence reduced the collection efficiency.

The fractional composition at different thermodenuder temperatures is shown in Figure A6a. Even at the highest temperatures, only 35% of mass is contained in the C\textsubscript{X} rBC fragments. This may appear to show that particles were still significantly coated, but there are two reasons that this is unlikely to be the case. Firstly, as rBC measured by the SP-AMS was biased low compared to the SP2, and this was most significant at higher temperatures, the true C\textsubscript{X} fraction is probably higher. Secondly, Figure A6b shows the organic mass spectrum at these temperatures. The majority of organic aerosol was composed of the CO\textsubscript{2}\textsuperscript{+} ion and associated fragments, with the remaining spectrum typical of Hydrocarbon-like Organic Aerosol (HOA). Onasch et al.(2012) reported a CO\textsubscript{2}\textsuperscript{+} fragment in the flame soot spectrum that was not measured with the laser off, suggesting it may due to be some form of refractory oxygenated soot. For this dataset the SP-AMS was run with the heater off, so we are unable to confirm that this CO\textsubscript{2}\textsuperscript{+} is refractory, but if this were the case, it would be more appropriate to think of this as rBC rather than organic.

If all the CO\textsubscript{2}\textsuperscript{+} fragments were associated with rBC, the ratio of CO\textsubscript{2}\textsuperscript{+}/rBC would hold constant for the entire dataset. Conversely, if the CO\textsubscript{2}\textsuperscript{+} was entirely organic, the CO\textsubscript{2}\textsuperscript{+} fraction would depend only on organic composition. In reality the data is probably somewhere between these two cases, but at the hottest thermodenuder temperatures the CO\textsubscript{2}\textsuperscript{+} fraction is significantly higher than is typical of even the most oxygenated organics (Ng et al., 2010). This, combined with the reduced C\textsubscript{X} collection efficiency through the thermodenuder (shown in Figure A3), demonstrates that it is likely that at the hottest thermodenuder temperatures, the majority of non-rBC material was removed.
Figure A5 – Campaign average thermodenuded mass fraction remaining, compared to ambient measurements, of species measured by the SP-AMS. Data have been corrected for thermophoretic losses by normalising to the SP2 rBC mass fraction remaining at the relevant temperature.
Figure A6 – (a) shows the fractional contributions to thermodenuded SP-AMS mass at different temperatures, and (b) the organics mass spectrum through the thermodenuder at temperatures >220°C. At these temperatures, 74% of organics are associated with the CO$_2^+$ fragment.
A5. Summary of $\rho_C$ and $n_C$ used in previous ambient SP2 core/shell studies

Previous publications studying ambient SP2 core/shell data have followed Bond and Bergstrom’s recommendations to varying degrees. Langridge et al. (2012) and Metcalf et al. (2012) used the highest refractive index recommended and the density in the middle of the range, whilst Subramanian et al. (2010) used the same refractive index but a higher density.

Shiraiwa et al. (2008) based their density $\rho_C = 1.77 \text{ g cm}^{-3}$ on denuded aerosol particle mass analyzer (APM) measurements of diesel soot. They explored the sensitivity of scattering cross section to core refractive index for graphite particles, but when modelling ambient data they used refractive indices for carbon black. Citing three measured values, they settled on the central value of $n_c = (1.87 - 0.56i)$ and estimated a 20% error in calculated absorption coefficient between the different values.

Schwarz et al. (2008a, 2008b, 2009) used a density $\rho_C = 2 \text{ g cm}^{-3}$ and refractive index of $n_c = (2 - 1i)$, to match that derived by Schnaiter et al. (2005) by comparing diesel soot size distributions to measured bulk optical properties, using a fractal particle model. They briefly investigated the effect of core refractive index and found little sensitivity to calculated absorption enhancement, though they calculated this at 1064 nm rather than a visible wavelength.

Unlike the other studies discussed, Kondo et al. (2011) and Moteki et al. (2012) focused on biomass burning aerosol, while Sahu et al. (2012) measured both fossil fuel and biomass burning emissions. They matched their refractive index and density to those used in the optical properties of aerosols and clouds (OPAC) software package (Hess et al., 1998), giving a density $\rho_C = 2 \text{ g cm}^{-3}$ and refractive index of $n_c = (1.76 - 0.44i)$. They also used the SP2’s scattering channel, at the onset of incandescence, to estimate the rBC core diameter, rather than using the incandescence channel. We investigated this method, but did not observe a clear scattering cross section of the rBC core, as shown in Laborde et al. (2012a), and use the incandescence channel to reduce ambiguity.
References


5.2 Paper B: “Comparison of measured black carbon mass absorption coefficient to modelled values during CalNex 2010.”

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Contributions from co-authors: James Allan helped run the field instruments, generated a time series of SP-AMS data and assisted with the preparation of the manuscript, including writing part of Section 2.5. Dantong Liu helped develop the code for the LEO fitting. Michael Flynn helped prepare the instrumentation for the field. Patrick Hayes and Jose Jimenez provided the AMS data. Barry Lefer, Nicole Grossberg and James Flynn provided the NO, NO$_2$ and NO$_Y$ data. Jessica Gilman and Joost de Gouw provided the GC-MS data. Hugh Coe assisted with the preparation of the manuscript.
Comparison of measured black carbon mass absorption coefficient to modelled values during CalNex 2010

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\textbf{Key points}

\begin{itemize}
  \item Black carbon mass absorption (MAC\textsubscript{BC}) coefficient measured in the Los Angeles area
  \item MAC\textsubscript{BC} increased by 15-25\% with photochemical ageing
  \item The core/shell Mie model agreed with measured MAC\textsubscript{BC} within 10\%
\end{itemize}
Index Terms

0305 (Atmospheric composition and structure: Aerosols and particles)
0394 (Atmospheric composition and structure: Instruments and techniques)
0345 (Atmospheric composition and structure: Pollution: urban and regional)
3311 (Atmospheric processes: Clouds and aerosols)
3359 (Atmospheric processes: Radiative processes)

Abstract

Variations in refractory Black Carbon (rBC) size distribution, coatings and Mass Absorption Coefficient (MAC$_{BC}$) were quantified using a single particle soot photometer (SP2) and PhotoAcoustic Soot Spectrometer (PASS) in Pasadena, California during CalNex 2010. Coatings were thickest in the afternoon, when an organic-rich processed plume advected to the site after several hours of processing. Measurements of coating composition, made with a Soot Particle Aerosol Mass Spectrometer (SP-AMS), showed organics composed a higher fraction of BC coating material than in bulk non-refractory aerosol, and secondary organics were likely responsible for the majority of coating growth. After around 1/3 of a day photochemical processing, MAC$_{BC}$ was 25% (at 532 nm and 781 nm) and 15% (at 405 nm) higher than in the freshest airmasses. The reduced change at 405nm may be due to interference from brown carbon and/or mineral dust. The measured changes in MAC$_{BC}$ were modest, and smaller than the factor of 1.5 expected due to ageing.

Core/shell Mie calculations using the measured SP2 data agreed with the measured MAC$_{BC}$ within 10%, though this was dependent on the assumed core refractive index. Artefacts of the core/shell Mie model include overestimation of absorption enhancement.
due to coatings and underestimation of absorption of the BC core. In this dataset these two effects largely cancelled out at 532 nm, and we were able to calculate MAC$_{BC}$ with high accuracy.

1. **Introduction**

Radiative forcing by aerosols represents a significant uncertainty in current climate models [Bond *et al.*, 2013]. Black carbon (BC) is the dominant absorbing aerosol, particularly in urban areas, and is therefore important in determining single scattering albedo (SSA) and consequently the magnitude and sign of aerosol radiative forcing [Haywood and Shine, 1995]. One source of uncertainty in climate models is BC mixing state; by condensation and coagulation, BC can become mixed with other species, which may increase its cloud condensation nuclei (CCN) activity [Khalizov *et al.*, 2009b]. This affects the rate at which BC is removed from the atmosphere, and hence creates uncertainty into its lifetime [Vignati *et al.*, 2010].

Fresh soot often takes the form of fractal chains of primary spherules, and condensation of secondary species can collapse aggregates to more spherical shapes, though laboratory studies present mixed results regarding the extent to which the collapse occurs [Zhang *et al.*, 2008; Xue *et al.*, 2009]. A concentric sphere core-shell configuration is often assumed for aged soot, and the optics of such a system are well characterized [Bohren and Huffman, 1983]. The coating acts as a lens, enhancing both scattering and absorption compared to that of the uncoated core, and this effect has been observed in numerous laboratory studies [e.g. Schnaiter *et al.*, 2005; Khalizov *et al.*, 2009a; Shiraiwa *et al.*, 2010]. Careful consideration of the mass absorption coefficient (MAC$_{BC}$, the ratio of absorption coefficient to BC mass concentration) is therefore important in radiative and climate models.
The concept of absorption enhancement ($E_{Abs}$) is often used to try to parameterize the effect of coatings, but the definition of $E_{Abs}$ can be ambiguous. Core/shell Mie modelling considers $E_{Abs}$ as the ratio of the absorption of a coated particle to that of the uncoated core. Studies using thermodenuders to remove coatings may empirically define $E_{Abs}$ as the ratio of ambient absorption (or $\text{MAC}_{BC}$) to denuded, though this can give mixed results depending on aerosol composition, as it is not guaranteed that all coating material is removed [Knox et al., 2009; Cappa et al., 2012, 2013]. Particle morphology could also have a significant effect; material coating a fractal core is less efficient at focusing the light, and hence the amplification effect of coatings is reduced [Adachi et al., 2010]. The collapse of the fractal structure and encapsulation in dielectric material may also inhibit interactions between the primary soot spherules, which are also thought to enhance absorption, and this would counteract the enhancement due to lensing [Fuller et al., 1999; Liu et al., 2008; Lewis et al., 2009].

The limitation of $E_{Abs}$ as a concept for use in climate modelling is the assumption that uncoated particles, whether fractal, spherical or denuded, are equivalent to freshly emitted particles found in the atmosphere. BC is always co-emitted with primary organics [Bond et al., 2004], and completely bare BC may not exist in the real atmosphere. In this study, we instead focus on changes in $\text{MAC}_{BC}$ as particles age. Bond et al. [2006] suggested absorption by aged black carbon may be around 1.5 times greater than that of fresh aerosol (at 550 nm), as fresh fractal BC changed to a coated core/shell morphology. This figure was reached as a balance between a decrease in absorption as the BC cores were restructured, combined with an increase in absorption by lensing. Under this model, the figure of 1.5 is sensitive to the initial coatings on the fresh BC, and the final shape of the coated particles.
Some studies have found evidence of coating enhancement in ambient aerosol \cite{Knox2009, Lack2012}, whilst others have found little change in MAC$_{BC}$ at visible wavelengths despite evidence of changes in coating thickness \cite{McMeeking2011, Cappa2012}. Organic brown carbon can be an important absorber in the ultraviolet, particularly in biomass burning aerosols \cite{Zhang2011, Lack2012}, but it is unclear to what extent brown carbon affects visible absorption compared to BC in urban areas \cite{Cappa2012, Thompson2012}.

Recently, \textit{Cappa et al.} [2012] presented ambient measurements of MAC$_{BC}$ taken during a similar time period as this study, some taken aboard a ship off the coast of California (also part of CalNex) and some taken in Sacramento, California during CARES (Carbonaceous Aerosols and Radiative Effects Study). They calculated $E_{Abs}$ by comparing ambient MAC$_{BC}$ to thermodenuded, and to a baseline value of 7.75 m$^2$g$^{-1}$ (at 532 nm) from \textit{Bond and Bergstrom} [2006]. While their results differed between the two locations, it was clear that Mie calculations (using SP-AMS data to calculate shell/core ratios) overestimated the measured $E_{Abs}$ in CalNex. When taking into account residual coating material present in the thermodenuded particles, this overestimation was diminished, though still significant at ~30% \cite{Cappa2013}.

Similar to \textit{Cappa et al.} [2012], in this analysis we used a Single Particle Soot Photometer (SP2, Droplet Measurement Technologies, Boulder, CO, USA) and PhotoAcoustic Soot Spectrometer (PASS, Droplet Measurement Technologies), which measure refractory BC (rBC) mass concentration and absorption respectively, to monitor changes in MAC$_{BC}$ in different aged airmasses in Pasadena, California in May-June 2010. However, instead of using the bulk SP-AMS data to calculate coating thickness we instead use the SP2, which can also measure rBC scattering on a single-particle basis \cite{Gao2007}. When input into an optical model the scattering measurements can be used to calculate coating
thickness. Although other morphologies are possible in the atmosphere [Adachi and Buseck, 2013], the SP2 cannot distinguish particle shape, and a core/shell configuration is typically assumed.

The meaning of the derived coating thicknesses has been discussed previously [Laborde et al., 2013; Taylor et al., 2013]. When used with appropriate parameters (core density and refractive index \(n_c\)), this technique can accurately predict the light scattered by externally-mixed rBC, any excess of which is indicative of nonrefractory material. For thickly coated particles, in an approximate core/shell morphology, it can accurately determine coating thicknesses. For intermediate particles, coating thickness is a useful qualitative measure of mixing state. For convenience, and because this is the optical model we use, we refer to rBC and non-BC components of soot as core and shell, though we acknowledge that the morphology of real soot is more complex.

These coating properties can be re-entered into the Mie model to calculate optical properties [Shiraiwa et al., 2008; Schwarz et al., 2009]. In this paper, we compare measured MAC_{BC} in different atmospheric conditions, and make comparisons to the model output in order to assess the validity of using SP2 data to model black carbon optical properties in an urban environment.

2. **Experimental**

The CalNex-LA ground site was located on the Caltech campus in Pasadena, California, and sampling took place during May-June 2010, though here we use only data after 17:15 27\textsuperscript{th} May – 07:00 16\textsuperscript{th} June (times in UTC), when data were available from all the instrumentation. Atmospheric composition at the site was a mixture of emissions found throughout the basin and an organic-rich processed plume, advected from the western LA basin, which reached the site during the afternoon after several hours processing [Hayes
Further details of the site and sampling system used for this study are provided in Taylor et al. [2013].

rBC was measured using an SP2 [Stephens et al., 2003; Schwarz et al., 2010], which uses light-induced incandescence to measure rBC mass on a single-particle basis. The SP2 also has two scattering detectors that measure the scattering cross-section of particles as they pass through the laser beam, and can be used to infer the amount of nonrefractory material on a particle (see Section 2.4).

The bulk composition of rBC core and coatings were measured by a soot-particle aerosol mass spectrometer (SP-AMS; Aerodyne Research Inc., Billerica, Massachusetts, USA). This is a standard high-resolution Aerosol Mass Spectrometer (AMS) modified to use a laser to selectively vaporize rBC-containing particles [Onasch et al., 2012]. Note here that we use the nomenclature recommended by Petzold et al. [2013] to refer to this material as rBC, though it might also be considered elemental carbon as it is detected as pure-carbon fragments in the mass spectra.

The sample line was dried to less than 40% relative humidity, and every ten minutes the SP2, SP-AMS and PASS all switched between an ambient inlet and a line through a thermodenuder that partially evaporated nonrefractory aerosol at different temperature steps [Huffman et al., 2008]. NO, NO$_2$ and NO$_y$ were measured by chemiluminescence using Model 42C-TL detectors (Thermo Fisher, Waltham, MA, USA) [Lefer et al., 2010; Luke et al., 2010], and we calculate $-\log(\text{NO}_y/\text{NO}_x)$ as a measure of photochemical processing, with propagated errors on each 5-minute average of around 9%. The calibration and operating procedure of the SP2, SP-AMS and chemiluminescence instruments were described in detail in Taylor et al. [2013]. Instrumentation not already introduced is described in the next section.
2.1. The PhotoAcoustic Soot Spectrometer

Aerosol light absorption was measured with a 3-λ photoacoustic soot spectrometer. Particle-laden air is drawn through an acoustic cavity, and lasers at 405 nm, 532 nm and 781 nm are pulsed at the cavity’s resonant frequency. Absorbing particles heat the surrounding air, causing a standing sound wave, the magnitude of which is proportional to the absorption in the cavity [Arnott et al., 1999]. The three lasers are pulsed at slightly different off-resonance frequencies, allowing separation of the absorption measurements in the same cavity at the same time using Fourier transforms [Lewis et al., 2009].

By default, the PASS records data every 2-3 s, and periodically switches to an internal filter and performs an acoustic calibration (using an internal piezoelectric speaker) and self-zero (to calculate and remove background absorption from gas-phase species), which takes approximately 17 s. During the measurements, it was observed that valve changes between the thermodenuder and bypass line introduced positive or negative offsets in the data that persisted until the next acoustic calibration and re-zero. This was likely due to small differences in the relative humidity between the two lines (as measured by an internal temperature and relative humidity sensor), caused by the charcoal denuder downstream of the thermal denuder exhibiting a ‘memory’ effect with changes in water vapour (and perhaps other trace gases) in the sampled air. Differences in pressure did not contribute to this artefact, as verified by the internal pressure sensor.

Irrespective of the cause, it was found that the valve switches were affecting the acoustic parameters of the cavity, manifesting as a change in the measured phase of the calibration signal. Because this phase is used in the Fourier transform retrieval of the signal, this artefact was not a simple offset to the derived data and as such, the data between valve changes and the next recalibration were regarded as unreliable and discarded. To
minimize the amount of data discarded, the frequency of recalibrations/zeros was increased from once every 200 points to 100 points on the 2\textsuperscript{nd} of June.

The 532 nm channel was calibrated using absorbing polystyrene spheres (APSS, Thermo Fisher Scientific, Waltham, MA, USA) using the absorption cross sections measured by Lack \textit{et al.} [2009], which were measured to within ±1.1%. APSS of 327 nm and 378 nm in diameter were nebulized, drawn through a diffusion drier and sampled with the PASS and SP2. The number concentration was counted using the SP2’s scattering measurement, corrected for coincidence, and used to calculate the absorption coefficient. The averaging times were long enough that statistical errors on each point were negligible, and the fit error was ±3%. This calibration was verified to within 20% after the campaign using a certified 5 ppm NO\textsubscript{2} standard (Cryoservice, Worcester, UK). We were unable to calibrate the 405 nm and 781 nm channels, and only consider relative changes at these wavelengths.

2.2. Aerosol mass spectrometer

A high resolution-time of flight aerosol mass spectrometer (Aerodyne Research Inc.) [DeCarlo \textit{et al.}, 2006; Canagaratna \textit{et al.}, 2007] measured size-resolved non-refractory aerosol composition of particles 50-1000 nm in diameter. Details of the sampling and data analysis procedures for CalNex are provided by Hayes \textit{et al.} [2013]. AMS data used were 2.5 minute averages, and only V-mode data are used in this analysis.

2.3. Gas Chromatography Mass Spectrometer

Chemically-speciated volatile organic compounds (VOCs) were measured by a gas chromatography mass spectrometer (GC-MS) [Goldan \textit{et al.}, 2004; Gilman \textit{et al.}, 2010]. Samples were taken for 5 minutes out of every 30 minutes, with 5-25% uncertainty in measured concentrations [Washenfelder \textit{et al.}, 2011]. The photochemical age, a measure
of the oxidation history of an airmass, was calculated using the ratio of benzene to 1,2,4-trimethyl-benzene [Parrish et al., 2007]. An average OH concentration of $1.5 \times 10^6$ molecules cm$^{-3}$ was used for consistency with Hayes et al. [2013]. For comparison, the campaign average daytime OH concentration during CalNex was $1.3 \times 10^6$ molecules cm$^{-3}$ [Hayes et al., 2013].

2.4. Measurements of rBC coatings

Two independent measures of rBC coating were determined. Firstly, the single particle soot photometer measures the scattering cross section of each particle before coatings begin to evaporate in the SP2’s laser. Single particle coated diameters were calculated by applying the Mie model described in Taylor et al. [2013] to measured SP2 data. An rBC core density of 1.8 g cm$^{-3}$ and refractive index of $n_c = (2.26 - 1.26i)$ were used, as recommended by Moteki et al. [2010]. When these parameters were input into the Mie model, particles thermodenuded to temperatures >220 °C showed minimal coatings in the freshest airmasses, in contrast to other values which have been used previously with ambient SP2 measurements [Taylor et al., 2013]. A non-absorbing coating refractive index was calculated using the relative amounts of different coating species measured by the SP-AMS, and applying the volume mixing method described by Stelson [1990]. To minimize bias due to particles that were too small or large to be properly detected, coatings were only calculated for particles with core diameters between 135 – 200 nm.

The second measure of rBC coatings presented is calculated from the SP-AMS which, unlike the SP2, quantifies coating composition. The ratio of nonrefractory coating to rBC mass also provides an indication of how thickly coated the particles are, though it does not explicitly provide particle diameters for optical modelling. This is also a bulk
measurement, meaning the data are representative of the distribution of particles, rather than individual particles.

Ideally, one would obtain closure between the SP2 and SP-AMS coating metrics, but this comparison is difficult to make. The SP2 reports a distribution of shell/core ratio and the median shell/core ratio provides a measure of coatings that is not biased by the detection range of the instrument [Taylor et al., 2013]. This measure is weighted towards the number mode in the shell/core ratio distribution within the specified core diameter range, whereas the mass-based SP-AMS is weighted towards the mass mode in coated particle diameter. This includes particles with small rBC inclusions which may not contribute much to overall rBC absorption, but may be numerous.

Such problems are confounded by the variable collection efficiency of the SP-AMS, which affected the instrument during CalNex [Taylor et al., 2013]. As a result, the SP-AMS was biased towards the largest, most coated particles in this dataset. Direct comparisons between the two instruments under controlled conditions would be necessary to fully explain the differences between the two instruments.

2.5. Positive matrix factorisation of SP-AMS data

Positive Matrix Factorisation (PMF) was applied to the SP-AMS data, using the high-resolution analysis of the V-mode data (and error matrices) using PIKA version 1.10H and the PMF Evaluation Tool (PET) [Paatero and Tapper, 1994; DeCarlo et al., 2006; Ulbrich et al., 2009]. While higher-resolution W-mode (the V and W refer to the path of the ions in the mass spectrometer, see Decarlo et al. [2006]) SP-AMS data was available, it was not used due to a low a signal-to-noise ratio. Only the analysis from the sampling bypassing the thermal denuder is presented here, as this is the focus of this work.
Because the sensitivity of the instrument was intrinsically linked to the amount of secondary material present, this introduced a large amount of covariance between all of the variables. Consequently, in spite of the large amount of overall variance, only three factors (shown in Figure 1) were reliably obtained before the onset of ‘splitting’ [Ulbrich et al., 2009]. An attempt to explore the rotational ambiguity was made by varying the ‘fpeak’ parameter [Paatero et al., 2002], however the algorithm did not converge if values other than 0 were used.

Within each of the three factors, a series of $C_x^+$ peaks were present with an identical profile in all factors. Because these are not normally encountered in normal AMS data and are observed in most rBC standards, these are almost certainly due to rBC. As such, the magnitudes of their signals have been scaled to take account of the difference in the relative ionisation efficiencies of organic aerosol and rBC [Onasch et al., 2012]. Through inspection of the organic mass spectra, the factors can be identified as a mixed rBC and Hydrocarbon-like Organic Aerosol (HOA) factor, and two Oxygenated Organic Aerosol (OOA) factors, which are normally associated with aged aerosol, though these also contain rBC peaks.

PMF factors derived from SP-AMS data are intrinsically different to those derived from the standard AMS, as the amount of non-BC material measured also depends on the amount of BC. We use the suffix SP when referring to SP-AMS PMF factors to reduce ambiguity. Due to the variable collection efficiency of the SP-AMS (see Taylor et al. (2013)), it was not possible to directly correlate our PMF factors with those reported from the standard AMS by Hayes et al. [2013], or to other tracers. Instead, we examine relative changes in the different factors in Section 3.

The fact that all factors contain rBC is noteworthy; if the organic species internally mixed with the primary rBC particles did not vary during its lifetime, the rBC would only be
associated with the primary factor (i.e. rBC/HOASP), however this is not the case. As the OOA$_{SP}$ factors must show a degree of covariance with the rBC that is independent of the primary HOA, it must be concluded that either there is a source of rBC present that is not co-emitted with HOA, or that some of the HOA is removed during the rBC’s lifetime, either through evaporation or oxidation.

All three factors are less oxidised than their equivalents in bulk nonrefractory aerosol reported by Hayes et al. [2013]. The SP-AMS is more sensitive to primary combustion aerosol, as it is more associated with rBC, so it may be better able to resolve the HOA from secondary material. There is also some trace of HOA-like peaks in the OOA-1$_{SP}$ and OOA-2$_{SP}$, which likely reduces their O:C and increases H:C.

3. **Changes in coating thickness and composition**

The bulk submicron aerosol composition in Pasadena has been extensively characterised by Hayes et al. [2013]. Organic aerosols comprised about half of the submicron mass, and a larger fraction during daylight hours. During most early afternoons a plume, advected from the western-LA basin, reached the site after several hours processing [Washenfelder et al., 2011]. This plume was the source of the highest rBC mass loadings, as shown in Figure 2a. The plume coincided with a small drop in rBC core mass median diameter (MMD), suggesting the plume was dominated by rBC that had not had time to coagulate, and was relatively fresh. Hayes et al. [2013] also showed hydrocarbon-like organic aerosol concentrations, also indicative of primary emissions, peaked at this time, but organic aerosol was largely secondary in nature, and the photochemical age peaked nearly at the same time as the plume reached the site. The larger MMD at other times suggests either rBC may have been recirculated or transported, or the source emissions profile varied throughout the day.
Inorganics were less influenced by the western-LA plume; ammonium nitrate formed nocturnally due to the low temperatures and high relative humidity, and evaporated during the day. Sulfate was present at similar mass concentration to nitrate, but with a flatter diurnal profile.

Figure 2b shows the diurnal profile of $-\log(\text{NO}_x/\text{NO}_y)$ and the VOC-based photochemical age. Between 0700 - 2300 these two metrics for photochemical processing show similar trends, and peaked in the early afternoon as the processed plume reached the site. This is because vehicular NO$_x$ and primary VOCs share similar source profiles, and in daylight hours are both oxidized primarily by OH. Between 2300 – 0700 the VOC-based photochemical age did not vary, but there was a secondary peak in $-\log(\text{NO}_x/\text{NO}_y)$. The absence of changes in organics is in accordance with low levels of nocturnal OH. NO$_x$ continued to be converted to NO$_y$ through the hydrolysis of N$_2$O$_5$ [Brown, 2004], and some of this will have been present as particulate nitrate (due to the lower night-time temperatures), which is detected by the NOy instrument [Luke et al., 2010]. The nighttime regime ended around 0700 as fresh NO$_x$ emissions and sunlight caused a shift to the daytime photochemistry, and an increase in temperature and drop in RH shifted the equilibrium of ammonium nitrate to the gas phase.

3.1. rBC coating composition

Figure 3 shows a comparison between the organic, NO$_3$ and SO$_4$ mass fractions measured in bulk nonrefractory aerosol by the AMS and in rBC coatings by the SP-AMS. In this dataset it is only meaningful to compare relative amounts of species due to the variable collection efficiency of the SP-AMS, discussed in Taylor et al. [2013]. The straight line fits to the data all show strong correlation, meaning that the relative amounts of each
species in the rBC coating vary in the same way as they do in the bulk nonrefractory aerosol.

Figure 4a and b show the composition measured by the SP-AMS during periods when the standard AMS measured low and high organic fractions. Data were stratified by the AMS organic fraction on a 5-minute time basis, and the average component mass were calculated from periods with organic fraction < 10th percentile and organic fraction > 90th percentile. Each of these periods represent the average of around 20 hours of ambient data. Although the inorganic fraction measured by the AMS during this time was >74%, inorganics only consisted 31% of SP-AMS composition, and 46% of rBC coating material. As the rBC/HOA\textsubscript{SP} fraction was dominated by rBC, this means most of the increased organics measured by the SP-AMS is in the OOA\textsubscript{1SP} fraction. As the more oxidised factor, this is often considered low-volatility, so it is possible the tungsten heater may not be able to vaporise all this material at 600°C. It may also be that the SP-AMS is more sensitive to this material (for example if it were only associated with soot). When the AMS measured a high organic fraction (>67%), 80% of the coating material reported by the SP-AMS was organic. The rBC/HOA\textsubscript{SP} and the rBC fractions are similar to Figure 4a, while OOA\textsubscript{1SP} is lower and OOA\textsubscript{2SP} is significantly higher. This suggests the standard AMS may be more sensitive to OOA\textsubscript{2SP} than OOA\textsubscript{1SP}, though it is not immediately clear why this is.

Figure 4c and d show the SP-AMS composition in the freshest and most processed airmasses measured. Data were stratified by \(-\log(\text{NO}_X/\text{NO}_Y)\) in a similar way to Figure 4a and b.

In the freshest airmasses, the dominant factor was rBC/HOA\textsubscript{SP}, confirming that this factor is primary. However, the majority of material was still associated with coating material. Some of this material is likely primary (HOA, and some refractory oxygen and primary
inorganics are possible [Toner et al., 2006; Onasch et al., 2012]), but some may also be
from aged background particles that were mixed in with the fresher emissions. As noted
previously, the SP-AMS described here was most sensitive to these larger, more coated
particles. In the most processed airmasses, the OOA_{SP} factors dominated, and this is in
agreement with Hayes et al. [2013], who reported large amounts of SOA formation linked
to photochemical processing. The low amount of the rBC/HOA_{SP} factor is interesting; the
reduction in this factor compared to the freshest airmasses is much larger than the
reduction in the fraction of rBC. This suggests that the primary HOA associated with this
factor was either oxidised or evaporated with time, meaning the atmospheric lifetime of
HOA is shorter than that of rBC.

Further insights into the OOA_{SP} factors are provided by the diurnal profile of the PMF
factors, shown in Figure 2d. The main variation in this is the increased prominence of
OOA-2_{SP} during the afternoon. This bears strong similarity to the diurnal profile of the
Semi-Volatile OOA (SV-OOA_{AMS}) factor presented by Hayes et al. [2013], attributed to
SOA formation. The diurnal profile of OOA-1_{SP} also appears qualitatively similar to that
of the Low-Volatility OOA (LV-OOA_{AMS}) factor presented by Hayes et al. [2013].

Overall, the PMF results are difficult to interpret due to the instrumental issues discussed
in Section 2.4 and by Taylor et al. [2013]. Any variation between factors is likely a
combination of real variation and instrumental artefact. We have provided speculative
explanations here, and these serve as an example of comparisons that would be useful
with a fully functioning (and well-characterised) instrument. However, we note that the
interpretation of the PMF factors does not affect the differences shown in Figure 3.
3.2. The diurnal profile of coating thickness

In Taylor et al. [2013] we showed that, to first order, rBC coatings increased with \(-\log(\text{NO}_x/\text{NO}_y)\), indicative of increased secondary aerosol condensation with increasing photochemical processing of the airmass. We used this, rather than VOC data, as measure of age as it produced a better correlation with the coating data. Here we discuss this topic in more detail in the form of diurnal profiles, which explain the correlation by showing that \(-\log(\text{NO}_x/\text{NO}_y)\) captures nocturnal chemistry and coatings better than the VOC-based ageing metric. We also use the SP-AMS data to explore the factors driving coating thickness.

Figure 2c shows the strong diurnal profile of rBC coatings, as measured by the SP2 and SP-AMS. The thickest coatings were measured during the afternoon, when the most photochemically processed airmasses reached the site. Figure 2d shows the diurnal cycle of fractional component mass measured by the SP-AMS; this does not directly show changes in the coating mass but is useful to explore coating composition at different times of day. It is clear from Figure 2d that the afternoon peak in coating thickness was related to the increase in OOA-2\text{SP} coating the particles as the Western-LA basin plume passed the site. In conjunction with the results of Hayes et al. [2013], this suggests that SOA formation was responsible for these changes. The number-based SP2 shell/core ratio peaked earlier than the mass-based SP-AMS coating/rBC mass ratio, highlighting the difference between the two metrics. This may be due to locally emitted less-coated particles reducing the median coating thickness, but condensation continuing to add mass to the coated particles.

Throughout the night, coating thicknesses were thinner and both aging metrics were lower, indicative of fresher local emissions becoming more prominent. The fraction of the rBC/HOA_{SP} component increased in agreement with this, though OOA-1_{SP} was also more
prominent, which may be indicative of aged background emissions mixed in. Between 
2300 – 0700 the nitrate fraction increased, as did the median shell/core ratio, suggesting 
some particles were coated by ammonium nitrate. The SP-AMS coating/rBC ratio 
appeared to remain fairly constant during this period, however for this dataset the SP-AMS rBC collection efficiency varied with inorganic concentration [Taylor et al., 2013], 
which may have affected this measurement.

Shiraiwa et al. [2007] and Moteki et al. [2007] showed that rBC coatings in the Western 
Pacific and Tokyo increased with photochemical age, and were largely controlled by 
organics and sulfate, with a contribution from nocturnal nitrate. Our findings confirm 
those of Metcalf et al.[2012] that sulfate has little influence on rBC coating thickness in 
the Los Angeles basin, due to its low mass fraction and slow formation rate compared to 
the residence time in the basin. In Pasadena the effect of organics during the afternoon 
outweighs that of nocturnal nitrate. Bearing in mind that any night-time coatings have 
little effect on direct radiative forcing, it is clear that fresh SOA formed from urban 
emissions is the main factor driving any enhancement in rBC absorption in Pasadena.

3.3. Changes in rBC properties with photochemical age

Figure 5 shows rBC size distribution and coating distributions, averaged over both the 
freshest and the most processed airmasses seen over the campaign. Between the least and 
most processed airmasses, there was a slight shift towards larger rBC cores, probably due 
to coagulation, and a clear shift to thicker coatings. In the freshest airmasses, the majority 
of particles registered shell/core ratios > 1, and in the most processed there were still 20% 
of particles that registered as externally mixed. While there is clearly always a 
distribution of coating properties in the real atmosphere, it is difficult to distinguish how 
much of this variation is real and how much is instrumental error. In a perfectly calibrated 
instrument, 50% of externally mixed particles would register some coating thickness due
to the instrumental error. The SP2 measurements presented here therefore represent an upper bound on the distribution of coatings in the freshest airmasses. For comparison, 56% of particles registered some coatings when sampling the freshest airmasses and thermodenuded to >220 °C.

*Cappa et al.* [2012] used the SP-AMS to calculate core/shell $E_{\text{Abs}}$ from the ship data, and calculated a mean shell/core ratio of around 2.5. These were significantly thicker coatings than those measured here by the SP2. As described in Section 2.4, we were unable here to perform a direct comparison of the SP2 and SP-AMS coating thicknesses due to biases in the SP-AMS data, but the photochemical ageing timescale was similar to the measurement period presented here. In order to explain this difference we recommend a direct comparison of the two techniques under controlled conditions, over a range of particle sizes, mixing states and morphologies.

4. **Changes in MAC$_{BC}$ with photochemical age**

As BC coating thickness increases, the Mie model predicts an increase in absorption. Figure 6 shows the change in measured MAC$_{BC}$ (at 532 nm) with age, and a comparison to calculated MAC$_{BC}$ using SP2 core/shell data, integrated over the entire rBC core size distribution. As in Figure 5, the 5-minute data were stratified by $-\log(\text{NO}_X/\text{NO}_Y)$, but here were divided into ten quantiles, over which average distributions of rBC core size and shell/core ratio were calculated. Measured MAC$_{BC}$ was corrected for rBC mass outside the SP2’s detection range, as shown in Figure 5, and the amount of undetected rBC mass ranged from 3 – 6 % over these periods. There is a clear trend of increased MAC$_{BC}$ in the more processed airmasses, which correspond to periods with thicker BC coatings measured by both the SP2 and SP-AMS. Measured MAC$_{BC}$ increased by 25% (at 532 nm) between the least and most aged conditions ($0.082 \leq -\log(\text{NO}_X/\text{NO}_Y) \leq 0.34$).
Comparing to Figure 2b and the photochemical ageing scale presented by Cappa et al. [2012] this corresponds to around 1/3 of a day of photochemical processing. This exceeds ambient coating enhancements previously reported from urban environments [Knox et al., 2009; Cappa et al., 2012], though it is still short of the factor of 50% recommended by Bond et al. [2006]. The range of measured data is within the \(7.8 \pm 1.2 \text{ m}^2\text{g}^{-1}\) recommended by Bond and Bergstrom [2006] (corrected from 550 nm to 532 nm assuming an Ångström exponent of 1), with the freshest measurements slightly below and the most processed slightly above. This means assuming this constant value would not significantly deviate from the measured data.

The coating thicknesses were calculated using a BC core refractive index of \(n_c = (2.26-1.26i)\), which generates the best agreement with thermodenuded SP2 scattering data at 1064 nm [Moteki et al., 2010; Taylor et al., 2013]. However, numerous studies have reported an increase in BC refractive index (real and imaginary) at infrared wavelengths [Bond and Bergstrom, 2006 and references therein]. We have therefore tested the effect of calculating optical properties at 532 nm using several other refractive indices more appropriate for use at visible wavelengths [Schnaiter et al., 2005; Bond and Bergstrom, 2006].

Using the refractive index derived by Moteki et al. [2010] results in a \(~25\%\) overestimation of MAC\(_{BC}\), similar in magnitude to the variation in the measured data. A refractive index of \(n_c = (1.95-0.79i)\) generates the best agreement with the measured data, and this is the highest value of those recommended by Bond and Bergstrom [2006].

The mean and standard deviation of the ratio measured/modelled MAC\(_{BC}\) using this refractive index is \(0.99 \pm 0.05\). The provides the accuracy and precision of this comparison, though we note that this is sensitive to the core refractive index and the calibration of the SP2 and PASS. Given the spread in the modelled values, it is clear that
BC core refractive index must be taken into account when considering optical closure, and these results suggest different refractive indices are needed at visible and infrared wavelengths, however we note that this conclusion is dependent on the optical model used.

When using a BC core refractive index of \( n_c = (1.95 - 0.79i) \), the calculated MAC\(_{BC}\) agrees with the measured data to within 10%. This is significant, as the recent results of Cappa et al. [2012, 2013] appeared to suggest that using the concentric core/shell Mie model would overestimate absorption by overestimating the enhancement due to coatings. However, detailed optical models also predict the core/shell model underestimates absorption by the rBC cores, as the centre of the spherical core is shielded by the edge [Liu et al., 2008; Kahnert et al., 2012]. In this case, taking into account distributions of both core diameters and coating thickness, it may be that these two effects cancel each other out.

Figure 7 presents normalized changes in MAC\(_{BC}\) with photochemical ageing, from both the measured data and Mie modelling from this study, at all three wavelengths measured by the PASS. As the PASS data at 405 nm and 781 nm were uncalibrated, the average MAC\(_{BC}\) at these wavelengths are normalized to the average at 532 nm, corrected to the relevant wavelength assuming an Absorption Ångström Exponent (AAE) of 1. This is not a robust calibration, but it is useful to qualitatively examine the data at these wavelengths. The increases in MAC\(_{BC}\) at 781 nm and 532 nm are similar, and both were around 25% higher in the most processed air masses than the least. The increase at 405 nm was more muted, at around 15%. The reasons for this are not immediately clear; both brown carbon and mineral dust may be expected to absorb strongly at UV wavelengths, but have a much more limited effect on visible absorption [Bergstrom et al., 2007; Zhang et al., 2011].
This would lead to an overestimate of the MAC$_{BC}$ of BC at shorter wavelengths, when these species were more prevalent. Brown carbon during CalNex increased at higher photochemical ages [Zhang et al., 2011], however the concentration of mineral dust was fairly constant [Hayes et al., 2013], meaning this may have dampened any increase in MAC$_{BC}$ with photochemical ageing at 405 nm.

As we have chosen the refractive index that generated the best agreement at 532 nm, the absolute agreement of modelled and measured MAC$_{BC}$ at 405 nm and 781 nm is dependent on the modelled AAE. In this comparison, the absolute agreement with the 781 nm data is similar to that at 532 nm, as the AAE calculated by the Mie model between 532 nm and 781 nm varied between 0.98 – 1.04. The absolute agreement at 405 nm is worse, as the AAE calculated by the Mie model here was 0.72 – 0.80.

Figure 7 also compares MAC$_{BC}$ with photochemical ageing from this study to similar ambient measurements by Cappa et al. [2012]. They reported ship-based measurements from along the Californian coast (also part of CalNex), and ground-based measurements conducted in Sacramento, California as part of CARES (Carbonaceous Aerosols and Radiative Effects Study). The campaigns all took place during May-June 2010. Cappa et al. [2012] reported the ratio of measured MAC$_{BC}$ to the fresh value recommended by Bond and Bergstrom [2006] for fresh soot (7.5 m$^2$g$^{-1}$ at 550 nm, corrected to the relevant wavelength using AAE=1). Here we have used this data to back out MAC$_{BC}$ to compare with our measurements. The CARES data are corrected by a factor of 1.3 for the erroneous photoacoustic calibration reported by Cappa et al. [2012].

At 532 nm all the measured MAC$_{BC}$ agree with the modelled values from this study to within 10%, though again we note that this will be dependent on the core refractive index chosen.
In contrast, the Mie calculations from this study underpredict the calibrated MAC$_{BC}$ reported by Cappa et al. [2012] at 405 nm by around 30%. As noted previously, the AAE calculated between 405 nm and 532 nm is ~0.75 which is low for soot, and the AAE using Cappa et al.’s data was 1.0 – 1.5. While Cappa et al. suggested that brown carbon may have influenced their dataset (which would increase the apparent MAC$_{BC}$), the main reason for the disparity between the good agreement at 532 nm but underestimation at 405 nm is the low calculated AAE between these wavelengths. The reason for the low AAE is that the shielding of the core centre by the its surface (which decreases MAC$_{BC}$ of the core) is a stronger effect at shorter wavelengths [Kahnert et al., 2012]. As the PASS data from this study were only calibrated at 532 nm, we are unable to assess the measured AAE for this dataset.

Bond et al. [2006] suggested absorption by aged black carbon is likely 1.5 times greater than that of fresh aerosol. This was made on the assumption that aged BC was found in a core/shell configuration, but that fresh fractal BC also had enhanced absorption (compared to a compacted sphere) due to interactions between primary spherules, which were inhibited as the particles became coated. The definitions of “fresh” and “aged” are somewhat ambiguous, in terms of time, chemistry and indeed the measurement technique used (see Figure 2). Further experimental work, including a direct comparison of the SP2 and SP-AMS, would help to remove some of the instrumental ambiguity. The range of photochemical ageing covered in Figure 7 is around half a day, which is relatively short compared to the lifetime of BC in the atmosphere [Bond et al., 2013], though particles are coated relatively rapidly. The data from this study (both measured and modelled) also appear to flatten off at the longer ageing times. Cappa et al. [2012] did make some measurements in more aged airmasses, but suffered limited signal/noise. It is not clear whether absorption will continue to increase at longer ageing timescales, or if the
core/shell configuration assumed by Bond et al. [2006] is ever fully reached. Similar measurements comparing MAC$_{BC}$ in fresh and more aged airmasses would help shed some light on this question.

5. Conclusions
Black carbon optical properties and coating thickness and composition were measured in an urban area under a range of different atmospheric conditions. Organics comprised most of coating mass, and the organic fraction in the coating material was higher than that of bulk nonrefractory aerosol. Secondary organics appeared to be responsible for the majority of coating growth, especially during daylight hours, which are relevant for direct radiative forcing.

Comparisons with a recent study by Cappa et al. [2012] showed good agreement with ambient MAC$_{BC}$ within ~10% at 532 nm, though in this study the rate of change of MAC$_{BC}$ was higher. MAC$_{BC}$ measured in the most processed airmasses was around 25% higher than in the freshest at 532 nm. The change in MAC$_{BC}$ is significantly less than the increase of 50% recommended by Bond et al. [Bond et al., 2006], the previous best estimate, but due to the relatively short ageing timescale compare to the lifetime of BC it is not clear if 50% is an overestimate.

The distributions of rBC core size and shell/core ratio were measured using an SP2, and these used to calculate MAC$_{BC}$. The absolute modelled values of MAC$_{BC}$ were dependent on the assumed refractive index of the BC core, but using the range recommended by Bond and Bergstrom [2006] bounded the measured data, whereas using the refractive index measured (in the infrared) by Moteki and Kondo [2010] overestimated MAC$_{BC}$ by around 25%. In order to obtain closure, it was necessary to assume a smaller core refractive index (real and imaginary) at 532 nm than in the near infrared. When using a
refractive index \( n_c = (1.95 - 0.79i) \) the modelled MAC\(_{BC} \) agreed with the measured values (and those reported by Cappa et al. [2012]) at 532 nm to within 10%. Several recent studies have focused on the core/shell model’s overestimation of absorption enhancement due to coatings, however detailed optical models also predict that the core/shell model underestimates absorption of the core as the core centre is shielded by its edge. In this dataset it appears these two effects largely cancel each other out at 532 nm. At 405 nm the modelled values underpredicted MAC\(_{BC} \) reported by Cappa et al [2012] by around 30%. This is in part because the shielding of the core centre by its edge is a stronger effect at shorter wavelengths. There may also be an additional impact of brown carbon and mineral dust, but it is not possible to quantify this effect from these measurements. Any inferences of the absorbing properties of brown carbon from measurements like these are dependent on the optical model used. It is possible that the predictive capability of optical properties may be improved further through the use of a more complex model than Mie, however these models would require additional parameters, which cannot be constrained within the data available here.

These results confirm a modest increase in MAC\(_{BC} \) with atmospheric ageing, and provide a yardstick against which models of BC ageing can be tested. Similar measurements in the future would provide greater confidence into the rate of change of MAC\(_{BC} \), which is likely to be different for biomass burning emissions, and measurements at longer timescales would be useful to further constrain this rate over the lifetime of black carbon.

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Figure 1 - Mass spectral profiles of the SP-AMS PMF factors. While all factors contained some rBC (contained in the \( C_x \) fragments), the rBC/HOA\(_{\text{SP}} \) contained significantly more than the other two, and is named to emphasise this. The rBC peaks have been corrected for a relative ionization efficiency of 0.2 [Onasch et al., 2012]. Note that the O:C and H:C ratios refer only to the organic components of the factors.
Figure 2 – The average diurnal cycle of (a) rBC mass concentration and core MMD, (b) atmospheric processing metrics, (c) rBC coating thickness measured by the SP2 and SP-AMS and (d) the mass fractions of rBC core and coating components measured by the SP-AMS. Errors bars in parts (a) – (c) represent the standard error of the mean. The sum of PMF factors was normalized to the sum of (rBC + organics) calculated using the fragmentation table. A discussion of the differences between the two rBC coating measures is presented in Section 2.4.
Figure 3 – Comparison of the relative amounts of rBC coating fractions, measured by the SP-AMS, and fractions of bulk aerosol measured by the AMS, for (a) organic aerosol and (b) inorganic aerosol. The black lines are orthogonal-distance relation (ODR) linear fits to the data. To reduce noise in the fit, data from periods when the SP2 rBC concentration was <0.3 µg m\(^{-3}\) have been excluded.
Figure 4 - Composition of rBC and coating material measured by the SP-AMS during different conditions. Parts (a) and (b) show composition when the organic fraction measured by the standard AMS was low (≤10th percentile, ≤26% organic) and high (≥90th percentile, ≥67% organic). Parts (c) and (d) show composition when in the freshest airmasses (defined by -log(NOXY/NOY) ≤ 10th percentile, ≤0.082) and most processed airmasses,) and the most processed ( defined by -log(NOXY/NOY) ≥ 90th percentile, ≥0.34).

The pie charts show the percentages of each PMF factor and inorganics, while the percentage of rBC in the corner represents the fraction of mass contained in the Cx peaks, (which are spread through the three PMF factors).
Figure 5 – Measured ambient rBC core and coating distributions in the freshest and most processed airmasses, defined in the same way as Figure 4. Part (a) shows the rBC core mass size distributions and double-lognormal fits, and part (b) shows the distributions of shell/core ratio. The shaded area in part (a) shows the range of rBC core diameters over which the fits were performed, and the vertical dashed line mark the range of core diameter over which coating properties were calculated. The discontinuity around 300 nm and the spike around 520 nm are due to detector saturation, and these regions were not used to perform the fits, nor were data below 100 nm when the SP2’s detection efficiency can be below unity [Schwarz et al., 2010]. Mass outside the SP2’s detection range was calculated by comparing the area under the measured and fitted curves, and was 5.8% in the freshest airmasses and 4.8% in the most processed.
Figure 6 – Comparison of absolute values of measured MAC\textsubscript{BC} at 532nm to that modelled using SP2 data. The modelled data were calculated using several different rBC core refractive indices, using the measured distributions of shell/core ratios, and integrated over the measured rBC core size distributions, the freshest and most processed of which are shown in Figure 5. The measured data were calculated as the gradient of a linear least-squares fit, with zero intercept, on a plot of absorption vs. rBC mass concentration, and corrected for BC mass outside the SP2’s detection range. Uncertainties were estimated from the fitting error. The SP2 core/shell data were calculated using $n_c = (2.26-1.26i)$, originally derived by Moteki et al. [2010] and shown in Taylor et al. [2013] to be the most appropriate to use in the infrared in this dataset.
Figure 7 – Comparison of the rate of change of measured $\mathrm{MAC}_{\mathrm{BC}}$ with photochemical ageing, at (a) 405 nm, (b) 532 nm and (c) 781 nm, showing measured data from this study and those reported in both locations by Cappa et al. The Mie modelled $\mathrm{MAC}_{\mathrm{BC}}$ from this study are the same as the red line in Figure 6, calculated with a core refractive index of $n_c = (1.95 - 0.79i)$, and composition-dependent coating refractive index. The 405 nm and 781 nm data are uncalibrated, but normalised to the 532 nm assuming AAE = 1.
5.3 Paper C: “Size-dependent wet removal of black carbon in Canadian biomass burning plumes”

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Size-dependent wet removal of black carbon in Canadian biomass burning plumes

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Abstract. Wet deposition is the dominant mechanism for removing black carbon (BC) from the atmosphere, and is key in determining its atmospheric lifetime, vertical gradient and global transport. Despite the importance of BC in the climate system, especially in terms of its ability to modulate the radiative energy budget, there are few quantitative case studies of wet removal in ambient environments. We present a case study of BC wet removal by examining aerosol size distributions and BC coating properties sampled in three Canadian boreal biomass burning plumes, one of which passed through a precipitating cloud. In this plume, the largest and most coated BC particles were found to be preferentially removed, suggesting that nucleation scavenging was the likely dominant mechanism. Calculated mass absorption coefficient (MAC) in the plumes showed no significant variation, as the shifts to smaller BC cores and thinner coatings had opposing effects. Similarly, calculated single-scatter albedo (SSA) showed little variation, as a large number of non-BC particles were also present in the precipitation-affected plume. The remaining BC size distribution was smaller than that observed in previous studies of BC in post-precipitation outflow over Asia, possibly due to the thick coatings associated with the biomass burning particles. This study provides important constraints to model parameterisations of BC wet removal in biomass burning regions, which will reduce uncertainty in radiative forcing calculations.
1 Introduction

Black carbon (BC) is the dominant absorbing aerosol in the atmosphere and its estimated radiative forcing is second only to \( \text{CO}_2 \) (Ramanathan and Carmichael, 2008; Chung et al., 2012; Bond et al., 2013). The optical properties of BC affect the single-scattering albedo (SSA) of an aerosol layer, which determines the sign of its radiative forcing (Haywood and Shine, 1995). Important uncertainties remain regarding global and local emissions of BC, as well as its lifetime and optical properties. Observations are required to further constrain and/or validate model parameterisations surrounding BC processes in the atmosphere. Open biomass burning (BB) is the largest source category of BC, responsible for \( \sim 40\% \) of total emissions in the year 2000 (Bond et al., 2013), and the size distribution and mixing state of BC from this source are known to exhibit systematic differences to fossil fuel emissions (Kondo et al., 2011; Sahu et al., 2012).

Wet deposition is the dominant mechanism for BC’s removal from the atmosphere (Textor et al., 2006), and consequently determines its lifetime and atmospheric burden to first order. As convection is often accompanied by precipitation, this also affects vertical profiles of number and mass concentration, which are important for determining radiative forcing (Samset et al., 2013). Such profiles are often poorly represented by models (Koch et al., 2009) as calculated removal rates are sensitive to the microphysical schemes used (Textor et al., 2006; Croft et al., 2010; Vignati et al., 2010).

In climate models, complex aerosol-cloud interactions must be simplified to reduce computing requirements, and many microphysical processes are sub-grid in both space and time. In-cloud scavenging occurs in two stages: aerosol activation to form cloud droplets, and removal of droplets by precipitation. Cloud droplet number concentration may be calculated based on empirical relations with updraft velocity and aerosol number concentration (Lohmann et al., 2007). Alternatively, many models use parameterisations designed to emulate size- and composition-based Köhler theory and the competition for water vapour between activated aerosols growing to cloud droplets (Ghan et al., 2011). Precipitation is determined by calculating autoconversion rates (the rates at which cloud water is converted to precipitation) which are tuned to simulate detailed microphysical schemes (Lin et al., 1983; Liu and Daum, 2004). Below-cloud scavenging is calculated by multiplying the precipitation rate by a scavenging coefficient, which may be size resolved, and again may be calculated empirically or based on theoretical considerations (Wang et al., 2010). Observations (particularly of size distribution, hygroscopicity and mixing state) are needed to constrain such schemes (Koch et al., 2011).

Fresh BC is generally considered hydrophobic, though it may act as a cloud condensation nucleus (CCN) in liquid cloud if coated with hydrophilic material (Khalizov et al., 2009; Liu et al., 2013). In biomass burning plumes this coating is thought to occur in the first few hours after emission (Abel, 2003; Akagi et al., 2012), and coatings are generally thicker than in fossil fuel emissions (Kondo et al., 2011; Sahu et al., 2012). BB emissions can be efficient CCN (Lathem et al., 2013), and can also act as ice nuclei (IN) (Petters et al., 2009), though different species in BB emissions may be
more effective than others. Several recent studies have suggested that non-nucleation scavenging (i.e. impaction) mechanisms may be more effective for BC removal, both in mixed-phase (Twohy et al., 2010) and ice clouds (Stith et al., 2011; Baumgardner et al., 2008).

The different scavenging mechanisms exhibit different size- and composition-dependent efficiencies. In liquid cloud, BC generally requires a soluble coating to activate, and larger particles are generally more effective CCN (Dusek et al., 2006). Larger particles are also more efficient IN (Hoose and Möhler, 2012), however soluble coatings have been shown to inhibit BC ice nucleation (Koehler et al., 2009). Falling ice and raindrops may scavenge coarse mode particles and liquid droplets, and hence remove particles that have already activated (Miller and Wang, 1991; Seinfeld and Pandis, 1998; Croft et al., 2009). This type of scavenging is also more efficient for Aitken mode aerosols. For typical BC size distributions, which span the Aitken and accumulation modes, impaction scavenging therefore favours smaller BC, whereas nucleation scavenging favours larger.

Recently, Oshima et al. (2012) calculated removal rates of diesel-dominated BC by liquid clouds in convective airmasses over the Yellow and East China Seas. By comparing BC/CO ratios in different air parcels, they calculated the transmission efficiency of BC \( TE_{BC} \), the fraction of BC not removed by precipitation. Moteki et al. (2012) showed that larger BC, which also had more coating material, were more efficiently removed during this process, meaning they must have been scavenged by nucleation. For airmasses in which the most BC was removed \( TE_{BC} < 0.3 \) the remaining BC core size distribution was similar to that seen by Schwarz et al. (2010b) in pristine conditions in the remote Pacific, suggesting a fraction of BC is not removed by wet processes and is able to travel long distances. In this manuscript, we present a case study of size-dependent wet removal of biomass burning BC, which may behave differently to diesel-dominated due to its contrasting microphysical properties. Firstly, we present an overview of the experiment, and use backtrajectories and weather satellite data to identify three plumes from Canadian boreal fires in the same region, one of which had passed through a region of precipitating cloud. We examine the aerosol size distributions and BC coating properties sampled in the three plumes and consider the effect this has on optical properties.

2 Experimental

2.1 BORTAS-B

BORTAS-B was the second phase of the BORTAS (Quantifying the impact of BOReal forest fires on Tropospheric oxidants over the Atlantic using Aircraft and Satellites) project (Palmer et al., 2013), and took place over eastern Canada and the north Atlantic during July–August 2011. The project aimed to study the chemistry of biomass burning plumes using a combination of airborne, ground and remote sensing measurements. This paper uses airborne aerosol measurements made aboard the UK BAe-146-301 Atmospheric Research Aircraft (ARA), and focuses on a single flight (B622) on 20 July 2011.
2.2 Instrumentation

2.2.1 The Single Particle Soot Photometer

The Single-Particle Soot Photometer (SP2, Droplet Measurement Technologies, Boulder, CO, USA) uses laser-induced incandescence to measure refractory black carbon (rBC; hereafter referred to as BC) on a single particle basis (Schwarz et al., 2006). Particles are drawn through a high-intensity 1064 nm Nd:YAG laser which heats BC-containing particles to incandescence. The incandescent light is detected by two photomultiplier tubes (PMTs), one fitted with a narrowband filter to determine incandescence temperature, and during BORTAS these were run at different gain settings to expand the dynamic range of the instrument. The signal these two PMTs detect is proportional to the mass of refractory black carbon present in the particle, regardless of mixing state (Slowik et al., 2007; Moteki and Kondo, 2007), and converted to mass-equivalent core diameter ($D_C$) using a density of 1.8 g cm$^{-3}$. The broadband PMT (measuring particles $60 \leq D_C \leq 275$ nm) was calibrated using several sizes of monodisperse Aquadag (Henkel Corporation, Bay Point, CA, USA), with particle mass calculated using the mass-mobility relationship reported by Gysel et al. (2011). This was then corrected for the difference in the response of the instrument compared to atmospheric BC (Baumgardner et al., 2012; Laborde et al., 2012b). The narrowband PMT (measuring $90 \leq D_C \leq 550$ nm) was then cross calibrated to the broadband in the overlap region. The instrument was run with sufficient laser power to ensure 100% detection efficiency for BC particles $\geq 1$ fg (femtogram) (Schwarz et al., 2010a). In plumes, the statistical uncertainty in BC mass concentration was typically $\sim 10\%$ for an averaging time of 10 s, and accuracy within 20% due to possible differences between the instrumental response to biomass burning BC and the calibrant (Laborde et al., 2012a).

The instrumental setup of the SP2 on the ARA was described by McMeeking et al. (2010), and is briefly summarised here. The SP2 sampled through a 1/4 inch stainless steel tube connected to a modified Rosemount inlet (Foltescu et al., 1995). Though recent results have shown that Rosemount inlets can enhance aerosol measurements at larger diameters and higher densities, the vast majority of BC mass is present in particles $< 600$ nm, where the efficiency is close to unity at densities typical of biomass burning emissions (Trembath et al., 2012). Losses between the inlet and the SP2 were minimised using a bypass flow of 1 l min$^{-1}$, and this also reduced the residence time in the inlet.

The SP2 is also capable of measuring light scattering particles (LSP, particles that do not contain BC), and the coating properties of BC-containing particles. Two avalanche photodiodes (APDs) detect scattered light at 1064 nm, and the detected signal is proportional to the scattering cross section of the particle. One APD is position-sensitive, and this provides a measure of the position of the particle in the laser (Gao et al., 2007). This allows calculation of the fractional laser power at the edge of the beam, as the laser has a Gaussian profile when configured correctly. Leading-edge only (LEO) fitting is then used to calculate the scattering cross section of the particle before it begins to evaporate. In this work we considered the leading edge as data from the baseline up to 5% of the...
maximum laser intensity.

Mie core/shell modelling is then used to infer the coated particle diameter ($D_P$), and hence coating thickness, though this is dependent on the assumed core density, and the refractive index of the BC core and coating (Taylor et al., 2013b). In this analysis we assumed a BC core density of 1.8 g cm$^{-3}$ (Bond and Bergstrom, 2006) and core refractive index $n = (2.26 - 1.26i)$ (Moteki et al., 2010). These parameters were shown by Taylor et al. (2013b) to be the most appropriate for use with fossil fuel BC, by comparing Mie calculations to the scattering by thermodenuded particles. As a similar analysis of biomass burning emissions has not been performed, we used these parameters on the assumption that the core properties of fossil fuel and biomass burning BC are broadly similar.

2.2.2 Aerosol mass spectrometer

Nonrefractory submicron aerosol mass concentration was measured with a compact time-of-flight Aerosol Mass Spectrometer (AMS, Aerodyne Research Inc, Billerica, MA, USA.) (Drewnick et al., 2005; Canagaratna et al., 2007). The AMS reports Organic Aerosol (OA), sulphate, nitrate, ammonium and chloride mass concentrations, though in this analysis we only consider the OA concentrations. The operation of the AMS on the ARA has been described previously (Crosier et al., 2007; Morgan et al., 2009). The AMS was connected to a Rosemount inlet and the aerosol flow is considered dry due to ram heating and the increase in temperature as the sample line passes into the cabin.

Data were processed as described by Morgan et al. (2010), using a collection efficiency of 0.5. Unfortunately, after landing on B622 the aircraft lost power, and the AMS had to be shut down before an Ionisation Efficiency (IE) calibration could be performed. For B622 the calibration for the following flight (B623) was applied, which may have introduced a systematic error in the AMS data. As an estimate of the size of this error, for the seven nitrate calibrations performed after B622, the standard deviation of the IE/airbeam was 13% of the mean. The calibrations before this were discarded because of a faulty power supply module in the AMS, which was replaced before B622. Also, in this case study the AMS data is only used to monitor relative changes in the OA/CO ratio, so this increased uncertainty does not affect the analysis method or conclusions.

2.2.3 Scanning mobility particle sizer

A custom-made Scanning Mobility Particle Sizer (SMPS) system, sampling from the same inlet as the AMS, measured particle mobility size distributions divided into 28 logarithmically-spaced bins in the range 20–350 nm. A custom-built low pressure Water-based Condensation Particle Counter (WCPC model 3786-LP, Aerosol Dynamics, Berkeley, CA, USA / Quant Technologies, Blaine, MN, USA) was connected to a TSI 3081 Differential Mobility Analyser (DMA). The WCPC drew 0.6 l min$^{-1}$, half of which was used as the sample flow, and the DMA sheath flow was 6 l min$^{-1}$. The data was inverted using routines developed by Zhou (2001), over a 30 s averaging time.
2.2.4 Supporting measurements

Aerosol light scattering coefficient ($B_{Sca}$) was measured using an integrating nephelometer (TSI 3563, St. Paul, MN, USA). Here we only consider the scattering measurement at 550 nm, though data from the instruments other two wavelengths were used to correct for truncation and the non-lambertian light source (Anderson and Ogren, 1998). Relative humidity (RH) measured in the nephelometer remained below 40%, so no scattering enhancements due to swollen aerosol are expected (Magi, 2003). CO was measured by vacuum-UV resonance fluorescence, with accuracy of ± 3 % and precision of 1 ppb at 1 Hz (Gerbig et al., 1999). CH$_3$CN (acetonitrile) was measured with a Proton-Transfer Reaction Mass Spectrometer (PTR-MS) (Murphy et al., 2010) and HCN (hydrogen cyanide) with a Chemical-Ionisation Mass Spectrometer (CIMS) (Le Breton et al., 2013).

2.3 Data analysis and plume identification

The SP2 and instruments listed in Sect. 2.2.4 record data at 1 Hz, and were averaged to 10 s. The AMS records data every 8 – 9 s and so, for comparison, CO was also averaged to the AMS time series. SMPS scans were averaged over the relevant in-plume periods. All aerosol measurements were corrected to standard temperature (273.15 K) and pressure (1013.25 kPa).

We identified three distinct plumes from B622 which were sampled during straight and level runs, flying at fixed heading and altitude. The times and locations of the plumes are listed in the supplementary material in Table S1. These plumes were selected as each plume had a large range of enhanced CO concentration above the regional background and good correlation ($R^2 \geq 0.55$) between CO and CH$_3$CN. Out-of-plume data were excluded using the thresholds defined by Palmer et al. (2013); only data with CH$_3$CN $\geq$ 150 ppt, CO $\geq$ 148 ppb and HCN $\geq$ 122 ppt were considered in-plume (see O’Shea et al. (2013) for a further discussion of the BORTAS airborne chemical climatology). These thresholds were determined from the 99th percentile measured in background air on flight B625 on 24 July 2011, on which no biomass burning plumes were detected (Palmer et al., 2013).

3 Results

3.1 Backtrajectories and meteorology

By examining Lagrangian back trajectories along with fire location, meteorological fields and satellite data, we can place each plume into the context of its contrasting airmass history. Five-day back trajectories were calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) (Draxler and Hess, 1998), and are shown in fig. 1. The trajectories were initialised using representative times and co-ordinates from the centre of each plume (defined as the mid-point of each straight-and-level run). The HYSPLIT model was driven with full vertical dynamics using
3-hourly NCEP GDAS reanalysis fields on a 1-degree global grid and 23 model (sigma) levels.

Although HYSPLIT (and indeed any Lagrangian model driven by coarse resolution meteorological fields) cannot capture convection (and hence transport) in isolated convective systems, it can effectively model vertical transport in mesoscale and synoptic features such as fronts (Stohl et al., 2001). As we shall discuss later when examining satellite imagery and meteorological fields, passage through cloud in our “precipitating” trajectory in this study was through frontal uplift in the region of active fires, which gives us confidence in the appropriate use of HYSPLIT in this convective regime. We limit our historical examination of these back trajectories to five days here due to the rapidly increasing uncertainty in the path of airmasses beyond this time, and the fact that we cannot trust the accuracy of trajectories that are suggested to have spent significant periods in the boundary layer or in close contact to the ground.

Moderate Resolution Imaging Spectrometer (MODIS) fire counts (Giglio et al., 2003) for 18–20 July are also shown in fig. 1, though this only shows fires that were not masked by cloud. The trajectories for all three plumes are seen to have passed over a large region of forest fires in northwest Ontario, to the southwest of Hudson Bay and east of Lake Winnipeg. Plumes 2 and 3 were sampled approximately ∼1 day after passing over the fires, while plume 1 was sampled after ∼2 days. The meteorology data used to calculate the HYSPLIT back trajectories does not take account of likely pyroconvection from the fires. Therefore the smoke plumes are expected to have formed a vertical emission profile which would be expected to join the trajectories at the altitudes shown over the region. It is therefore not possible to identify a particular fire as the source of a plume, but all three plumes are clearly observed to have passed over the same region of fires.

The back trajectory from plume 3 showed precipitation between 11:30–13:00 and 21:00–22:30 UTC on July 19 2011, as indicated by the aqua-coloured regions in fig. 1. The precipitation rates are calculated by HYSPLIT using the reanalysis meteorology data. Figure 2 shows cloud data measured by the Geostationary Operational Environmental Satellite (GOES) during these two time periods, and highlights the region where the three backtrajectories were at these times. The trajectories for plumes 1 and 2 clearly avoided regions of deep convective cloud, though plume 1 was below cloud at 14:45 – 13:00 UTC. During both periods that showed precipitation, the trajectory for plume 3 was co-located with a cloud system associated with a warm front, with effective cloud height in excess of 10 km and cloud depth up to 7 km, indicative of deep convection, potentially enhanced by pyroconvection at that time. The retrieved Ice Water Path (IWP) gives a qualitative indication of precipitation in these clouds. In fig. 2, it is clear that the frontal cloud that plume 3 passed through was not only 7 km deep but also has a core of IWP in excess of 1000 g m$^{-2}$, suggesting that this deep convective (frontal) cloud was actively precipitating.

Uncertainty in the calculated trajectories and the coarse resolution of the meteorology data used by HYSPLIT mean that the calculated precipitation rates cannot necessarily be considered accurate, but do highlight the presence of precipitating clouds in the area near where the plume passed. The
GOES data confirm the presence of a deep convective cloud in this region that was likely to have been precipitating. In the next section we examine aerosol emission ratios and demonstrate that most of the aerosol in this plume must have been removed by precipitation.

3.2 Emission ratios

Figure 3 shows the BC/CO, OA/CO and BC/B_{Sca} ratios for the three plumes. The gradients of BC/CO and OA/CO are listed in Table 1, while the BC/B_{Sca} gradients are listed in Table 3 and discussed later in Sect. 3.4. These ratios are a product of the initial emission ratios and physical processes between emission and measurement.

Both BC and OA may be affected by wet removal, and OA/CO may increase or decrease due to evaporation or condensation of OA. While there was some variation between Plumes 1 and 2, which did not show evidence of precipitation, this is not unexpected. Several studies have demonstrated the dependence of aerosol emission ratios on combustion conditions (e.g. McMeeking et al., 2009; Kondo et al., 2011), as BC is more associated with flaming combustion and OA with smouldering. Although CO_{2} data was available for the campaign, which can be used in conjunction with CO to characterise combustion efficiency (Ward and Radke, 1993), we did not consider this calculation robust as the variation in CO_{2} background was greater than the excess in the plumes, meaning the derived slopes (\partial CO/\partial CO_{2}) may be misleading (Yokelson et al., 2013). This issue did not affect the aerosol or CO measurements as the background variations were small compared to the excess levels in the plumes.

Table 1 presents a comparison of emission ratios with several other studies and emission inventory values. This is not intended to be a comprehensive review of all previous emission ratios, but to demonstrate the range of values typically observed. BC/CO in Plume 3 was significantly below the other reported values that were unaffected by precipitation, and was most similar to those measured during ICARTT in Alaskan/Canadian boreal plumes that were also affected by precipitation (Val Martín et al., 2006). BC/CO was an order of magnitude lower in Plume 3 than the average for plumes unaffected by precipitation. While the poor correlation between OA and CO in Plume 3 means this ratio cannot be considered reliably accurate, it is clear that it was also significantly below all other measurements listed. It is therefore clear that both BC/CO and OA/CO in Plume 3 were largely the result of the wet removal itself, rather than the initial combustion conditions.

Figure 3c shows the correlations between BC mass concentration and B_{Sca} measured by the nephelometer. For Plume 3, this provides a better comparison than BC/OA, as the AMS signal/noise was low at high altitude. There was excellent correlation in all three plumes, meaning there was no significant difference in the removal efficiencies of the bulk of BC and nonrefractory mass. Comparing the slopes in Fig. 3a and b, it is clear that the majority of BC and organics were removed in Plume 3.
3.3 Aerosol size and coating distributions

In this section we examine the effects of the precipitation event on particle size distributions. Biomass burning size distributions at source show a large amount of variation (Reid et al., 2005b). Additionally, aerosol concentrations in biomass burning plumes mean that coagulation can significantly affect the size distribution over timescales of hours (e.g. Capes et al., 2008). It is therefore not always possible to compare size distributions between different fires.

3.3.1 Bulk aerosol size distributions

Figure 4 shows SMPS size distributions for the three plumes in this case study. Plumes 1 and 2 had count median diameter (CMD) of 196 and 194 nm respectively, whereas Plume 3 had a CMD of 101 nm. The particles in Plumes 1 and 2 were larger than those reported for fresh Canadian boreal BB plumes during ARCTAS (Lathem et al., 2013), due to a different source profile and/or coagulation. The similarity between Plumes 1 and 2 is likely as they were from the same set of fires and had similar transport times. We can therefore infer that had Plume 3 not been affected by precipitation, it was likely have had a similar size distribution. As the particles in Plume 3 were much smaller than in Plumes 1 and 2, this suggests nucleation scavenging was the wet removal mechanism, as this process favours larger particles (Dusek et al., 2006). The remaining particles are likely interstitial in the cloud (i.e. not activated), and this is qualitatively consistent with the difference between cloud residual and interstitial size distributions seen previously (Allan et al., 2008).

3.3.2 BC core size distributions

Although coagulation can quickly affect bulk size distributions, BC-containing particles represent a small fraction of the total number concentration. Kondo et al. (2011) found little variation in BC core size distributions from Canadian biomass burning, meaning the effects of BC-BC coagulation are likely to be minor over the timescale of 1–2 days. Figure 5 shows the BC core size distributions in the three plumes, and a comparison to literature values of CMD and mass-median diameter (MMD) is presented in Table 2. The BC mass distributions of Plumes 1 and 2 were very similar, though there was a smaller mode in the number distribution for Plume 1, which may suggest some limited mixing with fossil fuel emissions in the boundary layer. This is unlikely to affect total BC mass as the mode is not clear in the mass distribution. The BC CMDs for Plumes 1 and 2 therefore show a difference of ∼10 nm whereas the MMDs are nearly identical.

The BC CMD is a more qualitative measurement than the MMD as it is more sensitive to the detection range of the instrument. The SP2 typically has good detection efficiency only for particles ≥ 1 fg. equivalent to ~100 nm in diameter (Schwarz et al., 2010a). For smaller BC cores, the detection efficiency drops down to zero, though the rate at which this occurs depends on the laser
power. Not only is it possible therefore that the BC CMD is sensitive to the instrumental setup of the
SP2, it is also possible that the true CMD is too small to be detectable at all (e.g. Liggio et al., 2012).
A significant fraction of the total BC number is < 1 fg, but as the smallest BC particles contribute
little to BC mass, the MMD is well above the cutoff of the instrument. We therefore consider MMD
a more robust variable to test for variation in BC size distribution.

The literature values of BC MMD in Table 2 range from 194–214 nm, and Plumes 1 and 2 fall
within the lower end of this range. These also compare very well to Canadian plumes from ARCTAS,
which were sampled close to emission (Kondo et al., 2011). Plume 3 shows a distribution skewed to
smaller sizes, with MMD of 152 nm, smaller even than measured in some fossil fuel emissions (Sahu
et al., 2012). The similarity of the size-dependence of wet removal between bulk aerosol and black
carbon (shown in Figs. 4 and 5 respectively) suggests that BC-containing particles were also removed
by nucleation scavenging, rather than another mechanism. As Fig. 3 shows the vast majority of BC
mass was removed in the plume, and Fig. 5 shows there was still a significant overlap in the size
distributions, this shows that the majority of BC particles across most of the size distribution were
removed by the precipitation event. In order to activate, BC requires coating by hydropphilic material
(Zhang et al., 2008; Khalizov et al., 2009). We examine coatings measured by the SP2 in the next
section.

3.3.3 BC coatings distributions

BC coatings were calculated for BC particles in the range $130 \leq D_C \leq 230$ nm. This range was
determined using the method outlined by Taylor et al. (2013b). Figure 6 shows the measured distrib-
utions of coating thickness, expressed in terms of shell/core ratio and absolute coating thickness.
The median coating thicknesses are also listed in Table 2. In all three plumes, nearly all particles
had measurable coatings. Plumes 1 and 2 had broadly similar distributions, with similar median
shell/core ratios of 2.34 and 2.35 and absolute coating thicknesses of 110 nm and 107 nm respec-
tively. Plume 2 had a slightly higher proportion of less-coated particles, probably due to mixing with
a small amount of anthropogenic emissions in the boundary layer. However, this does not appear to
have significantly affected the shape of the distribution, or the median values. Plume 3 had thinner
coatings overall, with median shell/core ratio of 2.02 and absolute coating thickness of 79 nm. This
suggests that the more coated particles were more effective CCN, and hence were removed more
efficiently.

Figure 5 compares the BC mass and number distributions to the range of BC core diameters that
was used for calculating coating properties, $130 \leq D_C \leq 230$ nm. For Plumes 1 and 2 this
range spans the mode of the mass distribution and is just above the mode of the number distribution,
whereas for Plume 3 it borders the mode of the mass distribution and is above the mode of the
number distribution. However, as this range is larger than the number mode in all three plumes,
the median coating properties are weighted towards the lower end of this range. The range is not
significantly far from the mass mode in Plume 3, and so it is likely representative of the bulk of BC mass in all three plumes.

### 3.4 The effect of wet removal on optical properties

Figure 3c shows correlations between BC mass loading and $B_{Sca}$, and the slopes are listed in Table 3. While there is over a factor of two spanning the slopes, this does not appear to be governed by the wet removal. The slopes for Plumes 1 and 2 show the greatest difference, meaning this is probably due to the initial combustion conditions and photochemical processing that occurred between emission and measurement, though Plume 1 has a possible minor contribution by mixing with other aerosols in the boundary layer. While the shift to smaller sizes will have reduced the per-particle scattering cross sections, it also reduced the average BC mass, and so this ratio was not as affected as the BC/CO or OA/CO. As noted in Sect. 3.3.2, the majority of BC particles were removed by the precipitation event over most of the size range.

Table 3 also lists the Mass Absorption Coefficient (MAC) for the three plumes, calculated at 550 nm using the SP2 data. This calculation is integrated over the entire measured BC size distribution (Taylor et al., 2013b). Though the coating properties were calculated using a BC core refractive index of $n_{core} = (2.26 - 1.26i)$ at 1064 nm, this is not appropriate for use at visible wavelengths when using the Mie model (Taylor et al., 2013a). We therefore used $n_{core} = (1.85 - 0.71i)$, the central refractive index listed by Bond and Bergstrom (2006). A sensitivity analysis of this assumption is presented in Table S2 in the supplementary material. We also assumed that BC coatings and particles not associated with BC did not absorb. While this assumption may not hold at shorter wavelengths, brown carbon absorption at 550 nm is highly uncertain (McNaughton et al., 2011; Kirchstetter and Thatcher, 2012; Lack et al., 2012), and we are unable to constrain this using these observations.

As the coating distributions were only measured in the range $130 \leq D_C \leq 230$ nm, coatings at other core sizes must be inferred from this size range. Table 3 presents MAC calculated assuming either a constant distribution of shell/core ratio or a constant distribution of absolute coating thickness, as shown in Fig. 6. A constant shell/core ratio distribution gives thicker absolute coatings to larger cores, whereas a constant absolute coating thickness distribution gives large shell/core ratios to smaller cores. The differences in calculated MAC between the two cases are 15 – 20%. A more realistic treatment of the variation in BC coatings with core size would require detailed modelling of condensation and coagulation processes, and is not in the scope of this analysis.

For comparison, McNaughton et al. (2011) separated out the different contributions of brown carbon, mineral dust and BC in boreal BB plumes during ARCTAS/ARC PAC, and reported average MAC of BC of $9.5 \pm 0.6$ m$^2$ g$^{-1}$ at 530 nm. We note however that this was derived using a filter-based absorption measurement, which suffer from systematic errors that must be corrected empirically (Lack et al., 2008; Cappa et al., 2008). MAC calculated in Plumes 1 and 2 using the absolute coating thickness distribution shows good agreement with this average, though absolute agreement
using the shell/core ratio distribution is possible if using a smaller (real and imaginary) core refractive index (see Table S2). Additionally, Table 2 shows the BC core size distributions discussed here were smaller than those measured during ARCTAS, which would have increased MAC. The coatings measured here were also thicker than those reported during ARCTAS/ARCPAC by Kondo et al. (2011), which would also increase MAC, though these measurements are not absolutely comparable due to the different methods used (Taylor et al., 2013b).

Regardless of which method was used to incorporate the coating distributions, the modelled MAC in the three plumes varies by < 10%. This is in spite of clear differences in the core size and coatings distributions between Plumes 1 and 2 and Plume 3. Figure 7 compares the BC core size distributions to the size-dependent MAC, calculated using the measured distribution of shell/core ratio for each plume. For a given core diameter, Plumes 1 and 2 have generally higher MAC than Plume 3, as they had thicker coatings. However, as the core size distribution in Plume 3 was smaller, this largely cancels out this change, and therefore the calculated MAC shows little variation between the plumes.

Multiplying the calculated MAC by the BC/CO ratios in Table 1 gives \( \frac{B_{\text{Abs}}}{\text{CO}} \), black carbon absorption per ppbv of CO. While there is some variation between Plumes 1 and 2, Plume 3 is an order of magnitude lower, due to its lower BC/CO ratio. As the MAC does not vary significantly between the plumes, BC/CO was the controlling factor determining aerosol absorption in these plumes. Combining these values with the measured BC/\( B_{\text{Sca}} \) one can calculate SSA using

\[
SSA = \frac{1}{1 + \frac{B_{\text{Abs}}}{B_{\text{Sca}}}} = \frac{1}{1 + \text{MAC} \times \frac{B_{\text{BC}}}{B_{\text{Sca}}}}
\]

Calculated bulk SSA are presented in Table 3. SSA was high in all plumes, even for aged smoke (Reid et al., 2005a), though this would be reduced slightly if absorption by brown carbon was included. They also compare well to SSA measured in boreal BB plumes during ARCTAS/ARCPAC (McNaughton et al., 2011). Though there was some variation between the plumes, Plume 3 was the central value. This shows that wet removal had only a minor effect on SSA compared to the burn conditions and secondary condensation.

4 Discussion

Moteki et al. (2012) listed CMD for BC core size distributions in Asian outflow after different amounts of wet removal. In free troposphere outflow the CMD was 132 nm (corrected to a BC core density of 1.8 g cm\(^{-3}\)) in airmasses with transmission efficiency \( TE_{\text{BC}} > 80\% \) and 100 nm for \( TE_{\text{BC}} < 30\% \). While this shows excellent agreement with the CMDs measured in this analysis, the CMD is sensitive to the detection efficiency at the lower cut-off of the BC number distribution.

Moteki et al. (2012) also listed \(< m >\), the mean BC mass per BC-containing particle. Based on their fit data, this ranged from 5.87 fg for \( TE_{\text{BC}} = 1 \) and 2.74 fg for \( TE_{\text{BC}} = 0 \). For comparison, \(< m >\) was 3.65 fg, 4.17 fg and 1.86 fg for Plumes 1, 2 and 3 respectively. We have not quantified
in this study, though based on the BC/CO ratios it is $\sim 0.1$. As the initial size distributions and coatings were different it is difficult to say conclusively if the removal efficiency was the same between the two studies. The size distributions of BC remaining after wet removal were qualitatively similar, though the initial and remaining mass distributions were both smaller in this study. What is clear between the two cases is that nucleation scavenging was an effective mechanism for removing coated BC, and that only the smallest particles were left behind. In this study we have also demonstrated that less coated BC are also less effectively removed.

The MMD in Plume 3 was significantly smaller than those measured in remote Pacific airmasses by (Schwarz et al., 2010b), which were consistently within a few nm of 186 nm (corrected to BC core density of 1.8gcm$^{-3}$). Schwarz et al. (2010b) suggested the consistency (and narrow shape) of this size distribution implied more than one process was responsible for regulating this distribution, one which preferentially removed larger BC cores and ones which removed smaller. Considering our results and those of Moteki et al. (2012), it is clear that nucleation scavenging is an effective mechanism for shifting BC core size distributions to smaller sizes. Additional measurements of BC wet removal in different environments (and involving different mechanisms) are required to further constrain these processes.

The result that wet removal did not significantly affect the SSA and MAC of Plume 3 is important. Many climate models divide BC into two modes with different hydrophilicity, and assume a conversion from the hydrophobic to the hydrophilic mode over time. Bond et al. (2006) recommended a simple optical aging scheme in which the hydrophobic mode had the optical properties of fresh BC, and the hydrophilic had that of aged BC, and some models have implemented this scheme (e.g. Goldenson et al., 2012). This was based on the assumption that coatings were the only factor responsible for BC hydrophilicity. In this case study both hydrophobic and hydrophilic BC had similar MAC, as the BC core size distribution was different between the two modes. This provides a point of reference for models, and highlights the fact that coatings are not the only factor that affects MAC.

The fact that the SSA was not significantly affected by precipitation suggests that some fraction of nonabsorbing particles also did not activate, presumably because they were too small. For comparison, the mean BC number concentration in Plume 3 was 34 scm$^{-3}$, whereas the mean number concentration of LSP measured by the SP2 was 718 scm$^{-3}$. A range of hydrophilicity and size-dependent activation efficiency would be expected of all particles, and these results show that BC activated with similar efficiency to LSP.

5 Conclusions

We have presented a case study of black carbon wet removal by comparing three biomass burning plumes from the same region of fires. Through the use of backtrajectories and weather satellite data we identified that one of these plumes convected up into a likely precipitating cloud. The
BC/CO and OA/CO ratios in this plume were much lower than those in the other two plumes, and almost all those found in literature. The only comparable literature values were BC/CO ratios in plumes that had also been affected by precipitation. Taken together, the backtrajectory, satellite and emission ratios suggest that most of the aerosol in this plume had been removed by precipitation. By comparing particles in this plume to the two unaffected by precipitation, we have made deductions about the properties of the particles that were rained out.

Upon examination of the bulk size distributions it was clear that the larger particles were preferentially scavenged, meaning nucleation scavenging must have been the wet removal mechanism. Similarly, the largest and most thickly coated black carbon particles were also removed more efficiently, meaning they must have undergone the same nucleation mechanism. Removing particles with the largest BC cores and also those with the thickest coatings has opposing effects on MAC, and so the calculated values were similar in all three measured plumes. A large number of LSP were also present in the precipitation-affected plume, so similarly the SSA (based on measured scattering and calculated absorption) was not obviously altered by the precipitation event.

The size-dependence of wet removal is an important process for moderating BC lifetime, vertical profile and transport to remove environments. While the observation that larger particles were more efficiently scavenged is similar to those of Moteki et al. (2012), the residual size distribution measured here was smaller. This may be due to thicker coatings on these particles or simply because the original size distribution was smaller than Moteki et al. (2012). To date there have been very few studies of BC wet removal. Further measurements of BC wet removal in different environments are required to improve model parameterisations and reduce what is currently a major source of uncertainty in radiative forcing calculations.

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Table 1. Ratios of BC/CO and OA/CO from this study and several previous measurements. The emission ratios from this study were calculated from Fig. 3, and listed errors are the fit errors.

<table>
<thead>
<tr>
<th>Project/plume</th>
<th>Description</th>
<th>BC/CO (µg sm$^{-3}$/ppmv)</th>
<th>OA/CO (µg sm$^{-3}$/ppmv)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plume 1</td>
<td>Canadian boreal forest</td>
<td>3.28 ± 0.06</td>
<td>174 ± 5</td>
<td>This study</td>
</tr>
<tr>
<td>Plume 2</td>
<td>Canadian boreal forest</td>
<td>5.4 ± 0.5</td>
<td>78 ± 5</td>
<td>This study</td>
</tr>
<tr>
<td>Plume 3</td>
<td>Canadian boreal forest</td>
<td>0.61 ± 0.04</td>
<td>0.4 ± 0.3</td>
<td>This study</td>
</tr>
<tr>
<td>ARCTAS</td>
<td>Asian boreal forest</td>
<td>9 ± 5</td>
<td>110$^a$</td>
<td>Hecobian et al. (2010); Kondo et al. (2011)</td>
</tr>
<tr>
<td>ARCTAS</td>
<td>Canadian boreal forest</td>
<td>2 ± 2</td>
<td>120</td>
<td>Hecobian et al. (2010); Kondo et al. (2011)</td>
</tr>
<tr>
<td>ARCTAS</td>
<td>Californian boreal forest</td>
<td>3.4 ± 1.4</td>
<td>100</td>
<td>Hecobian et al. (2010); Kondo et al. (2011)</td>
</tr>
<tr>
<td>TexAQS</td>
<td>Unknown BB</td>
<td>9 ± 2</td>
<td>-</td>
<td>Schwarz et al. (2008)</td>
</tr>
<tr>
<td>ICARTT non-precip.</td>
<td>N. American boreal forest</td>
<td>2.5 – 8.4</td>
<td>39.4 – 125.6</td>
<td>Sullivan et al. (2006); Val Martín et al. (2006)</td>
</tr>
<tr>
<td>ICARTT precip.</td>
<td>N. American boreal forest</td>
<td>0.47 – 2.2</td>
<td>-</td>
<td>Sullivan et al. (2006); Val Martín et al. (2006)</td>
</tr>
<tr>
<td>Prescribed burn</td>
<td>Large shrubs</td>
<td>18</td>
<td>82</td>
<td>Pratt et al. (2011)</td>
</tr>
<tr>
<td>Emission inventory</td>
<td>Extratropical forest</td>
<td>6.5 ± 3.2</td>
<td>150 – 170$^b$</td>
<td>Andreae and Merlet (2001)</td>
</tr>
</tbody>
</table>

$^a$ Estimated from Siberian and mixed Siberian + Asian BB.

$^b$ Assuming OM:OC ratio of 1.5 (Reid et al., 2005b).
Table 2. BC core size distribution properties for the three plumes, and a comparison of literature values.

<table>
<thead>
<tr>
<th>BC Core</th>
<th>CMD (nm)</th>
<th>MMD (nm)</th>
<th>( \sigma_{geo} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plume 1</td>
<td>128</td>
<td>196</td>
<td>1.49</td>
<td>This study</td>
</tr>
<tr>
<td>Plume 2</td>
<td>137</td>
<td>194</td>
<td>1.38</td>
<td>This study</td>
</tr>
<tr>
<td>Plume 3</td>
<td>100</td>
<td>152</td>
<td>1.37</td>
<td>This study</td>
</tr>
<tr>
<td>ARCTAS Asia</td>
<td>146</td>
<td>214</td>
<td>1.37</td>
<td>Kondo et al. (2011)</td>
</tr>
<tr>
<td>ARCTAS Canada</td>
<td>141</td>
<td>194</td>
<td>1.32</td>
<td>Kondo et al. (2011)</td>
</tr>
<tr>
<td>ARCTAS-CARB California</td>
<td>146</td>
<td>200</td>
<td>1.33</td>
<td>Sahu et al. (2012)</td>
</tr>
<tr>
<td>TexAQS biomass burning</td>
<td>140</td>
<td>210</td>
<td>-</td>
<td>Schwarz et al. (2008)</td>
</tr>
<tr>
<td>CARB fossil fuel</td>
<td>119</td>
<td>175</td>
<td>1.36</td>
<td>Sahu et al. (2012)</td>
</tr>
</tbody>
</table>

* Literature values are corrected to BC core density of 1.8gcm\(^{-3}\).*
Table 3. BC optical properties (at 532 nm) in the three plumes. BC/B_{Sca} are the slopes from Fig. 3c, calculated using ODR fits with zero offset. The listed errors are the fit errors. MAC was calculated using the measured BC core size and coating distributions, integrated over the entire BC size distribution, assuming either a constant distribution of shell/core ratio or absolute coating thickness from Fig. 6. The stated values were calculated using BC core and coating refractive indices $n_{\text{core}} = (1.85 - 0.71i)$ and $n_{\text{coating}} = (1.50 - 0i)$. $B_{\text{abs}}/\text{CO}$, and errors are the standard deviation of the corresponding range in Table S2. SSA were calculated by combining the calculated MAC with measured BC/CO and BC/B_{Sca}.

<table>
<thead>
<tr>
<th></th>
<th>Calculated MAC $\text{m}^2\text{g}^{-1}$</th>
<th>$B_{\text{abs}}/\text{CO}$ (Mm$^{-1}$/ppmv)</th>
<th>BC/B_{Sca} (µg sm$^{-3}$/Mm$^{-1}$)</th>
<th>SSA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Using shell/core ratio distribution</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plume 1</td>
<td>10.64 ± 0.64</td>
<td>34.9 ± 0.6</td>
<td>2.38 ± 0.03</td>
<td>0.975</td>
</tr>
<tr>
<td>Plume 2</td>
<td>10.95 ± 0.63</td>
<td>59 ± 5</td>
<td>5.55 ± 0.09</td>
<td>0.943</td>
</tr>
<tr>
<td>Plume 3</td>
<td>10.24 ± 0.68</td>
<td>6.2 ± 0.4</td>
<td>4.36 ± 0.15</td>
<td>0.957</td>
</tr>
<tr>
<td><strong>Using coating thickness distribution</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plume 1</td>
<td>9.10 ± 0.53</td>
<td>29.8 ± 1.8</td>
<td>2.38 ± 0.03</td>
<td>0.979</td>
</tr>
<tr>
<td>Plume 2</td>
<td>9.27 ± 0.55</td>
<td>50 ± 5</td>
<td>5.55 ± 0.09</td>
<td>0.951</td>
</tr>
<tr>
<td>Plume 3</td>
<td>8.79 ± 0.55</td>
<td>5.4 ± 0.5</td>
<td>4.36 ± 0.15</td>
<td>0.963</td>
</tr>
</tbody>
</table>
Fig. 1. 5-day HYSPLIT backtrajectories, starting at the time and location sampled (the square markers) and with triangular markers every 6 hours. Parts (a) and (b) show the horizontal and vertical tracks respectively. The aqua-coloured parts of the trajectories are regions with HYSPLIT precipitation, and the yellow dots show MODIS fire data between 18–20 July 2011.
Fig. 2. Cloud data from the GOES satellite from 19 July 2011. The retrievals are from the periods when the meteorology data in the backtrajectory for plume 3 showed precipitation. Parts (a) and (b) show effective cloud height, (c) and (d) show cloud depth (calculated as the difference between effective cloud height and cloud bottom) and parts (e) and (f) show ice water path. The coloured circles show the locations of the backtrajectories at the time of the GOES retrievals.
Fig. 3. Correlations of (a) OA/CO, (b) BC/CO and (c) BC/$B_{\text{Sca}}$ in the three plumes. The slopes (which were calculated by orthogonal distance regression) are listed in Table 1 for (a) and (b) and Table 3 for (c).
Fig. 4. Average normalised bulk size distributions measured by the SMPS.
Fig. 5. Normalised average BC core size distributions for the three plumes. Part (a) presents the number distribution, and part (b) the mass distribution. The discontinuity at \( \sim 300\text{nm} \) is due to saturation of the broadband detector and switching to the narrowband. The grey shaded regions show the range of core diameter used for calculating coating properties.
Fig. 6. Distributions of measured coating thicknesses expressed in terms of (a) shell/core ratio and (b) absolute coating thickness. The first bin \((D_P = D_C = 1, \text{uncoated particle})\) also contains all particles with measured scattering less than that predicted for an uncoated core (equivalent to \(D_P < D_C\)). Such particles are a result of random variations in the detected scattering, however as the result \(D_P < D_C\) is nonphysical they are assigned the nearest realistic value.
Fig. 7. BC core size distributions and size-dependent MAC for the three plumes, calculated using $n_{core} = (1.85 - 0.71i)$ and assuming a constant distribution of shell/core ratio.
Supplementary material for:

Size-dependent wet removal of black carbon in Canadian biomass burning plumes

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Table S1. Plume locations and sampling times on 20 July 2011. Plumes 2 and 3 were sampled continuously during the time periods listed, whereas Plume 1 was encountered on 4 straight and level runs, totalling 40 minutes, during the time period listed.

<table>
<thead>
<tr>
<th>Plume name</th>
<th>Altitude (m)</th>
<th>Latitude (°N)</th>
<th>Longitude (°W)</th>
<th>Time (UTC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plume 1</td>
<td>1570 – 1990</td>
<td>47.70 – 48.04</td>
<td>69.08 – 78.62</td>
<td>16:00:00 – 18:01:10</td>
</tr>
<tr>
<td>Plume 2</td>
<td>4700 – 4790</td>
<td>46.57 – 46.59</td>
<td>72.83 – 73.81</td>
<td>18:40:40 – 18:48:40</td>
</tr>
<tr>
<td>Plume 3</td>
<td>7540 – 7580</td>
<td>46.42 – 47.54</td>
<td>65.82 – 67.80</td>
<td>15:25:00 – 15:46:20</td>
</tr>
</tbody>
</table>

Table S2. Calculated MAC in m² g⁻¹ using different $n_{core}$ in the range recommended by Bond and Bergstrom (2006), and the measured relative and absolute coating thickness distributions.

<table>
<thead>
<tr>
<th>$n_{core}$</th>
<th>Plume 1 Relative</th>
<th>Plume 1 Absolute</th>
<th>Plume 2 Relative</th>
<th>Plume 2 Absolute</th>
<th>Plume 3 Relative</th>
<th>Plume 3 Absolute</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.75 – 0.63i)</td>
<td>9.78</td>
<td>8.37</td>
<td>10.04</td>
<td>8.53</td>
<td>9.33</td>
<td>8.05</td>
</tr>
<tr>
<td>(1.80 – 0.67i)</td>
<td>10.22</td>
<td>8.75</td>
<td>10.51</td>
<td>8.92</td>
<td>9.80</td>
<td>8.43</td>
</tr>
<tr>
<td>(1.85 – 0.71i)</td>
<td>10.64</td>
<td>9.10</td>
<td>10.95</td>
<td>9.27</td>
<td>10.24</td>
<td>8.79</td>
</tr>
<tr>
<td>(1.90 – 0.75i)</td>
<td>11.03</td>
<td>9.42</td>
<td>11.36</td>
<td>9.61</td>
<td>10.65</td>
<td>9.13</td>
</tr>
<tr>
<td>(1.95 – 0.79i)</td>
<td>11.40</td>
<td>9.72</td>
<td>11.75</td>
<td>9.92</td>
<td>11.05</td>
<td>9.45</td>
</tr>
</tbody>
</table>

References

Chapter 6

Conclusions

Ambiguities surrounding the physical and optical properties of black carbon represent a significant source of uncertainty in current understanding of man’s influence on the climate system. Despite complex soot morphologies and variable mixing with other species, most current climate models are limited to considering soot in a spherical geometry due to computational constraints. At best, they may consider a BC core surrounded by a nonrefractory coating in a concentric core/shell configuration.

State of the art climate models use 2-D matrices of particle size and BC fraction, which provide room for the wide range of core size and mixing states observed in the atmosphere, including externally mixed BC and LSP. Such schemes allow for detailed aerosol dynamic and wet removal processes, but there is question as to the accuracy of optical properties calculated using the core/shell model, and few reliable observations to constrain such calculations. By providing measurements of core/shell parameters under different environments, this thesis aimed to provide data required to test such schemes, which are scarce in previous literature. Additionally, by comparing modelled optical properties to those measured using modern instruments, this thesis aimed to gauge how accurately the core/shell approximation can predict these properties in ambient environments.

This chapter will summarise the key findings, discuss their implications and propose further work to reduce uncertainty in estimate of BC’s effects on the climate system.
6.1 Instrumental conclusions

6.1.1 The SP2

A large part of the instrumental work described in this thesis surrounded the derivation of core/shell parameters using the SP2. Chapters 3 and 4 described the practical aspects of generating this data within the framework used by the Manchester SP2 analysis software, which had not been done previously. Several studies have used this method before to derive coating thicknesses, but a variety of different BC core densities and refractive indices were used, with little or no consideration as to the effects this might have on the data. Section 5.1 outlined the sensitivity of the technique to these parameters, and demonstrated that the parameters derived by Moteki et al. (2010a) were the most appropriate for use with ambient BC. It was also shown that the use of different parameters caused systematic bias in the derived coating properties, meaning that this must be taken into account when comparing between different studies, and if comparing modelled core/shell data (for example in a climate model) to measurements.

Similarly, most studies consider core/shell properties only for a narrow range of core diameters. Metcalf et al. (2012) reported coating properties over a wide range of core diameters, and considered the lower detection limit only in terms of the limits of their Mie table, rather than the detection efficiency of the instrument. Schwarz et al. (2008b) considered upper and lower bounds of calculated core/shell absorption enhancement by assuming particles that were not optically sized as either externally mixed or the thickest coating that would not be detected by the SP2, but this assumed a constant cutoff diameter, which the work described in Section 5.1 shows is not the case. Section 5.1 also outlined a method to determine a range of core diameter that is the least biased by the detection limits of the instrument. The median coating thicknesses generated in this range are unaffected by the detection limits, and the range was chosen to minimise the effects of the lower and upper detection limits on measurement of the least and most thickly coated particles respectively. This is more difficult to compare between projects, as the most appropriate range is dependent on the setup of the instrument and the properties of the BC being studied. The work presented here at least serves to highlight the fact that core/shell parameters must be compared only with consideration of the range of core diameters in which they were calculated. This range is likely to be widened due to recent upgrades to the SP2, which provide greater dynamic range on all detectors.
6.1. INSTRUMENTAL CONCLUSIONS

6.1.2 The SP-AMS

Section 3.3 highlighted several areas of uncertainty regarding mass quantification of both BC and coatings using the SP-AMS. During CalNex the variable collection efficiency (caused by temporal variations in particle size and shape), led to some difficulty in analysing the data, and only relative changes in composition could be considered. It also appeared to cause some mixing between the PMF factors usually observed, meaning it is not clear how much of the variation in composition seen by the SP-AMS is due to real variation and how much is due to instrumental artefact. The SP-AMS is a relatively new instrument, and technical issues such as these often have to be identified and overcome through a process of iteration. Massoli et al. (2012) experienced similar problems with poor SP-AMS collection efficiency, and noted that these size-dependent effects were being investigated, however the issue was not discussed by Cappa et al. (2012), so it unclear to what extent this may have affected their data.

Figure 6.1 shows an example of an experiment which would be needed to investigate the sources of uncertainty in mass quantification of BC and coatings in the SP-AMS. The soot source could be a nebuliser providing standardised test particles, a propane burner or similar, or a diesel engine/test bench, which may be run under different conditions to generate different amounts of BC and primary organics. The coating chamber may be filled with organic substances such as DOS or oleic acid, or sulphuric acid, which has previously been very effective at collapsing soot cores (Zhang et al., 2008). Bypassing the catalytic stripper would then allow selection of coated particles of known BC and coating mass. When running through the catalytic stripper, the majority of coating material would be removed, allowing for separate investigation of shape and size effects. For such experiments, ideally the coating species would be easily removed, so semi-volatile species such as methanol may be a good candidate. Comparison between the SP2, AMS and SP-AMS would be useful to determine the relative collection efficiencies of BC and coatings in the SP-AMS, while the DMPS would be useful to compare size distributions, and constrain the width of the distributions of particles transmitted by the CMPAs. It would also be useful to investigate the properties reported of small BC cores (< 90 nm), which represent the bulk of BC number but usually contribute little to total BC mass. When these particles are thickly coated, the properties reported by the two instruments are likely to be very different, as the SP2 may struggle to detect smaller BC cores and may report particles as LSPs, whereas the SP-AMS may report very thick BC coatings.
Figure 6.1: Suggested experimental setup to investigate the effects of particle shape and size on the SP-AMS. Test aerosol are mass-selected by CPMA 1, then may be coated (and possibly collapsed) by in the coating chamber. The catalytic stripper may remove coatings, before the particles are again mass-selected by CPMA 2, before being sampled by several aerosol measurement instruments.
6.1.3 The PASS

In Chapter 3 and Section 5.2, a method was described to calibrate the 532 nm channel of the PASS using APSS, and this was checked using NO$_2$. The APSS are a useful calibrant as they are easy to deploy in the field, using equipment (a nebuliser and DMA) that are often used during calibration of aerosol instrumentation. Unfortunately, it was not possible to calibrate the other channels using the APSS, as no absorption cross-section data are currently available at 405 nm (though there are plans to measure these (Daniel Lack, personal communication)), and they do not absorb significantly at 781 nm. It was also not possible to calibrate these channels with NO$_2$ as this is photolysed by the laser at 405 nm and does not significantly absorb at 781 nm. While relative changes can be monitored at all wavelengths, it is recommended that calibration of all three wavelengths would be useful, and this is planned using O$_3$ as the calibrant.

6.1.4 The Sunset OC/EC instrument

Section 5.1 demonstrated the excellent correlation between the rBC measured by the SP2 and the Sunset instrument’s ‘optical EC’ measure. This compares to worse agreement using the standard thermal EC measure, with a lower correlation coefficient and scatter plot gradient further from unity. As the SP2 mass measurement is not affected by the mixing state of the particles, this suggests that this relatively unused ‘optical EC’ measure may be surprisingly reliable, despite its limitations as a filter-based measurement. The reasons for the lack of absolute agreement could be related to the calibration of each instrument, particularly the empirical calibration of the Sunset instrument. Further comparison in different environments should be undertaken to determine if this good agreement is consistent, as the comparison may not always be as favourable, particularly in environments with large amounts of BrC.

6.2 The use of core/shell schemes in climate models

The core/shell model is not an accurate representation of the morphology of fresh, fractal BC aggregates, and this has been known for many years. However, this does not necessarily mean that it cannot be used to model the optical properties of ambient BC. Modelling studies show that fractal externally mixed BC may absorb more, the same or less than equivalent spheres, depending on the spherule size, number of spherules,
shape, refractive index and wavelength (Liu et al., 2008; Adachi et al., 2010; Kahnert, 2010a; Chung et al., 2012a). MAC may be increased by multiple scattering or decreased due to light being unable to penetrate through the outer shell of an absorbing sphere. The concentric core/shell model is generally considered to be an upper bound on the absorption enhancement due to coatings, and any deviation from such a configuration is expected to decrease absorption (Adachi et al., 2010). Many authors therefore state that the core/shell model overestimates absorption enhancement (compared to that of an uncoated core), and consequently also overestimates ambient MAC.

Cappa et al. (2012) (and subsequently Cappa et al. (2013)) was an important paper, presenting evidence that large absorption enhancements (compared to a less coated core), such as those calculated by Jacobson (2012), may not be observed in the real atmosphere. These were not the first observations of ambient absorption enhancement; Knox et al. (2009) observed 2–42% in downtown Toronto, depending on the age of the airmass, and Lack et al. (2012a) observed up to 40% enhancement (at 532 nm) in biomass burning emissions. The novelty of Cappa et al.’s work was their detailed Mie calculations, and the systematic disagreement between these and measured absorption enhancement. However, their coating thicknesses were calculated from the SP-AMS data, and it is not certain that these data are necessarily representative of the bulk of BC mass. The core/shell absorption enhancement calculated based on these data were 1.5 – 2.2, which is large compared to previous core/shell measurements (Schwarz et al., 2008a; Shiraiwa et al., 2008), and the work presented here.

But it is not the core/shell absorption enhancement that matters when calculating DRF_{BC}. This (albeit useful) diagnostic does not appear in Equation 1.4. To suggest that absorption enhancement and MAC are equivalent is to ignore the dependence on BC core size shown in Figure 2.1b, and the dependence on the assumed refractive index of the BC core. It is also to assume that freshly-emitted soot particles are made of spherical BC, which do not vary within their lifetime. Within the core/shell model, fresh soot is a distribution of spherical BC cores, some of which may be coated in primary organics. The MAC of fresh soot is 7.5 ± 1.2 m^2 g^{-1} at 550 nm (Bond & Bergstrom, 2006). Within the core/shell Mie model, this value could be achieved by many different combinations of core size distribution, refractive index and primary coatings. And when detailed optical models underpredict this range (e.g. Kahnert, 2010b), they may be less accurate than the Mie model. Ageing processes in the climate models will then determine how the coating and core size distributions will change
over time, and much of the change described in this work may be sub-grid in a global model.

This work does not confirm that 2D mixing state schemes such as those in WRF-Chem (Matsui et al., 2013) and GATOR (Jacobson, 2012) can accurately calculate MAC using the core/shell Mie model. In the case of GATOR it suggests it is over-estimated, though Jacobson (2012) reported MAC at ambient RH, and the effects of humidity on MAC are not well known. But it suggests that these models may be able to do a reasonable job if their condensation/coagulation processes produce core and coating distributions similar to those measured by the SP2. As they are based on different physics and emission/chemistry processes, there is no guarantee that this will be the case, though Matsui et al. (2013) showed their scheme captured the overall features well compared to SP2 measurements. Even if it emerges that 2D core/shell schemes do overestimate absorption, they would still be an improvement over previous schemes that combine all BC (internally and externally mixed) and nonrefractory aerosol (internally and externally mixed) into one internally mixed mode. Matsui et al. (2013) demonstrated that these schemes overestimate absorption by 40% compared to 2-D core/shell schemes, though when using these simpler schemes to calculate wet removal processes, much of the BC was removed, cancelling out this effect when considering total absorption.

In the wider context, if 2D mixing state schemes are to improve predictions of direct effect forcing, they must achieve not only improved accuracy in the calculation of MAC, but of AOD, SSA, backscatter fraction and transport (both vertical and horizontal) of all aerosols. For BC, these schemes provide space for different mixing between BC and co-emitted aerosol, as well as aerosol from other sources. Bond et al. (2013) demonstrated that Jacobson’s model agreed better with remote measurements of BC than most. But this does not guarantee that this is due to the mixing state scheme, as differences in transport, meteorology and wet removal schemes are also a large source of model diversity. Exercises like AEROCOM are useful to identify areas where models differ (both from each other and from observations), but thusfar have not been able to test whether 2D core/shell schemes are an improvement over simpler schemes as GATOR (the only global model with such a scheme) has not been included. To test if the increased detail generates better agreement with observations, such comparisons may need to take place within the context of the models in which they are applied.
6.3 Further work

If 2D core-shell schemes are to be implemented in more climate models than is currently the case, there are several key areas in which their core and shell distributions require input data and testing. Any model (including alternatives to 2D core/shell schemes) should ideally be able to accurately calculate key properties of particles, and these must be tested against observations. The following section discusses the observations that are required, both within the context of a 2D core/shell scheme and for any model, to improve constraint on the effects of BC and other aerosols in the climate system.

6.3.1 Testing models with core/shell observations

Equation 1.4 highlighted several factors that are useful to identify sources of uncertainty in $\text{DRF}_\text{BC}$. Again, it is convenient to consider these terms separately.

While there is uncertainty into BC emissions estimates, the amount and distribution are at least standardised for model comparisons in the near future (Lamarque et al., 2010). Characterisation and use of emission sources in the developing world are somewhat lacking, though the United Nations are co-coordinating an effort to create a standardised emission inventory using emissions data gathered by different nations (Laursen, 2013). However, emission inventories do not constrain primary particle size or mixing state. Measurement of the core size and coating distributions of primary emissions would need to be carried out for each of the different major BC sources. There is evidence that in developed nations there can be significant differences between fossil fuel combustion (i.e. diesel emission) and open biomass burning emissions in terms of both the core size distribution and coating thicknesses (Kondo et al., 2011b; Sahu et al., 2012). Large differences are also to be expected in biomass burning emissions under different conditions and fuel types (e.g. McMeeking et al., 2009; Kondo et al., 2011b), and these should be investigated and taken into account. Emissions from residential cooking/heating are a major source of BC emissions but appear to be rarely measured, probably because they are most prevalent in developing nations. Huang et al. (2011) showed the core size distribution in the Pearl River Delta region of China (an area with high levels of industry) were larger than typically observed in western diesel emissions, though this may be in part due to increased coagulation due to high mass loadings. Characterisation of these primary emissions would also be useful input to climate models. Of course, such experiments would also need to report the amounts
and size distributions of co-emitted LSP in order to fully populate the 2D matrix of particle size and mixing state.

Next, the ageing schemes (based on condensation and coagulation) must be tested to see how well these processes can capture changes in core/shell parameters. As Jacobson (2013) pointed out, at high RH any soluble material mixed with BC would grow hygroscopically, leading to thicker coatings. Thusfar, all SP2 measurements have been carried out under dry conditions, however NOAA have tested the use of a humidified SP2 (including a humidified sheath flow) and successfully demonstrated particle growth at higher RH, and this may be a useful addition to the suite of BC measurements. McMeeking et al. (2011) described the use of a combined HTDMA-SP2 technique, and these measurements would also be useful to test BC growth at high RH. Modelling of SOA formation in different environments is highly uncertain (Hallquist et al., 2009) and modelling of nitrate is often absent in global climate models (Myhre et al., 2013), meaning testing these processes will have implications outside of just BC.

Wet removal is the dominant deposition route for BC (and all accumulation mode aerosols), so parameterisations of wet removal are important for determining lifetime (and hence burden and transport). The data presented in Section 5.3 are useful to inform and test these parameterisations, as are those reported by Moteki et al. (2012) and Oshima et al. (2012). Section 5.3 is an interesting case study, but to some extent it was found accidentally (investigating aerosol wet removal was not one of the objectives of BORTAS) and therefore there was no measure of the conditions of pyroconvection and little information on the cloud conditions available. A more systematic way to investigate wet removal would be to observe the properties of an aerosol layer through the convection process, such that the properties of the particles before, during and after uptake into cloud droplets may be reported and linked within the same airmass. Ideally this would also include measurement of aerosol within the liquid/ice cloud particles (e.g. Twohy et al., 2010), to obtain closure between the particles removed from the aerosol phase and the particles observed in the cloud phase. There are very few observations of the effect of cloud processing on soot (i.e. activation followed by evaporation) and Jacobson (2006) predicted this may be an important means by which BC may become internally mixed and its core size distribution modified.

Any experiments such as these must consider the limitations of the instruments used to measure such properties and processes. While the SP2 is capable of measuring the majority of accumulation mode BC mass distribution, it is limited in the range of
particles for which it can detect coatings. Though the dynamic range of the instrument has recently been upgraded, there will still be limits on the smallest and largest particles it can reliably detect. For the sake of argument, if the SP-AMS were modified such that it could accurately measure 100% of BC and coating materials, the coating/BC mass ratio it reports would still be based on different particles than that reported by the SP2. Regardless, the SP-AMS would be a useful tool to determine the processes that lead to internally mixed BC, by measuring the composition of material it is mixed with.

### 6.3.2 Testing models with bulk observations

Even if models can produce core and coating distributions that agree well with observations, there is still uncertainty regarding how accurately these schemes can calculate optical properties. This means as well as testing modelled distributions, it is also necessary to compare to measured optical properties. Due to the artefacts related to filter-based absorption and EC techniques, reliable measurement of MAC can only take place using instruments such as the SP2 and PAS, which do not suffer from such artefacts. Where absolute values of MAC are compared, care should be taken to cross-calibrate instruments where possible, to reduce uncertainty relating to different calibrations. Cappa et al. (2012) showed evidence (though this was not conclusive) that even well-calibrated systems may suffer systematic uncertainties due to unknown factors in the calibrations.

Key environments to study are those in which BC, and aerosol in general, have the biggest climate forcing. These include high emission regions such as China, South and Southeast Asia, as well as megacities all over the world. Recently, several studies reporting SP2 measurements in China have been published (e.g. Huang et al., 2011, 2012) but Lan et al. (2013) is the only study to have measured MAC. Industrial coal and biofuel cooking are large sources of BC in East Asia (Bond et al., 2013), and these are poorly characterised. The Indian subcontinent is an important region of study due to the high aerosol mass loadings and the effects this may have on the Asian Monsoon. One SP2 has been deployed near Bangalore, but a recent more comprehensive aerosol study was cancelled due to logistical difficulties. These regions are particularly important as they are areas where emission reductions would have the largest effect. To some extent the optical properties of diesel emissions in western nations have been characterised, but less efficient emissions from regions with fewer regulations, industrial coal burning, biofuel and open biomass burning are less well studied. The properties of BC transported to the Arctic are also important due to its high climate sensitivity, and to
remote regions due to the large area these cover.

The techniques developed in this thesis are being used to analyse data from several of these environments. The SP2 and PASS were used in London in January – February and July – August 2012 as part of the ClearfLo (Clean air for London) project. The SP2 was deployed to measure biomass burning aerosols in the Amazon in September 2012 as part of the SAMBBA (South AMerican Biomass Burning Analysis) project, and in the Arctic in March – April and July – August 2013 as part of the ACCACIA (Aerosol-Cloud Coupling and Climate Interactions in the Arctic) project.

The SP2 is very sensitive at sampling BC mass concentrations; Schwarz et al. (2010a) showed it can be used to report mass concentrations < 1 ng m\(^{-3}\) for 60 s averages in the remote Pacific, and reported mass distributions from these regions, though these were averaged over a wide area. The ability to report mass distributions suggests coating distributions may also be possible in such environments if the averaging time is long enough. The PASS used in this thesis is not sensitive enough for such environments. More precise PAS measurements are achievable: Lack et al. (2012b) reported a 1 Hz sensitivity of < 1.5 Mm\(^{-1}\) at 532 nm, and hope to improve this to \(\sim 0.1\) Mm\(^{-1}\) by increasing the laser power. This would correspond to \(\sim 15\) ng m\(^{-3}\) at 1 Hz, and \(\sim 2\) ng m\(^{-3}\) for a 60 s average.

MAC is not the only variable that determines aerosol radiative forcing. While it is useful to constrain the effects of BC, direct radiative forcing is determined by SSA, \(B_{Ext}\), and backscatter fraction at different wavelengths, and the vertical profile of these variables all must be tested. This would require measurement of particles other than BC, and also of scattering/extinction as well as absorption to calculate SSA. While MAC may increase with ageing, a corresponding increase in scattering would mean SSA may increase, meaning the radiative forcing of BC and co-emitted species would decrease (in absolute terms).

Ideally, measurements would take place in a Lagrangian style, first characterising sources and then observing changes as aerosols aged photochemically and were transformed (or removed) by clouds. This would reduce uncertainty due to calibrations (as relative changes could always be observed) and allow MAC to be characterised for specific source regions over their entire lifetime. This may be achieved using an aircraft platform, such as that used in Section 5.3, and Langridge et al. (2012) and Lack et al. (2012b) described a suite of instrumentation to measure SSA at three wavelengths using photoacoustic and cavity ring-down spectrometers, suitable for operation on a research aircraft. A dedicated measure of BrC (such as that described by Zhang et al.
would also be a useful addition to this suite of measurements, as otherwise the amount and properties of BrC required to agree with bulk optical measurements are dependent on the optical model assumed (e.g. Lack et al., 2012a). These measurements would also be useful at multiple wavelengths, as the optical properties of BrC are uncertain as well as its abundance.

### 6.4 Closing Remarks

Several papers in the last few years have used complex optical models to criticize the concentric core/shell model (e.g. Liu et al., 2008; Adachi et al., 2010; Kahnert, 2010a; Chung et al., 2012a; Kahnert et al., 2012; Adachi & Buseck, 2013; Kahnert et al., 2013). Criticism generally has focused on specific aspects of a particular particle; absorption of externally mixed particles compared to a compacted sphere, or absorption enhancement due to coatings. Any differences between the complex models and coated sphere approximation are then used to infer that the coated sphere approximation is ‘wrong’ and cannot possibly be used to calculate BC’s optical properties with any degree of accuracy. It is almost universally ignored that many of the differences (underprediction of absorption in large cores but over-prediction of absorption enhancement due to coatings) cancel out, and all these effects vary with the sizes and refractive indices of the core and coating, the shape of the particles and the wavelength of light.

There are very few measurements of any of these effects. Only one study has used measured core/shell distributions to calculate ambient MAC and then compared this to that measured using reliable, modern techniques. That is the work presented here. In this comparison, the core/shell model was used to calculate MAC with reasonable accuracy, though this in no way guarantees that this would be the case using a climate model that may generate different core and shell distributions than those measured here. At present, the SP2 is the only tool capable of reporting these distributions, and this work has presented a methodology for determining measured core and coating distributions and using them to calculate optical properties.

What, then, is the outlook for BC modelling in the future? The best model is the one that can most accurately reproduce all properties when compared to observations, whilst also using the least computing power. This includes not only MAC but SSA, backscatter fraction, hygroscopicity and vertical and horizontal transport. Many of these variables are relatively poorly represented in current models. It remains to be
seen whether models using 2D core/shell parameterisations can generate better agreement than previous schemes for any of these variables, though preliminary results from Matsui et al. (2013) appear promising.

Few realistic alternatives are presented in literature, though some authors have made attempts. Kahnert (2010a) incorporated optics of externally-mixed fractal BC into a climate model, but did not consider mixing or changes of shape. Adachi et al. (2010) used particle shapes observed in Mexico city to calculate a single value of MAC, and calculated radiative forcing using this single, static value. These approaches do not take into account variations in size, shape and mixing that their optical models are capable of, as processes such as mixing and aggregate compaction are very poorly understood, and would be extremely complex to calculate. One credible alternative may be the core-grey-shell model proposed by Kahnert et al. (2013). To demonstrate that any one alternative would be an improvement on current climate models, one would need to demonstrate systematically improved agreement with measured properties. Further observations like those described in this thesis will be required to determine whether or not this is the case.
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