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OPTICAL PROPERTIES OF ATMOSPHERIC AEROSOLS
USING FILTER-BASED ABSORPTION PHOTOMETERS

JOHN BACKMAN

Division of Atmospheric Sciences
Department of Physics
Faculty of Science
University of Helsinki
Helsinki, Finland

Academic dissertation

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Author's Address: Department of Physics
P.O. Box 64
FI-00014 University of Helsinki
john.backman@helsinki.fi

Supervisors: Docent Aki Virkkula, Ph.D.
Finnish Meteorological Institute

Professor Tuukka Petäjä, Ph.D.
Department of Physics
University of Helsinki

Reviewers: Professor Jorma Keskinen, Ph.D.
Department of Physics
Tampere University of Technology

Docent Jorma Joutsensaari, D.Sc. (Tech.)
Department of Applied Physics
University of Eastern Finland

Opponent: John A Ogren, Ph.D.
Earth System Research Laboratory
National Oceanic and Atmospheric Administration

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John Carl Gustav Backman
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Abstract

Aerosol particles are part of the Earth's climatic system. Aerosol particles comprise a minute amount of aerosols by volume. However, aerosol particles can significantly impact the climate. The ability of aerosol particles to do so depends mainly on the size, concentration and chemical composition of the particles. Aerosol particles can act as cloud condensation nuclei (CCN) and can therefore mediate cloud properties. Aerosol–cloud interactions can extend the lifetime of clouds and make them brighter. Aerosol particles can thus perturb the energy balance of the Earth through clouds. Aerosol particles can also directly interact with solar radiation through scattering, absorption, or both. The climatic implications of aerosol–radiation interactions depend on the Earth's surface properties and the amount of light-scattering in relation to light absorption as well as how the particles are spread throughout the atmosphere. Light absorbing aerosol particles, in particular, can alter the vertical temperature structure of the atmosphere and inhibit the formation of convective clouds. The net change in the energy balance imposed by perturbing agents, such as aerosol particles, results in a radiative forcing. Globally, aerosol particles have a net cooling effect on the climate, but, not necessarily on a local scale.

Accurate measurements of the optical properties of aerosol particles are needed to estimate the climatic effects of aerosols. A widely used means of measuring light absorption by aerosol particles is to use a filter-based measurement technique. The technique is based on light-transmission measurements through the filter when the aerosol sample is drawn through the filter and particles deposit onto the filter. As the sample deposits, it will inevitably interact with the fibres of the filter and the interactions needs to be taken into account. This thesis investigates different approaches to dealing with filter-induced artefacts and how they affect aerosol light absorption using this technique. The study highlights that different methods for deriving light-absorption using the technique can lead very different outcomes. Moreover, different data treatment methods can be a source of uncertainties when comparing the spectral dependence of light absorption by aerosol particles when using the technique.

In addition, the articles included in the thesis report aerosol optical properties at sites that have not been reported in the literature before. The locations range from an urban environment in the city of São Paulo, Brazil, an industrialised region of the South African Highveld, to a rural station in Hyytiälä in Finland. In general, it can be said that sites that are distant from urban areas tend to scatter more light in relation to light absorption. In urban areas, the aerosol particle optical properties show the aerosol particles to be darker.

Keywords: atmospheric aerosol particles, aerosol optical properties, aerosol light absorption, aerosol light scattering, filter-based absorption measurements, Ångström exponents

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Nomenclature

Symbol	Explanation
σ_{AP}	Light absorption by aerosol particles (m^{-1})
σ_{SP}	Light scattering by aerosol particles in all directions (m^{-1})
σ_{EP}	The sum of light scattering and absorption by aerosol particles known as light extinction (m^{-1})
σ_{BSP}	Light scattering by aerosol particles back towards the light source known as hemispheric backscattering (m^{-1})
AOD	Aerosol optical depth – a measure of how much light is obscured by atmospheric aerosol particles (unitless)
σ_0	Uncorrected absorption coefficient i.e. without considering filter-induced artifacts (m^{-1})
b	Hemispheric backscatter fraction – the amount of light scattered backwards divided by the light scattered in all directions σ_{BSP}/σ_{SP} (unitless)
β	Up-scatter fraction – the amount of light scattered back into space by aerosol particles (unitless); b and β are related, but there is no one-to-one relationship between them
Q	Efficiency factor by which aerosol particles interact with light in relation to their physical size used in Mie formalism (unitless)
x	Size parameter that describes aerosol particle size in relation to the wavelength of light used in Mie formalism (unitless)
m	Complex index of refraction and absorption.
AAE, α_{AP}	Absorption Ångström exponent describing the spectral dependence of light absorption by aerosol particles (unitless)
SAE, α_{SP}	Scattering Ångström exponent describing the spectral dependence of light absorption by aerosol particles (unitless)
MAC	Mass absorption cross-section – the amount of light absorption divided by the mass of the absorbing material ($m^2 g^{-1}$)
SSA, ω_0	Single-scattering albedo – a measure of the darkness of aerosol particles (unitless): 0=black and 1=white
EBC	Mass concentration of light-absorbing matter determined by optical means and a presumed MAC ($g m^{-3}$)
Tr	Transmission of light through a filter (unitless)
s	Scattering correction factor. The factor compensates for light scattering by the aerosol that is interpreted as absorption by the instrument; known as apparent absorption.

List of Publications

The thesis consists of an introductory review, followed by five research articles. In the introductory part, these papers are cited using roman numerals. All the papers included in this thesis are reprinted under the Creative Commons License.

- I. Backman, J., Virkkula, A., Petäjä, T., Aurela, M., Frey, A., and Hillamo, R.: Impacts of volatilisation on light scattering and filter-based absorption measurements: a case study, *Atmos. Meas. Tech.*, 3, 1205–1216, 10.5194/amt-3-1205-2010, 2010.
- II. Backman, J., Virkkula, A., Vakkari, V., Beukes, J. P., Van Zyl, P. G., Josipovic, M., Piketh, S., Tiitta, P., Chiloane, K., Petäjä, T., Kulmala, M., and Laakso, L.: Differences in aerosol absorption Ångström exponents between correction algorithms for a particle soot absorption photometer measured on the South African Highveld, *Atmos. Meas. Tech.*, 7, 4285–4298, 10.5194/amt-7-4285-2014, 2014.
- III. Backman, J., Rizzo, L. V., Hakala, J., Nieminen, T., Manninen, H. E., Morais, F., Aalto, P. P., Siivola, E., Carbone, S., Hillamo, R., Artaxo, P., Virkkula, A., Petäjä, T., and Kulmala, M.: On the diurnal cycle of urban aerosols, black carbon and the occurrence of new particle formation events in springtime São Paulo, Brazil, *Atmos. Chem. Phys.*, 12, 11733–11751, 10.5194/acp-12-11733-2012, 2012.
- IV. Virkkula, A., Backman, J., Aalto, P. P., Hulkkonen, M., Riuttanen, L., Nieminen, T., dal Maso, M., Sogacheva, L., de Leeuw, G., and Kulmala, M.: Seasonal cycle, size dependencies, and source analyses of aerosol optical properties at the SMEAR II measurement station in Hyytiälä, Finland, *Atmos. Chem. Phys.*, 11, 4445–4468, 10.5194/acp-11-4445-2011, 2011.
- V. Laakso, L., Vakkari, V., Virkkula, A., Laakso, H., Backman, J., Kulmala, M., Beukes, J. P., van Zyl, P. G., Tiitta, P., Josipovic, M., Pienaar, J. J., Chiloane, K., Gilardoni, S., Vignati, E., Wiedensohler, A., Tuch, T., Birmili, W., Piketh, S., Collett, K., Fourie, G. D., Komppula, M., Lihavainen, H., de Leeuw, G., and Kerminen, V.-M.: South African EUCAARI measurements: seasonal variation of trace gases and aerosol optical properties, *Atmos. Chem. Phys.*, 12, 1847–1864, 10.5194/acp-12-1847-2012, 2012.

1 Introduction

The inherent properties of atmospheric aerosol particles affect the radiative budget of the Earth and thus make them a part of the climatic system (Haywood and Shine 1995, Haywood and Boucher 2000, Lohmann et al. 2010). The inclusion of aerosol particles in climate models is of profound importance in the quest to predict climate sensitivity and future climate scenarios (Shindell et al. 2009). Aerosol—cloud interactions remain one of the great uncertainties in future climate predictions, and the full extent of anthropogenic climate perturbations is not certain (Lohmann et al. 2010). Aerosol particles are even known to affect the hydrological cycle (Ramanathan et al. 2001, Lohmann and Feichter 2005). Moreover, aerosol particles are known to affect human health and mortality (Nel 2005, Pope and Dockery 2006).

The physical and chemical properties of aerosol particles determine the particles' behaviour in the atmosphere. The heterogeneity of atmospheric aerosols makes climatic predictions a major challenge for the scientific community. Perturbing agents, such as aerosol particles, which affect the instantaneous net radiative balance of the atmosphere, impose radiative forcing (RF). The more recently introduced effective radiative forcing (ERF, IPCC 2013) includes rapid adjustments imposed by the perturbing agent, rather than instantaneous perturbations. Aerosol particles are important for the microphysical processes of cloud formation, because they can act as cloud condensation nuclei (CCN, Andreae and Rosenfeld 2008). The ability of aerosol particles to do so depends greatly on the size and to a certain degree on the chemical composition of the particles (Dusek et al. 2006, Hudson 2007, Andreae and Rosenfeld 2008, Zhang et al. 2008, Pöschl et al. 2010). An abundance of CCN can modify cloud properties by decreasing cloud droplet size, and consequently, increasing atmospheric lifetime of clouds, suppressing precipitation, and making clouds more reflective (Rosenfeld 2000, Andreae and Rosenfeld 2008). CCN-mediated cloud properties alter the Earth's radiative balance and are referred to as aerosol-cloud interactions (aci) of the ERF; in conjunction ERF_{aci} (IPCC 2013).

Furthermore, aerosol—radiation interactions (ari) can alter the radiative balance directly by scattering and absorbing incoming solar radiation (Haywood and Boucher 2000, Andreae et al. 2005, Ramanathan et al. 2007b, Stier et al. 2007, Lohmann et al. 2010, IPCC 2013). This direct interaction with radiation is referred to as 'ERF_{ari}' (IPCC 2013). Light scattering, absorption, or both, will reduce the incoming solar radiation at the surface (e.g. Ramanathan et al. 2001, Satheesh et al. 2010). An aerosol particle-laden layer of strongly light-absorbing particles will absorb solar radiation that is converted into heat, and thus perturbs the temperature of the layer. A redistribution of energy by a strongly absorbing aerosol layer can inhibit the formation of convective clouds (Koch and Del Genio 2010). Furthermore, strongly light absorbing particles can rapidly adjust the temperature profile of the atmosphere (IPCC 2013).

Much attention has been paid to 'black carbon' (BC) aerosol particles, which originate from incomplete combustion. Over the last decade the focus has shifted from a pollution perspective to the role BC plays in the Earth's climate (Hansen et al. 2000, Jacobson 2000, Jacobson 2001, Bond et

al. 2013). The interest in atmospheric BC has grown considerably since the climatic relevance of BC aerosol particles was recognised (Moosmüller et al. 2009, Bond et al. 2013, IPCC 2013). BC is the most potent particulate absorber of light in the atmosphere, although mineral dust and some organics also contribute to light absorption in the atmosphere. BC is the second most potent radiative forcing agent, second only to carbon dioxide (Bond and Bergstrom 2006, Ramanathan and Carmichael 2008, Bond et al. 2013). In addition, naturally occurring wildfires and wind-driven suspension of mineral dust are also sources of light-absorbing aerosol particles. In addition to BC aerosols that are black in appearance, species exist that absorb light predominantly at the lower end of the visible spectrum and appear brown, giving rise to the term brown carbon (BrC, Andreae and Gelencsér 2006, Sun et al. 2007). However, not all organic carbon (OC) absorbs light and therefore scatters light instead. Sulphates and nitrates scatter light too and they are common aerosol particle constituents (Pöschl 2005, Jimenez et al. 2009). These light-scattering species counteract the impact of positive radiative forcers since they have a negative net ERF (e.g. Charlson et al. 1992, Tang 1996, Andreae et al. 2005).

Aerosol particle optical properties are wavelength-dependent. This dependency is often described by a simple power law relationship where light scattering, light absorption, or both (known as light extinction), or aerosol optical depth (AOD) vary with the wavelength. The exponent in the formula used to describe the wavelength dependency is called the Ångström exponent, here AE. It was named after the Swedish scientist Anders Ångström, who noticed that the wavelength dependence of AOD followed such a formula (Ångström 1929). More specifically, absorption Ångström exponents (AAE) can be used as a proxy for the chemical composition of the absorbing particulate species (Bergstrom et al. 2007). The light-scattering Ångström exponent (SAE) relates to the size distribution of aerosol particles (Bohren and Huffman 1998, Schuster et al. 2006). Thus, AEs provide additional information about the aerosol that can be retrieved from satellite data (e.g. Eck et al. 1999, Russell et al. 2010, Bréon et al. 2011, Moosmüller and Chakrabarty 2011).

Ground-based in situ measurements of aerosol light absorption have often been conducted using filter-based absorption photometers such as the Aethalometer (Hansen et al. 1984, Weingartner et al. 2003), the particle soot absorption photometer (PSAP, Bond et al. 1999, Virkkula et al. 2005) and the multi-angle absorption photometer (MAAP, Petzold and Schönlinner 2004, Petzold et al. 2005). These instruments can provide a high temporal resolution. Thus the dynamic processes that aerosol particles are subject to can be derived by ground-based measurements. However, as for all measurements, filter-based absorption measurements are associated with uncertainties (Müller et al. 2011a). A global assessment of the extent of the climatic impact of light-absorbing aerosol particles is uncertain, although there is a scientific consensus on a net warming effect (Bond et al. 2013). Accurate measurements of both light absorption and light scattering by aerosol particles are needed to estimate the climate impact they impose on a global and regional scale (Mishchenko et al. 2004, Bond et al. 2009).

The objectives of this thesis are to contribute to the knowledge of key aerosol particle optical properties at different locations using ground-based in situ measurements. This includes exploring the possible causes and effects of the observations. In science, the practice is to scrutinise methods and facts continuously. This practice is also part of the thesis, in particular with emphasis on the widely used method of filter-based absorption photometers. Filter-based absorption measurements are a widely used technique to determine the amount of light absorption by aerosol particles. Apart from the objectives above, this thesis comprises the following individual goals:

- to determine the characteristics and features of the optical properties of aerosol particles at previously unreported locations, including a rural site in southern Finland, an industrialised region in South Africa and the megacity of São Paulo (**Paper I–V**);
- to investigate the features of submicron aerosol in a megacity that extensively uses bioethanol as a vehicle fuel (**Paper III**);
- to improve our understanding of the uncertainties associated with filter-based absorption measurements (**Paper I and II**).

2 Background and physical concepts

2.1 Aerosol size distributions and chemical composition

Size is the most fundamental property of an aerosol particle and there is always a distribution of differently sized particles in the atmosphere. Size determines the dynamics of aerosol particles, how they interact with light, and whether they can act as CCN (Heintzenberg 1989, Andreae and Rosenfeld 2008, Moosmüller et al. 2009). Aerosol particles are larger than the molecules of air that suspend them and small enough to be suspended without being quickly removed by gravitational settling. Thus aerosol particles range in size from a nanometer to roughly 100 μm . Particles with a size of less than 1 μm are classified as fine-mode particles, whereas larger particles are classified as coarse-mode particles (Seinfeld and Pandis 2006). The fine mode can be further divided into a cluster mode (1–3 nm), a nucleation mode (3–25 nm), an Aitken mode (25–100 nm), and an accumulation mode (100–1000 nm) (Kulmala et al. 2001, Seinfeld and Pandis 2006, Kulmala et al. 2007, Kulmala et al. 2012). This division is made because the different modes are governed by different physical processes. The fine and coarse modes comprise aerosol particles with different origins. Atmospheric aerosols can be introduced into the atmosphere directly as particles called primary aerosol particles; they are not formed in the atmosphere. Secondary aerosol particles, however, are formed in the atmosphere from gas-phase precursors.

The anthropogenic sources of primary aerosol particles are vehicles and industries which emit soot, metals and organics into the atmosphere, and they reside mostly in the fine-mode size range. In addition, construction and agriculture can introduce soil into the atmosphere, mostly as coarse-mode aerosol particles. There are also naturally occurring primary aerosol particles. Arid regions are

sources of wind-driven suspension of desert dust and vegetation debris, forested areas are sources of biogenic material such as pollen, and breaking waves produce sea-salt aerosols, not to mention the volcanic ash that a volcanic eruption can introduce. All of these are predominantly coarse-mode aerosol particles (e.g. Koçak et al. 2007, Cozic et al. 2008, Petäjä et al. 2012). A natural source of primary aerosol particles in the fine-mode range is smoke from wildfires containing soot and organics.

Anthropogenic emissions of precursor gases for secondary aerosol particles come from vehicular emissions, industry and agriculture. Natural emissions of secondary aerosol particle precursors are volatile organic compounds (VOCs) and their oxidation products from plants (Ehn et al. 2014) and dimethyl sulphide from marine phytoplankton (Andreae and Crutzen 1997). Secondary aerosol particles, since they are formed in the atmosphere, start from the very smallest of aerosol particles and scarcely ever reach the size range of the coarse mode simply by coagulation and condensation (Kulmala et al. 2007, Kulmala et al. 2013). There is little mass exchange between the fine and coarse mode (Hinds 1999).

Different processes govern the behaviour and fate of aerosol particles in the atmosphere and depend on particle size and the chemical composition of the particles. The fate of coarse-mode aerosols is governed by how efficiently the particles are removed by gravitational settling and dry deposition, and to some extent scavenged by precipitation. Fine-mode aerosols are more intricate by nature (Heintzenberg 1989). The atmospheric processes of fine-mode aerosols include gas-to-particle conversion of vapours, coagulation, cloud processing, and wet and dry deposition (Fenton et al. 1980, Raes et al. 2000, Andreae and Rosenfeld 2008, Kroll and Seinfeld 2008).

Aerosol particles suspended in air are not stationary, even though they get transported with the air movement, because they are subject to Brownian motion and diffusion in the suspended gas (Hinds 1999, Seinfeld and Pandis 2006). As particle size increases, so Brownian motion decreases, and consequently so does the diffusivity of the particles in air. Both the nucleation and Aitken mode will coagulate with each other (and larger particles) due to Brownian motion and concurrently the total number of suspended particles will decrease, assuming that no additional particles are introduced. Particles that have grown into the accumulation mode regime are often the result of cloud processing and heterogeneous chemistry (Hoppel et al. 1986, Jacob 2000, Andreae and Rosenfeld 2008). CCN activated particles will acquire additional aerosol mass through the aqueous phase chemistry of water soluble gases within the cloud drop, in particular between acids and the base ammonia to form inorganic salts (e.g. ammonium nitrate and ammonium sulphate). Through cloud processing, particles will accumulate in the accumulation mode where removal processes are weak (Raes et al. 2000).

Secondary aerosol particles can form in the atmosphere from precursor vapours through gas-to-particle conversion processes (e.g. Kulmala et al. 2004, Kulmala et al. 2014). The formation of secondary aerosol particles requires precursor gases that can form low enough vapour pressure species in abundance. The initial steps in the formation of secondary aerosol particles involve the clustering of oxidised vapours that nucleate or form kinetically (Vehkamäki and Riipinen 2012,

Kulmala et al. 2014). Recent advances in the understanding of the process have found that, in addition to sulphuric acid, low-volatile oxygenated organic compounds and acid-stabilising agents such as ammonia and amines are important for the formation of cluster-sized particles (Sipilä et al. 2010, Almeida et al. 2013, Schobesberger et al. 2013, Ehn et al. 2014, Riccobono et al. 2014). In addition to the formation of new particles, the evolution of gas-phase precursors can — through various pathways — make pre-existing aerosol particles gain secondary aerosol mass (Zhang et al. 2000, Kroll and Seinfeld 2008, Hallquist et al. 2009). Secondary organic aerosol (SOA) is a substantial constituent of the ambient aerosol particle and forms through gas-to-particle conversion processes in the atmosphere (Hallquist et al. 2009).

Soot particles consist of almost pure carbon spherules (10–50 nm in size) made of graphene layers that form agglomerates immediately after combustion (Andreae and Gelencsér 2006, Bond and Bergstrom 2006). Soot particles that enter the atmosphere as primary aerosol particles are initially externally mixed with the pre-existing aerosol. Soot will then gradually start to mix with the aerosol through coagulation, and will gain secondary aerosol mass through condensation (Saathoff et al. 2003, Moffet and Prather 2009, Khalizov et al. 2013). This will result in a change of the mixing state of the soot aerosol from externally mixed to internally mixed and the fractal like structure of fresh soot will collapse (Mikhailov et al. 2006, Zhang et al. 2008). Since soot aerosol is the most potent absorber in the visible spectrum, the mixing with other particles — predominantly non-absorbing — will change the optical properties of the aerosol particles and thus their climatic implications (Jacobson 2001, Lack and Cappa 2010).

The nomenclature associated with strongly light absorbing 'black carbon' (BC) aerosols has been debated in the literature and is not always congruent (Andreae and Gelencsér 2006, Bond and Bergstrom 2006, Bond et al. 2013, Petzold et al. 2013). As pointed out by Petzold et al. (2013), the classification of carbonaceous species is not a straightforward task since it would require multiple properties of the constituent to be determined concurrently, which is not feasible with a single instrument. Thus the determination of BC is inevitably related to the instrument (or instruments). For BC determined by optical means, the term equivalent black carbon (EBC) has been devised to avoid confusion with other methods of determining BC (Andreae and Gelencsér 2006, Petzold et al. 2013). Soot, which is black in appearance, is used here to refer to particles that originate from incomplete combustion of carbon containing fuels, and thus refers to the process through which the particles were formed (Petzold et al. 2013). Hence the optical properties of soot can vary depending on the combustion process through which they were formed.

Soot is an important aerosol constituent in the sub-micron range and abundant in urban areas (e.g. Putaud et al. 2004, Wang et al. 2006). In addition to soot, sulphates, nitrates, ammonium and many organics constitute the total suspended particulate matter (Jimenez et al. 2009). Of these constituents, soot is the most refractory (heat resistant) component. Inorganic particulate salts, such as ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$, ammonium bisulphate NH_4HSO_4 , and ammonium nitrate NH_4NO_3 are volatile by nature (Jacob 2000, Tiitta et al. 2010). Moreover, the reaction that forms NH_4NO_3 is reversible and, therefore, depends on the relative abundance of the individual gas phase

components that produce particulate NH_4NO_3 . Thus a change in the concentrations of the precursors (nitric acid HNO_3) and ammonia (NH_3) can cause particulate NH_4NO_3 to evaporate (Meng et al. 1997). A general feature of inorganic salts is that they do not absorb light in the visible spectrum, whereas some organics (not all) can absorb light at the lower end of the visible spectrum and in the ultraviolet (UV) region (Jacobson 1999).

2.2 Aerosol optical properties

2.2.1 Essential optical properties of aerosol particles for estimating direct radiative forcing

Atmospheric aerosol particles are a highly heterogeneous mixture of different species that differ in shape, size and chemical composition. Moreover, a single particle need not be composed of a single constituent but comprises a number of optically different species. Therefore, the optical properties of an aerosol particle ensemble are the result of a complex mixture of particles all contributing to the optical properties of the particles.

A beam of light that traverses a volume filled with aerosol particles is subject to light scattering and absorption by the particles, in addition to light scattering and absorption by gas molecules. The amount of light that is removed from the beam either through, absorption, scattering, or both (referred to as light extinction) is described by the Bouguer–Lambert–Beer law

$$I_p = I_i e^{-\sigma_{EP}(\lambda)L} \quad (1)$$

where σ_{EP} is the particle light extinction coefficient (in units of m^{-1}), λ is the wavelength of light and L is the path length in metres (Perrin 1948, Seinfeld and Pandis 2006). The beam intensity will drop from I_i to I_p ; the subindexes represent incident and passed intensities, respectively. In Eq. (1), σ_{EP} can be substituted by σ_{SP} and σ_{AP} to give the light scattering and light absorption coefficients of aerosol particles, respectively. In this thesis, light scattering coefficients have been measured with an instrument called a Nephelometer. The light absorption coefficients presented in this thesis were measured with different types of filter-based absorption photometers. Both the Nephelometer and the different types of absorption photometers will be discussed in more detail further on in the text. The coefficients are often expressed Mm^{-1} , which is $10^6 \text{ m}^{-1} = \text{Mm}^{-1}$, and thus circumvents writing out powers of ten. The light extinction coefficient is directly related to atmospheric visibility (Koschmieder 1925).

The amount of light scattering by aerosol particles can further be divided into light scattering in a backward direction to yield the hemispheric backscattering (σ_{BSP}), which is light scattered at angles of 90° – 180° (Fig. 1). There are commercially available Nephelometers that are able to measure both hemispheric back-scattering by aerosol particles and light scattering by the particles in all directions (σ_{SP}). The ratio between light scattered in a backward direction and light scattered in all directions gives the hemispheric back-scatter fraction as

$$b(\lambda) = \frac{\sigma_{\text{BSP}}(\lambda)}{\sigma_{\text{SP}}(\lambda)}. \quad (2)$$

Furthermore, the parameter b can be used in radiative transfer calculations to estimate the impact of the aerosol aerosol particles on the radiative forcing (e.g. Marshall et al. 1995, Andrews et al. 2006). The figure illustrates how differently sized particles scatter visible light in different directions. A 10 nm particle scatters visible light in equal amounts in a forward and backward direction. For larger particles (200 and 1000 nm), this is no longer the case.

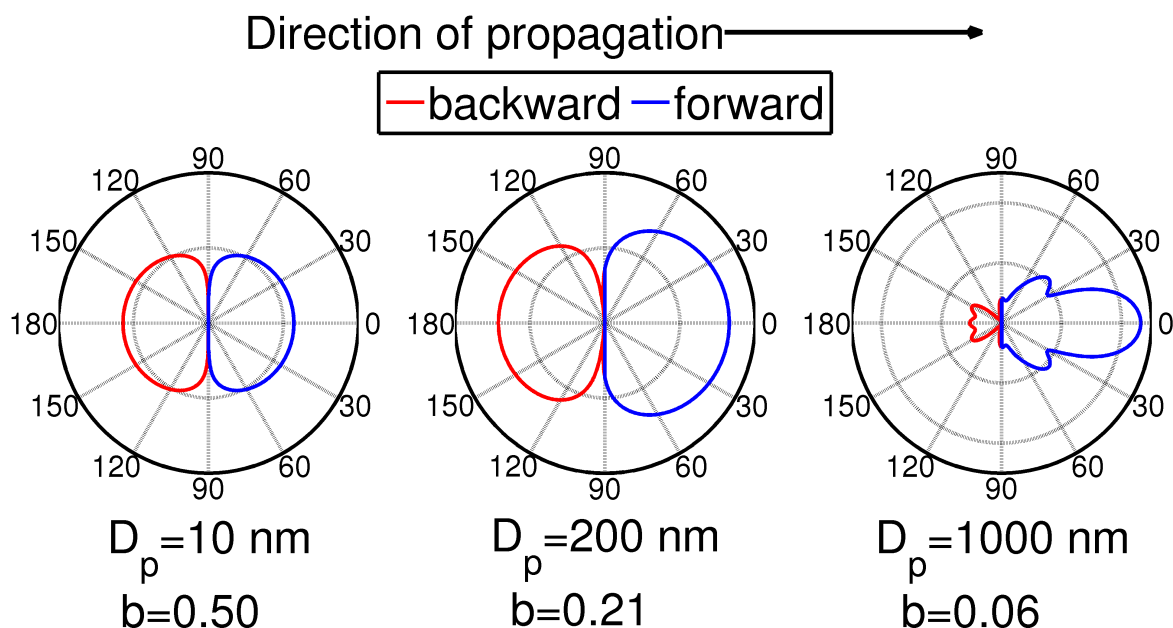


Figure 1: Illustration of hemispheric back-scatter fractions for differently sized particles; light propagates from left to right. For clarity, the figure depicts parallel polarised light calculated using the Mie codes of Mätzler (2002) and a refractive index $m=1.521+i0.02$ at a wavelength of 550 nm.

Radiative transfer calculations also require the aerosol–radiation interactions of the whole atmospheric column — from the surface to the top-of-atmosphere (TOA) — given as

$$AOD(\lambda) = \int_0^{\text{TOA}} \sigma_{EP}(\lambda, z) dz. \quad (3)$$

The integral will yield the unitless aerosol optical depth (AOD, Kokhanovsky 2008). The higher the AOD the more the aerosol interacts with incident radiation and the less radiation reaches the surface.

An important parameter for the radiative forcing potential of aerosol particles is the single-scattering albedo (SSA, Seinfeld and Pandis 2006). The SSA is the fraction of light scattered by the aerosol in relation to light extinction as

$$\text{SSA}(\lambda) = \frac{\sigma_{\text{SP}}(\lambda)}{\sigma_{\text{EP}}(\lambda)} = \frac{\sigma_{\text{SP}}(\lambda)}{\sigma_{\text{AP}}(\lambda) + \sigma_{\text{SP}}(\lambda)}. \quad (4)$$

In other words, the SSA is a measure of the darkness of the aerosol. An SSA of unity means that all of the light extinction is only due to light scattering, whereas an SSA of zero means that all light extinction is due to light absorption alone. However, SSA values that are close to zero are in practice encountered when particles are much smaller than the wavelength of light (Moosmüller et al. 2009).

As discussed above, both light scattering and absorption by aerosol particles depend on the wavelength of light. The wavelength dependency is expressed in terms of the so-called Ångström exponent (AE) by a power-law relationship as $\text{AOD}(\lambda) = K\lambda^{-\text{AE}}$ (Ångström 1929). The Ångström exponent can also be calculated from light scattering, absorption or extinction coefficients as

$$\sigma(\lambda) = K\lambda^{-\text{AE}} \quad (5)$$

to give the scattering Ångström exponent (SAE), absorption Ångström exponent (AAE) and extinction Ångström exponent (EAE), respectively (Schuster et al. 2006, Moosmüller et al. 2009, Moosmüller et al. 2011). The constant K is the approximated AOD at a wavelength of 1 μm , known as the turbidity of the aerosol (Schuster et al. 2006).

The essential parameters governing the aerosol–radiation interactions of aerosols for an optically thin atmosphere can be summarised in one equation as the radiative forcing efficiency (i.e. the radiative forcing ΔF per unit of AOD)

$$\frac{\Delta F}{\text{AOD}} = -DS_0T_{\text{at}}^2(1 - A_c)\text{SSA}\beta \left[(1 - R_s)^2 - \left(\frac{2R_s}{\beta} \right) \left[\left(\frac{1}{\text{SSA}} \right) - 1 \right] \right] \quad (6)$$

(Sheridan and Ogren 1999). In the equation above, D is the daylight fraction, S_0 the solar constant, T_{at} the atmospheric transmissivity, A_c the cloud cover fraction, R_s the surface reflectance (or surface albedo), and β the average up-scatter fraction. The equation only takes into account the effect of aerosols under clear sky conditions and assumes all aerosol particles are in the atmospheric boundary layer. Furthermore, the atmospheric transmissivity is the transmissivity of the overlaying atmosphere excluding aerosol particles, whereas the up-scatter fraction is the up-scatter fraction of aerosol particles (Charlson et al. 1991). The up-scatter fraction is a function of the solar zenith angle (θ_0) so that $\beta(\theta_0=0^\circ) = b$ and is related to the back-scatter fraction (see Fig. (1), Wiscombe and Grams 1976, Seinfeld and Pandis 2006). The up-scatter fraction can be estimated from b although there is not a one-to-one relationship between β and b (Marshall et al. 1995). Thus Eq. (6) depends on the light scattering, and absorption of the aerosol through the SSA, and the magnitude of the forcing through the AOD. Although still wavelength-dependent, both SSA and β are not explicitly expressed as functions of wavelength in Eq. (6) and calculations require spectral weighing (Haywood and Shine 1995).

The critical SSA (SSA_c), where the radiative forcing efficiency changes sign (at $\Delta F/\text{AOD}=0$), is a function of β and R_s and can be solved from Eq. (6). Figure (2) depicts a combination of parameters

at which the radiative forcing changes from net cooling to net warming, as given by Haywood and Shine (1995). Over a dark surface (R_s is low), the aerosol is more likely to act as a cooling agent than over bright surfaces. Over bright surfaces, such as sea ice and fresh snow, the range in which the aerosol has a cooling effect becomes narrower as the surface reflectance increases. Thus accurate measurements of both light scattering and absorption are needed to correctly assess the implication of the aerosol, especially in polar regions.

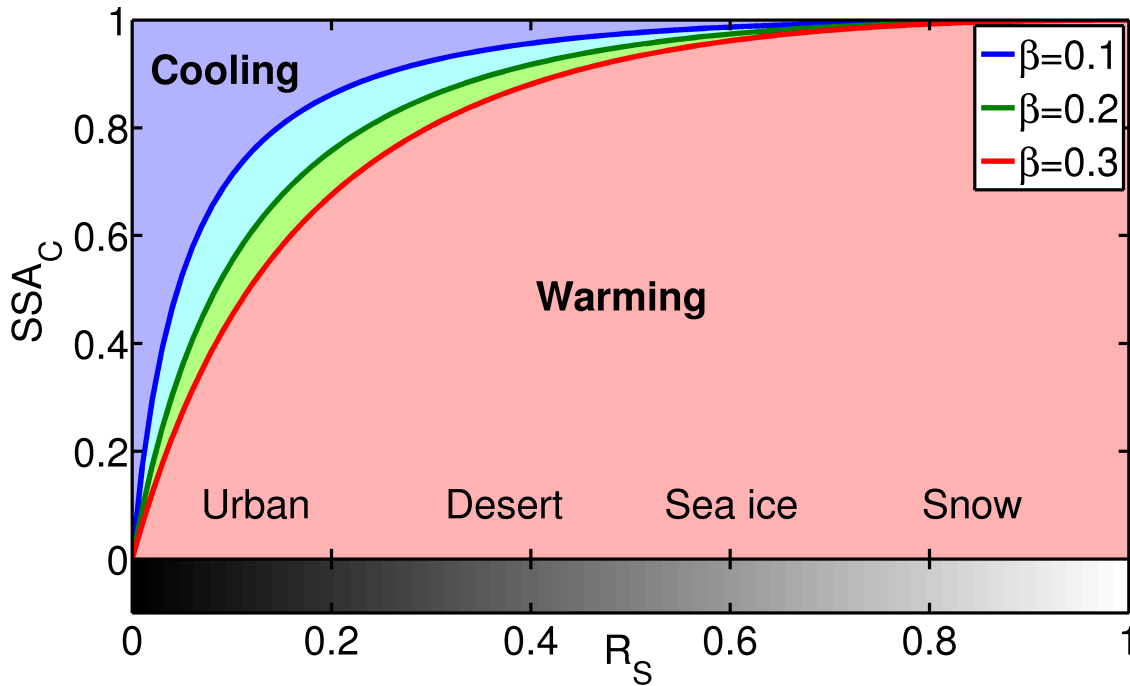


Figure 2: Critical single-scattering albedo (SSA_C) as a function of surface reflectance (R_s) for a range of up-scatter fractions (β) as given by Haywood and Shine (1995).

2.2.2 Size dependence of aerosol particle optical properties

In this section some basic optical properties of single particles are described since they are useful in understanding the optical properties of aerosol populations, i.e. aerosol particle number size distributions. It also should be emphasised that all particles here are treated as spheres even though in nature particles exist in numerous different shapes (e.g. Kokhanovsky 2008, Kahnert and Rother 2011). For spherical particles or layered spheres analytical solutions can be applied to derive the scattering, absorption and extinction of light (Liou 1977, Bohren and Huffman 1998). The approximation and analytical solutions yield the Mie formalism (or Mie theory), which provides a means to describe the general features of how aerosol particles interact with light (e.g. Barber and Hill 1990, Bohren and Huffman 1998). In this section, the size dependence of aerosol optical properties are shown using Mie formalism.

Aerosol particles interact differently with visible light depending on particle size and the wavelength of light. Following Mie formalism, the efficiency (Q) by which a particle interacts with

light is expressed in terms of the ratio between optical cross-section (C) and the geometrical cross section, which for a spherical particle with a diameter (D_p) is given by

$$Q_{EP} = \frac{4C_{EP}}{\pi D_p^2}. \quad (7)$$

The extinction cross-section C_{EP} can be substituted with the scattering (C_{SP}) or absorption (C_{AP}) cross-section to yield the scattering and absorption efficiencies Q_{SP} and Q_{AP} , respectively. These efficiencies are measures of the ability of particles to scatter and absorb light in relation to their physical size.

For spherical particles, a scale-invariant size parameter (x) describes how a particle interacts with incident light of wavelength λ as $x = \pi D_p / \lambda$ (Bohren and Huffman 1998). The unitless size parameter x is often used to distinguish between three different regimes of aerosol optics. Particles that are much smaller than the wavelength of light ($x \ll 1$) interact with light in the Rayleigh regime (Young 1982, Moosmüller and Arnott 2009). When particles are roughly the same size as the wavelength of light ($x \approx 1$), this is referred to as the Mie (or resonance) regime (Bohren and Huffman 1998). For larger particles ($x \gg 1$), the interaction with light follows geometrical optics, hence is called the geometric regime.

The computation of particle properties using Mie formalism requires knowledge of the complex refractive index $m = n + ik$ (e.g. Bohren and Huffman 1998). The real and imaginary part of m represents the non-absorbing and absorbing components of the particle, respectively. Thus, in a medium with m that is equal to n , no absorption will take place. It should be noted that the complex refractive index of the aerosol particles is likely to be different in different size ranges. For clarity, a constant complex refractive index is used here.

To illustrate which particle sizes are responsible for light scattering, a scattering size distribution can be calculated for particles with a diameter D_p as

$$\frac{d\sigma_{SP}}{d\log D_p} = Q_{SP}(\lambda, D_p, m) \frac{\pi D_p^2}{4} \frac{dN}{d\log D_p}, \quad (8)$$

if the complex refractive index of the particles are known. The term $\pi D_p^2/4$ of Eq. (8) is the cross section of a spherical particle. The amount of total light scattering is the integral of Eq. (8). Moreover, light absorption and extinction by particles can be calculated using Eq. (8) by substituting Q_{SP} with Q_{AP} and Q_{EP} , respectively.

Depicted in Fig. (3a) are Q_{SP} and Q_{AP} , a particle number size distribution (Fig. 3b) and the corresponding scattering size distribution (Fig. 3c) calculated using Mie codes by Mätzler (2002). The figure shows that particles in the Rayleigh regime neither efficiently scatter nor absorb light (Fig. 3a). In the scattering size distribution of Fig. (3c), the nucleation mode is shown to have little influence on the total scattering. However, in the Mie and geometric regime, the situation is very different. In the Mie and geometric regime — due to the physical size of the particle — mutual constructive and destructive interference of internal wavelets (individual scatterers) increases and

appears as a resonance pattern seen in Q (Fig. 3a). In the Rayleigh regime, these interactions diminish since the individual scatterers of the particles are in phase (Moosmüller and Arnott 2009).

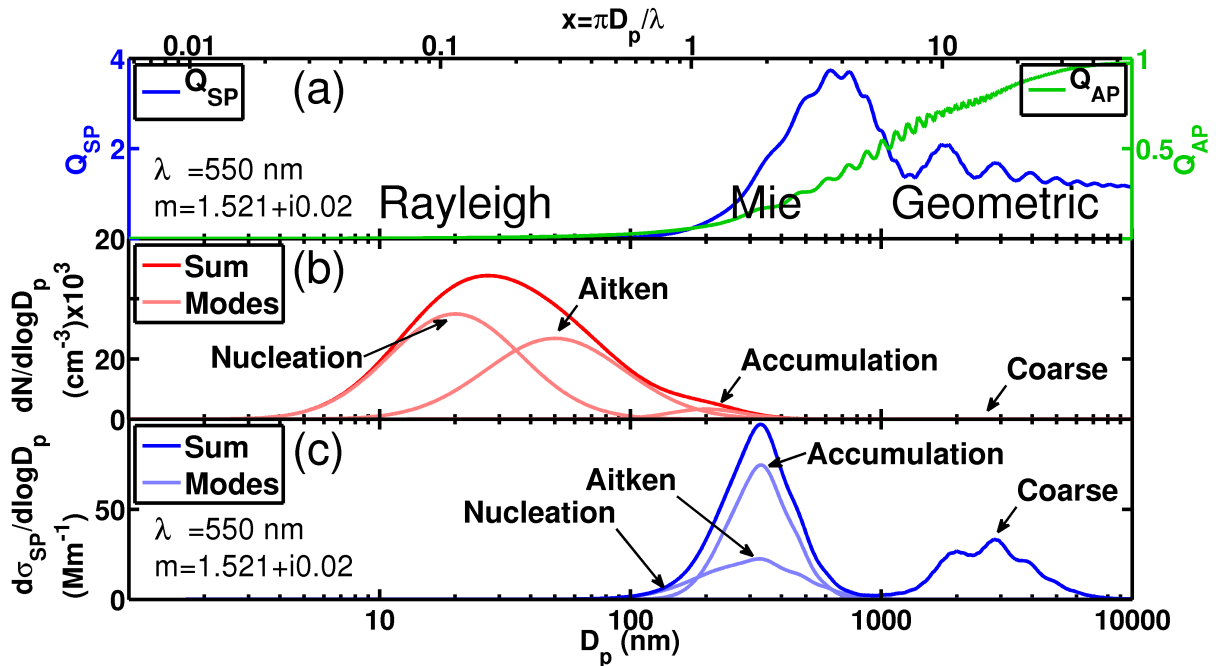


Figure 3: (a) Scattering (Q_{SP}) and absorption (Q_{AP}) efficiencies in the Rayleigh, Mie, and geometric regimes. (b) A typical particle number size distribution in an urban environment (partly from **Paper III**). (c) Scattering size distribution calculated using Eq. (8). The aerosol was given a complex refractive index m of $1.521 + 0.02i$ at a wavelength of 550 nm.

As was shown previously in Fig (1), the hemispheric back-scatter fraction (Eq. 2) is different for different particle sizes. In Fig. (1), the 10 nm particle represents the Rayleigh regime ($x \ll 1$), where light is scattered in equal amounts in a backward and forward direction. The 200 nm particle of Fig. (1) represents the Mie regime ($x \approx 1$). For large particles ($x \gg 1$), most of the light is scattered in the near forward direction and is represented by a particle of 1000 nm which is characteristic of the geometric regime.

The spectral dependence of light scattering by the aerosol is related to particle size. In the Rayleigh regime, the light scattering is proportional to λ^{-4} (Moosmüller and Arnott 2009). This implies that particle scattering in the Rayleigh regime has an SAE of 4; see Eq. (5). In the geometric regime, the wavelength dependency of light scattering will diminish. Therefore, SAE values below unity are indicative of light scattering in the geometric regime.

Light absorption by aerosol particles is a function of particle size, although not in the same way as for light scattering. Of the atmospherically relevant species, soot is the most potent light absorber, and therefore has a high imaginary part of the refractive index in comparison to other species. For small particles ($x \ll 1$), soot particles are volume absorbers whereas large particles ($x \gg 1$) are surface absorbers. In other words, for large soot particles absorption only takes place at the surface of the

particle since light does not fully penetrate into the particles. This behaviour can be shown by introducing the concept of mass absorption cross-section (MAC). The mass absorption cross-section is the light absorption coefficient divided by the mass concentration of the light absorbing material (m_{abs}) as

$$\text{MAC} = \frac{\sigma_{\text{AP}}}{m_{\text{abs}}} \quad (9)$$

The MAC is often expressed in units of $\text{m}^2 \text{g}^{-1}$ (e.g. Seinfeld and Pandis 1998, Moosmüller et al. 2009). When soot particles are volume absorbers, an increase in the mass (and volume) corresponds to an equal amount of increased absorption, thus the MAC remains constant. This changes when light is absorbed only at the surface of large particles, when light does not penetrate the particles fully. Then, light absorption is proportional to the surface area and the mass of the particle is proportional to the volume of the particle. Figure (4) depicts the transition of a strongly absorbing particle, with the imaginary part of the refractive index being 0.67, from a volume absorber to a surface absorber in the size range of 1 nm to 10 μm . A particle density of 1.8 g cm^{-3} was assumed in the figure.

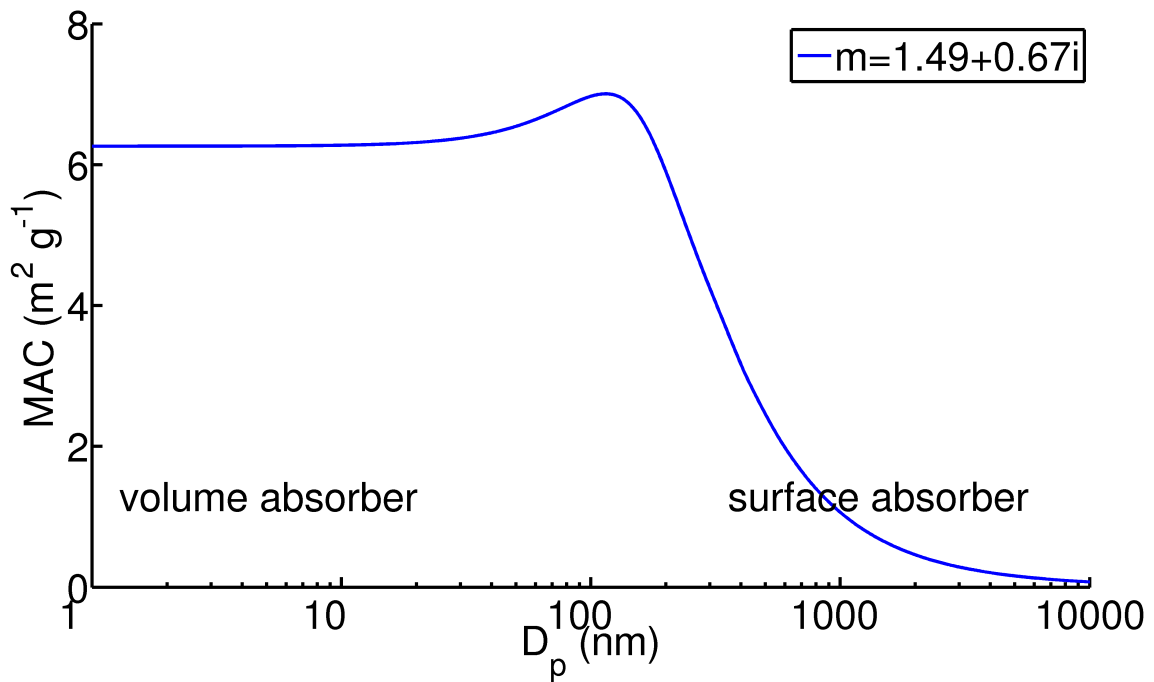


Figure 4: Mass absorption cross section (MAC) of a strongly absorbing spherical particle with a density of 1.8 g cm^{-3} at a wavelength of 550 nm and a refractive index of diesel soot (Schnaiter et al. 2003).

3 Measurements and methods

3.1 Measurement sites

The work included in the thesis was carried out at four different measurement sites on three continents. The demographics and climate of the sites ranged from a scarcely populated rural site to an urban site in a megacity. Of the four sites included in the thesis, the São Paulo site was temporary and was established for the sole purpose of the study, whereas the other sites were long-term measurement sites.

The SMEAR III (Station for Measuring Ecosystem–Atmosphere Relations) station, where the study of **Paper I** was carried out, is located 5 km north-northeast of the city centre of Helsinki. The measurement location is, therefore, a semi-urban location. The station was established in 2004 to extend the SMEAR network to include urban air pollution measurements. The station is a joint undertaking of the University of Helsinki and the Finnish Meteorological Institute. In addition to particulate air pollution related measurements turbulent exchange and meteorological measurements are conducted at the site (Järvi et al. 2009).

The Elandsfontein site of **Paper II** and **Paper V** is located on the South African Highveld in the province of Mpungalunga. The Highveld is an inland plateau with an elevation of 1400 to 1600 metres above mean sea level. The outskirts of the Johannesburg–Pretoria conurbation begin roughly 140 km from the site, to the west-northwest. The area that surrounds the site is home to heavy industry and is considered to be one of the NO₂ pollution hot-spots in the world (**Paper V**, Lourens et al. 2012). There are also several strong air pollution point-sources surrounding the site ranging from mining associated industry such as metallurgical industries, coal-fired power plants, and petrochemical sites. In addition to heavy industry sources, anthropogenic emissions from vehicles and wood burning for domestic uses contribute to the air pollution at the site. There is also a biomass burning season at the end of the dry season which contributes to the air pollution at the site (**Paper V**, Eck et al. 2013).

In **Paper III**, the urban measurement site in São Paulo was a temporary measurement site established for the BIOFUSE (Effects of intensive BIO-Fuel production and USE on regional air quality and global climate) project. The measurement site was located at the University of São Paulo campus area at the western edge of the most densely populated area of São Paulo. The campus area is 7.4 km² and consists of parks and campus buildings. The measurement site was constructed on the roof of a four storey building surrounded by tree canopy at the centre of the campus area. The metropolitan area of São Paulo is home to 20 million inhabitants making it the biggest conurbation in South America. A large proportion of the light-duty vehicular fleet of São Paulo consists of flexible-fuel vehicles which can either run on pure ethanol or gasoline-ethanol mixtures.

The measurements of **Paper IV** were carried out at the SMEAR II site, located in a rural area in south-western central Finland (Hari and Kulmala 2005). The site is surrounded by a coniferous

boreal forest with little settlements within its vicinity. The largest city, with roughly 200 000 inhabitants is located some 60 km from the site. The SMEAR II station has been operated continuously since 1995 to provide a comprehensive and long-term dataset at the ecosystem-atmosphere boundary. The suite of instruments at the site far exceeds those covered by **Paper IV**, which focused on aerosol particle optical properties and how these are related to particle size distributions.

3.2 Instruments

This section describes the key measurement techniques used in the articles of the thesis, their working principles and the associated data processing.

3.2.1 Filter-based absorption photometers

Light absorption by aerosol particles is a key parameter when estimating the effective radiative forcing of aerosol–radiation interactions (ERFari, IPCC 2013). A common method for measuring aerosol light absorption is to measure the reduction of light passing through a fibre filter while aerosol particles deposit onto the filter. These instruments are commonly referred to as filter-based absorption photometers. The working principle of the instrument is fairly straightforward. Artefacts will occur, however, since aerosol–filter interactions are inevitable. This section covers the working principles of the Aethalometer (AE-31, Magee Scientific), the Particle Soot Absorption Photometer (PSAP, Radiance Research), and the Multi-Angle Absorption Photometer (MAAP, Thermo Scientific). Both the Aethalometer (Hansen et al. 1984, Weingartner et al. 2003) and the PSAP (Bond et al. 1999, Virkkula et al. 2005) are multi-wavelength instruments, whereas the MAAP is not (Petzold and Schönlinner 2004).

Light absorption by particles reduces the intensity of the light passing through the filter. The intensity reduction from the initial intensity I_i to the passed intensity I_p can be described by the Bouguer–Lambert–Beer law (Eq. 1). However, the law as such describes the optical properties of the filter and the deposited aerosol as a whole. Moreover, since for most atmospheric monitoring purposes a high temporal resolution is desired, the intensities of Eq. (1) are substituted with the subsequent change in the transmitted intensities. Thus, by this convention, the optical properties of the filter will initially be avoided, and so will the optical depth of the filter. Equation (1) then becomes

$$\sigma_0 = \frac{A}{Q_f \cdot \Delta t} \ln \left(\frac{I_{t-\Delta t}}{I_t} \right) \quad (10)$$

after some rearrangement yielding the uncorrected absorption (σ_0) (Bond et al. 1999, Virkkula et al. 2005). In Eq. (10), the pathlength L has been replaced with the aerosol sample column drawn through the filter where A is the sample spot size, Q_f the flow rate and Δt the time between the subsequent measurements of the transmitted intensities I_t and $I_{t-\Delta t}$ at time t and $t-\Delta t$, respectively. Both the Aethalometer and PSAP relies on Eq. (10).

As is the case for all filter-based absorption measurements, a pristine filter will gradually accumulate deposited aerosol particles and become laden by them. The evolution from a pristine filter to a particle laden one is expressed in terms of filter transmittance $Tr = I_t/I_0$ in the PSAP; I_0 is the light intensity transmitted by a pristine filter and I_t is the light intensity at the time t when aerosols have deposited onto the filter (Virkkula et al. 2005). The Aethalometer expresses the state of the filter in terms of filter attenuation as $ATN = -\ln(I_t/I_0)$ (Weingartner et al. 2003). This gives the relationship between Tr and ATN as $ATN = -\ln(Tr)$.

It is well established that σ_0 is not equal to the light absorption by aerosol particles when suspended and is greatly dependent on the aerosol loading of the filters (e.g. Bond et al. 1999, Sheridan et al. 2005, Virkkula et al. 2005). This difference is the result of filter-induced artefacts when light absorbing aerosol particles embed in filters. Embedded particles are subject to multiple scattering by light scattered by the fibres in the filter. Incident light upon the filter will be scattered multiple times inside the filter resulting in an increased optical path. Multiple scattering will thus increase the light incident upon an absorbing particle embedded in the filter and enhance the amount of light absorbed by the embedded particles. For a pristine filter, the multiple scattering enhancement can result in roughly twice the absorption of the same particles when suspended. A scattering aerosol particle that deposits on the filter can further increase the optical path of light traversing the filter and thus further enhance light absorption by the pre-deposited aerosol (commonly called apparent absorption); purely scattering aerosol particles will also increase the reflectivity and give rise to apparent absorption. The enhancement of the optical path will, however, gradually decrease as the filter gets laden with absorbing aerosols. Moreover, the penetration depth of the particles, which is size dependent, will influence the amount of multiple scattering the embedded particles are subject to and thus impact the instrument response (VanOsdell et al. 1990, Lack et al. 2009, Moteki et al. 2010, Nakayama et al. 2010). These issues, which concern the technique, result in artefacts and they need to be corrected for.

There are a number of different empirical correction functions and algorithms that convert the uncorrected absorption (σ_0) to light absorption coefficients. Correction algorithms for the PSAP and Aethalometer instruments have been developed separately, although both instruments use the same technique to acquire σ_0 . As discussed above, the state of the filter will dictate the magnitude of the artefacts and the filter states are expressed differently in the PSAP and the Aethalometer. Thus, the corrections for the Aethalometer have been derived using ATN , whereas the corrections for the PSAP have been derived using Tr .

The work of Bond et al. (1999) provided a method to minimise systematic errors between different instruments. Furthermore, the study introduced a scattering correction factor s in addition to the empirical filter transmittance correction function $f(Tr)$ to give the equation

$$\sigma_{AP} = f(Tr)\sigma_0 - s\sigma_{SP}. \quad (11)$$

In Eq. (11), a fixed amount s of light-scattering (σ_{SP}) is subtracted. Since the work of Bond et al. (1999), the coefficients of the filter transmittance correction function have been updated and the method elaborated to avoid inconsistencies when the correction is applied (Ogren 2010). In addition

to the original form of the Bond et al. correction, another filter transmittance correction function was developed for a three wavelength prototype of the PSAP which takes the SSA of the aerosol into account (Virkkula et al. 2005). These two algorithms were used to derive σ_{AP} in **Paper I** and **Paper II**. Recently, the work of Müller et al. (2014) provided a more theoretical approach in the form of a constrained two-stream algorithm to determine light absorption coefficients from a PSAP.

A study by Springston and Sedlacek (2007) showed that the detection limit of the PSAP can be improved significantly by data post-processing to improve the precision of the instrument. Furthermore, the study highlighted that boxcar averaging is not the most efficient method to reduce measurement noise due to the measurement technique itself. The post-processing makes use of the change in the transmitted intensities between time t and $t+\Delta t$ in Eq. (10) for an arbitrary time interval which is not the same as averaging one second data between t and $t+\Delta t$. The noise of the instrument has been reported to be proportional to $\Delta t^{-1.31}$ when using the method (Springston and Sedlacek 2007). All PSAP data presented in the thesis were calculated using this method.

The Aethalometer provides real time measurements of EBC by measuring the attenuation of light through the filter. The Aethalometer converts the uncorrected absorption coefficients obtained using Eq. (10) into EBC mass concentration using an MAC proportional to λ^{-1} (see Eq. 9). As such, the Aethalometer will not take the state of the filter into account and thus requires a correction to be applied. There are a number of correction algorithms for the Aethalometer data to derive light absorption coefficients which include some method for taking light scattering coefficients into account. An overview of various corrections for the Aethalometer is provided by Collaud Coen et al. (2010). In the work presented in this thesis, the correction algorithm of Arnott et al. (2005) was used because it is based on multiple scattering theory in combination with analytically derived scattering and filter-loading corrections.

The MAAP uses radiative transfer equations to provide light absorption by the aerosol particles deposited in the filter. The radiative transfer scheme is a two-stream approximation for determining the radiative properties of the aerosol-loaded filter layer. The scheme treats the filter matrix as a two-layer system because the sample aerosol deposits onto the uppermost layer of the filter, whereas the rest of the filter remains devoid of the sample aerosol. To determine the radiative transfer of light in the filter by the two-stream approximation, light scattered back from the filter has to be measured at multiple angles. These measurements can differentiate between diffusely back-scattered and Gaussian-distributed back-scattered radiation that are different for different aerosol particle types (Petzold and Schönlinner 2004). The filter transmittance is measured by one detector since the light is diffuse once it exits the filter. An iterative procedure can then deduce the SSA and the optical depth of the aerosol-loaded filter layer (Petzold and Schönlinner 2004). In brief, the deduction is done by matching the measured back-scattered and transmitted radiation of the filter to the radiative transfer scheme (Petzold and Schönlinner 2004). Thus, the MAAP is not solely based on the Bouguer-Lambert–Beer law.

3.2.2 Integrating Nephelometer

A nephelometer is an instrument that provides measurements of aerosol light-scattering coefficients when in a suspended state. The principles of the instrument originate from the 1940s and were originally intended for atmospheric visibility applications for the military (Beuttell and Brewer 1949, Heintzenberg and Charlson 1996). The development of the principle ultimately resulted in instruments that were sensitive enough to measure Rayleigh scattering by air, which is in the order of 12 Mm^{-1} at a wavelength of 550 nm at standard atmospheric pressure (1013 hPa) and temperature (273 K) (Bodhaine 1979, Heintzenberg and Charlson 1996). Correct assessment of Rayleigh scattering is of profound importance since this signal is subtracted from the measurements and thus yields the amount of light scattered by the aerosol particles.

The geometry of an integrating Nephelometer is such that it performs a geometrical integration of the scattered intensity in different directions (Anderson et al. 1996, Heintzenberg and Charlson 1996). The design of the instrument has a orthogonal geometry between a Lambertian light source (emits diffuse light) and a light detector (Hasan and Lewis 1983). The orthogonal geometry means that the Lambertian light source is aligned at 90° to the light detector. The enclosed sensing volume of the Nephelometer is coated black so that only the light source illuminates the sample. Furthermore, the Lambertian light source weighs the sample in the sensing volume by $\cos(\theta)$ within the sensing volume; θ is the scattering angle. The orthogonal geometry, therefore, weighs the scattered light intensity by $\cos(90^\circ - \theta) = \sin(\theta)$ as seen from the detector. A $\sin(\theta)$ weighted signal is desired since the integral that yields the desired light-scattering coefficient is $\sin(\theta)$ weighted by definition (Heintzenberg and Charlson 1996). The instrument geometry, however, does not allow for a geometric integration from $0-180^\circ$ since the detector must not be blinded by the light source. In practice, the viewing geometries are roughly $7-170^\circ$ and part of the light scattering is truncated (Anderson et al. 1996). In addition to the total light scattering by particles, a back-scatter shutter can be used to block the light source from illuminating half of the sensing volume. The back-scatter shutter, as the name suggests, blocks light from the light source at angles between $0-90^\circ$ from the sensing volume so that the light that reaches the detector is scattered in a backwards direction by the aerosol sample (ideally from $90-180^\circ$) and thus yield back-scatter coefficients. The Rayleigh scattering in the backwards direction is half of the total Rayleigh scattering (see Fig. (1), Anderson et al. 1996).

The light intensity that reaches the detector depends on the intensity of the light source and the signal depends on the sensitivity and dark counts of the detector. A rotating shutter between the light source and the detector allows for the assessment of dark counts by the detector. Dark counts are measured when the part of the shutter that prevents all light from reaching the detector is between the lamp and the detector. Fluctuations in the light intensity of the lamp is monitored by the shutter calibration section which directs part of the light from the lamp to the detector (Bodhaine et al. 1991). Both temperature and pressure are needed to calculate the Rayleigh scattering of air, which is then subsequently subtracted from the signal. The temperature and pressure measurements are needed because the instrument cannot distinguish between light that is scattered by aerosol particles

and light scattered by air molecules. The instrument signal is calibrated using particle-free air and a span gas with known Rayleigh scattering coefficients (usually carbon dioxide) which provides the offset and slope of the instrument relative to known span-gas values (Anderson et al. 1996).

Because of the geometry of the sensing volume of an integrating Nephelometer, the light scattering by the aerosol cannot be detected from 0–180° (Anderson et al. 1996, Heintzenberg and Charlson 1996). Particles that are in the geometrical optics regime tend to scatter light predominantly in a forward direction (Fig. 4). Moreover, forward scattering is the greatest at angles close to 0° in relation to the direction of the radiation (near forward scattering). The truncation of light due to the geometric design of the instrument will result in that part of the scattered light not being detected at angles close to 0° and 180°. The result is that more light is truncated for the coarse-mode aerosol than for the fine-mode aerosol (Anderson and Ogren 1998). Moreover, a Lambertian light source does not produce an ideal cosine-weighted illumination of the sensing volume as desired (Anderson and Ogren 1998, Müller et al. 2009). A study by Anderson and Ogren (1998) shows how these pitfalls affect the submicron and supermicron aerosol-scattering coefficients differently and provides a correction that compensates for these factors. The study also highlights that the non-ideal Lambertian light source influences the submicron aerosol particles the most. The truncation correction as suggested by Anderson and Ogren (1998) was applied to the dataset of **Paper I, III** and **IV** for the TSI 3563 integrating Nephelometer. In **Paper II**, the truncation correction of Müller et al. (2011b) was used for the Ecotech Aurora 3000 integrating Nephelometer, which is similar to the correction of Anderson and Ogren (1998).

3.2.3 Aerosol number size distribution measurements

The determination of aerosol particle number size distributions is often done according to their electrical mobility in size ranges from a few nanometres to one micrometre (McMurry 2000). A charged particle which is subject to an electric field will move towards the opposite polarity with terminal velocity. The electrical mobility of the particle yields the mobility-equivalent size of the particle, which is called the electrical mobility diameter.

The classification of a disperse aerosol particle population can be done using a differential mobility analyser (DMA, Hewitt 1957, Knutson and Whitby 1975). Prior to entering the DMA, the aerosol particles are neutralised with a radioactive source to a known charge equilibrium (Wiedensohler 1988). In the work presented in this thesis, a Vienna-type DMA was used (Winklmayr et al. 1991). The geometric layout of the Vienna-type DMA is coaxial with a central electrode and a cylindrical outer wall. The working principles of a DMA require laminar flows of particle-free air and the sample aerosol. When a voltage is applied to the central electrode, particles that are oppositely charged will start to migrate through the DMA according to their electrical mobility and only particles of a certain size are collected (Zhang and Flagan 1996). These selected particles can then be counted with a condensation particle counter (CPC). In a CPC, particles are grown to optically detectable sizes by supersaturation of vapours that condense onto the particles (McMurry 2000). The combination of a DMA and a CPC to differentiate between the number of particles of a certain

size is called a differential mobility particle sizer (DMPS) if the voltage of the central electrode is changed stepwise (Aalto et al. 2001).

Other means to measure aerosol particle-number size distributions exist, especially for coarse-mode aerosol particles. In that size range, the size distribution can be determined directly by optical means using an optical particle counter (OPC, Heim et al. 2008) or according to their aerodynamic inertia using an aerodynamic particle sizer (APS, Chen et al. 1985). These diameters, however, do not necessarily correspond to the electrical mobility diameters measured using a DMPS.

3.2.4 Thermodenuder

A thermodenuder (TD) consists of a heating section that heats the aerosol sample in order to evaporate volatile constituents from the particulate phase and a denuding section where the volatilised constituents are removed from the sample air. There are a couple of designs for the denuding section, which contains activated carbon as a sink for the volatilised constituents; the denuding section can be either heated or cooled (Wehner et al. 2002, Fierz et al. 2007, Cappa 2010). Whatever the method, the principle is that the surface area of the denuding section is greater than the aerosol surface area so that it will strip out volatilised gas phase constituents so that they do not re-enter the particulate phase post-TD and pre-measurement. In the set-up of **Paper I**, no activated carbon denuding section was present to replicate the method used by the continuous soot monitoring system (COSMOS, Miyazaki et al. 2008). A TD model study by (Cappa 2010) showed that the inclusion of a denuding section is of particular importance for semi-volatile constituents. However, the design of the thermodenuder of **Paper I** is similar to the set-up described by Ehn et al. (2007), which showed little difference between a thermodenuder including an activated carbon denuding section and one without one, when measuring ambient urban aerosol in Helsinki. Furthermore, the work by Saleh et al. (2011) concluded that re-condensation of volatilised constituents is minimal for short TD residence times (such as in **Paper I**) under atmospherically relevant concentrations.

4 Results and discussion

The purpose of this chapter is to summarise the key findings about aerosol-particle optical properties studied in **Papers I–V**. The reader is encouraged to read the articles for more detailed information about the findings discussed in this thesis. The papers included in the thesis cover aerosol measurements conducted on three continents, from urban areas (**Paper I** and **Paper III**) and an industrialised part of South Africa (**Paper II**, **Paper V**) to a rural site in a boreal forest in southern Finland (**Paper IV**). These observations are put into context here by comparing the observations with other locations. Table (1) provides an overview of the extensive aerosol particle optical properties of light scattering (σ_{SP}) and light absorption (σ_{AP}), as well as the intensive aerosol optical particle properties of SSA, SAE and AAE. The last column of Table (1) represents the fraction of light scattered by fine-mode aerosol particles (PM_1) and the amount of light scattered by both coarse and fine-mode aerosol particles (PM_{10}).

Table 1 : Overview of different aerosol optical properties (and standard deviations) conducted during the measurements in this thesis. The table consists of values reported in **Papers I–V**, whereas some are supplementary.

Site	σ_{AP} (Mm ⁻¹)	σ_{SP} (Mm ⁻¹)	SSA	SAE	AAE	$\sigma_{SP, PM1}/\sigma_{SP, PM10}$
Hyytiälä	1.9 (2.1) ^c	14 (16) ^c	0.88 (0.07) ^c	1.7 (0.5)	1.4 (0.3) ^d	0.90 ⁱ
Helsinki^a	4.8 (4.0) ^c	29 (21) ^c	0.73 (0.11) ^d	2.0 (0.2)	N/A	0.85 ⁱ
Helsinki^b	5.3 (3.3) ^d	5.3 (3.1) ^f	0.50 (0.10) ^e	N/A	1.1 (0.1) ^g	N/A
São Paulo	20 (16) ^c	65 (54) ^c	0.70 (0.13) ^c	1.47 (0.24)	N/A	N/A
Elandsfontain	8.4 (8.7) ^c	50 (50) ^c	0.84 (0.08) ^c	1.55 (0.38)	1.3 (0.3) ^h	0.91 ⁱ

^aAmbient aerosol properties

^bAerosol properties after denuding

^cAt a wavelength of 637 nm

^dCalculated using the Arnott et al. (2005) algorithm

^eAt a wavelength of 880 nm

^fAt a wavelength of 545 nm

^gCalculated from σ_0 because of no multiwavelength scattering information.

^hCalculated from PSAP data using the correction function of Ogren (2010) and a $Tr > 0.7$

ⁱCalculated from particle number size distribution measurements using a constant refractive index.

4.1 Optical properties of aerosol particles with different levels of anthropogenic influence

Although urban areas cover a small proportion of the world's land surface area, they are significant contributors to aerosol particle pollution on a global scale (Hidalgo et al. 2008, Seto and Shepherd 2009). In urban areas, traffic is the most obvious contributor particulate pollution (Grimm et al. 2008, Beirle et al. 2011). However, major conurbations require infrastructures, such as factories and power plants, and can therefore be accompanied by heavy industry that exacerbates impaired air quality further. The lifetime of aerosol particles is generally no longer than a few weeks (e.g. Haywood and Boucher 2000, Raes et al. 2000, Ramanathan et al. 2001). In the meantime, aerosol particles can be transported a long way. In the atmosphere, the aerosol particles continue to evolve both chemically and physically (e.g. Crutzen and Zimmermann 1991, Jacob 2000, Zhang et al. 2000, Kroll and Seinfeld 2008, Hallquist et al. 2009). Thus, during atmospheric transport, aerosol particles will gain secondary aerosol mass. During transport, additional sources add to the aerosol particle population, and some aerosol will be lost due to wet and dry deposition. Moreover, aerosol particles that travel long distances from strong-source regions to remote areas will also disperse on the way.

In general, measurements that are conducted far away from pollution hotspots tend to show less scattering and absorption by aerosol particles and a higher SSA (see Fig. 5). When aerosol particles gain secondary aerosol mass, both the SSA and the size of the particles will increase (e.g. Schnaiter et al. 2005). There are large differences in the amount of light absorption and scattering by aerosol

particles at different sites. Although the SSA of Beijing and Hyytiälä are quite close (Fig. 5a), the extensive properties of light-scattering and absorption are certainly not (Fig. 5b). The new measurement locations included in this thesis, shown in Fig. (5), add to the information about intensive and extensive aerosol particle optical properties. The new sites are not outliers, and fall in the range of previously reported values reported for sites elsewhere (e.g. Delene and Ogren 2002, Garland et al. 2008, Lyamani et al., 2008, Garland et al. 2009, Marley et al. 2009).

At the Hyytiälä station (**Paper IV**), which is a background station in southern Finland, aerosol particles comprise natural and anthropogenic components. The boreal forest of Scandinavia has been shown to be a substantial source of aerosol particles both in terms of mass and by numbers (Tunved et al. 2006). Using back trajectories, **Paper IV** showed that increased light scattering and

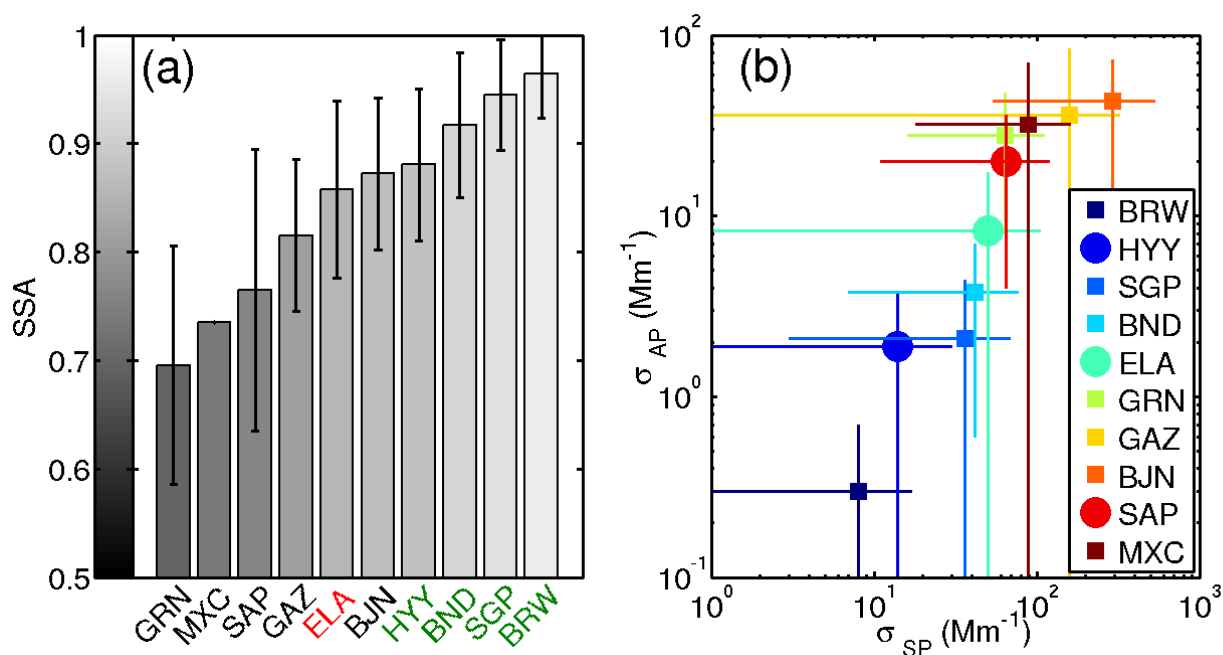


Figure 5: Aerosol optical properties in urban, industrial, and remote sites. The left panel (a) shows the SSA of different sites sorted according to the SSA of the aerosol at the site. The colour of the x-axis labels in the left panel represents urban sites (black), industrialised region (red), and continental and remote sites (green). The abbreviations and the studies from which the values were obtained are: GRN: Granada, Spain (Lyamani et al., 2008), MXC: Mexico City, Mexico (Marley et al. 2009), SAP: São Paulo, Brazil (data from **Paper III**), GAZ: Guangzhou, China (Garland et al. 2008), ELA: Elandsfontain, South Africa (data from **Paper V**), BJN: Beijing, China (Garland et al. 2009), HYY: Hyytiälä, Finland (**Paper IV**), BND: Bondville, USA, SGP: Lamont, USA, and BRW: Barrow, USA (Delene and Ogren 2002). Panel (b) shows the scattering and absorption coefficients reported for the different sites; adapted from **Paper V**. The whiskers in both panels indicate the standard deviations. In panel (b), the circles indicate values from the measurements in this thesis.

absorption coefficients were associated with air-masses originating from continental Europe. Back trajectory analysis is a method when a spatial model of air-mass movement is used to associate — in the case of **Paper IV** — aerosol scattering and absorption measurements of air-masses that have arrived from a certain region (Scheifinger and Kaiser 2007, Riuttanen et al. 2013). Numerous back-trajectories can be used to find source regions. In **Paper IV**, it was argued that the site — from the point of view of the optical properties of aerosol particles — is a result of continental aerosol pollution during winter and biogenic aerosol particles during summer. The highest SSA in Hyytiälä occurred during the summer months, during the growth season of the forest. The forest is known to produce organic vapours that evolve in the atmosphere, and can then condense onto pre-existing particles or form new particles (e.g. Kerminen et al. 2012, Kulmala et al. 2013, Paasonen et al. 2013). Thus, the forest can change the SSA of aerosol particles.

Of the four background stations shown in Fig. (5), Hyytiälä (HYY) had the lowest SSA. Both the light scattering and absorption coefficients at Hyytiälä were lower than for Bondville (BND) in Illinois and Southern Great Plains (SGP) in Oklahoma (see the figure for references). The Bondville station was located some 16 km from an area populated by 100,000 inhabitants and was thus closer to an urban area than Hyytiälä is. The Southern Great Plains station was located far from urban areas, although there were large point sources (oil refineries and power plants) close by. The Barrow (BRW) station in Alaska is the most remote of the background stations and had the highest SSA and the lowest light scattering and absorption coefficients of all the stations. The message of Fig. (5) is that the background stations HYY, BND, SGP and BRW have a higher SSA and lower light scattering and absorption coefficients than the urban stations. Moreover, Fig. (5b) shows that light scattering coefficients, and to a even greater extent light absorption coefficients, are lower at background stations than at stations that are subject to anthropogenic pollutants. In comparison to the background stations of Fig. (5), urban aerosol particles generally have a lower SSA than aerosol particles observed at remote regions, and can be explained by the high soot content of urban aerosol particles. In addition to the megacities of Mexico City (MXC), São Paulo (SAP), Guangzhou (GAZ) and Beijing (BJN) the Granada (GRN) station is also shown in the figure due to its exceptionally low SSA.

A substantial aerosol particle constituent that is common in urban areas is soot, which originates from incomplete combustion of carbon-containing fuels (e.g. Cass et al. 2000, Cabada et al. 2004, Putaud et al. 2004). In contrast to the rather short study of combustion-related aerosol particles in Helsinki (**Paper I**), a more comprehensive study of particulate urban air pollution was conducted in **Paper III** in São Paulo, a megacity with 20 million inhabitants. Prior research using filter sampling analysis concluded that traffic-related pollution and re-suspended soil dust are substantial contributors to the air pollution in the city (Castanho and Artaxo 2001). The study further concluded that the coarse-mode aerosol particles in São Paulo mostly consist of dust, whereas fine-mode aerosol particles do not. In **Paper III** the submicron aerosol particles were shown to have a lower SSA than the Asian cities of New Delhi and Beijing.

A plausible explanation for higher SSAs of aerosol particles in Asia is that the particulate pollution within the cities is mixed with the atmospheric brown cloud (ABC) that is associated with the region (Ramanathan et al. 2007a). A combination of the higher SSA of the ABC than that of the aerosol particle sources within the cities would lead to higher aerosol particle SSAs within the cities. The ABC over the Indian Ocean has been shown to be largely due to combustion of fossil fuels on the Indian sub-continent (Ramanathan et al. 2001). China and India are the world's most populous countries and Asia represents 60% of world population, whereas South America accounts for roughly 8% (United Nations, 2013). Furthermore, the most populous city in South America is São Paulo. Thus, the aerosol particles measured in São Paulo should to a greater extent be local compared to more densely populated areas in Asia.

Because aerosol particle pollution in urban areas is to a great extent related to traffic emissions, the diurnal variation of traffic affects the pollution within cities. In **Paper III**, it was found that boundary layer dynamics affect how aerosol particle pollution evolves within a city, which is in agreement with earlier studies (Bischoff-Gauß et al. 1998, Castanho and Artaxo 2001). There was a sharp increase in total particle number concentrations from night-time concentrations to morning rush-hour concentrations. Concurrently, light absorption and light scattering coefficients increased to peak diurnal values. A diurnal minimum in the SSA of the aerosol particles occurred during the morning rush hour. There was no clear afternoon rush hour detected by the optical instruments although it occurred at around 18:00 local time as measured in tunnels in the city (Brito et al. 2013). The observed morning rush hour occurred during stagnant and stable atmospheric conditions whereas the absence of an afternoon rush hour peak was argued to be due to a wind shift towards the edge of the city in addition to convective mixing of aerosol particles throughout the atmospheric boundary layer. The absence of an afternoon rush-hour peak has been reported for other megacities (e.g. Baumgardner et al. 2007, Garland et al. 2009).

In an urban area, such as São Paulo, the aerosol pollution within the city is substantially affected by the traffic, and traffic has a pronounced diurnal cycle. Thus, the aerosol particles within cities are affected by traffic patterns. At sites that are distant from urban areas, or in areas where anthropogenic aerosol particulate pollution is continuous throughout the day, the diurnal behaviour is different. In areas with constant emissions, aerosol particulate pollution is more related to the evolution of the boundary layer during the course of the day than in urban areas. Figure (6) shows the diurnal behaviour of light absorption coefficients in São Paulo and how it differs from Elandsfontain, which represents an industrialised area (anthropogenic emissions are more steady throughout the day) and the background site of Hyytiälä. Thus the anthropogenic component at Elandsfontain and Hyytiälä, since they are distant to major traffic sources, does not show the characteristics of an urban site, namely rush-hour peaks in light absorption coefficients in the morning. Furthermore, the absolute amount of light absorption by the aerosol particles vary substantially between the sites in Fig. (6), as indicated by the different y-axis scales of the panels.

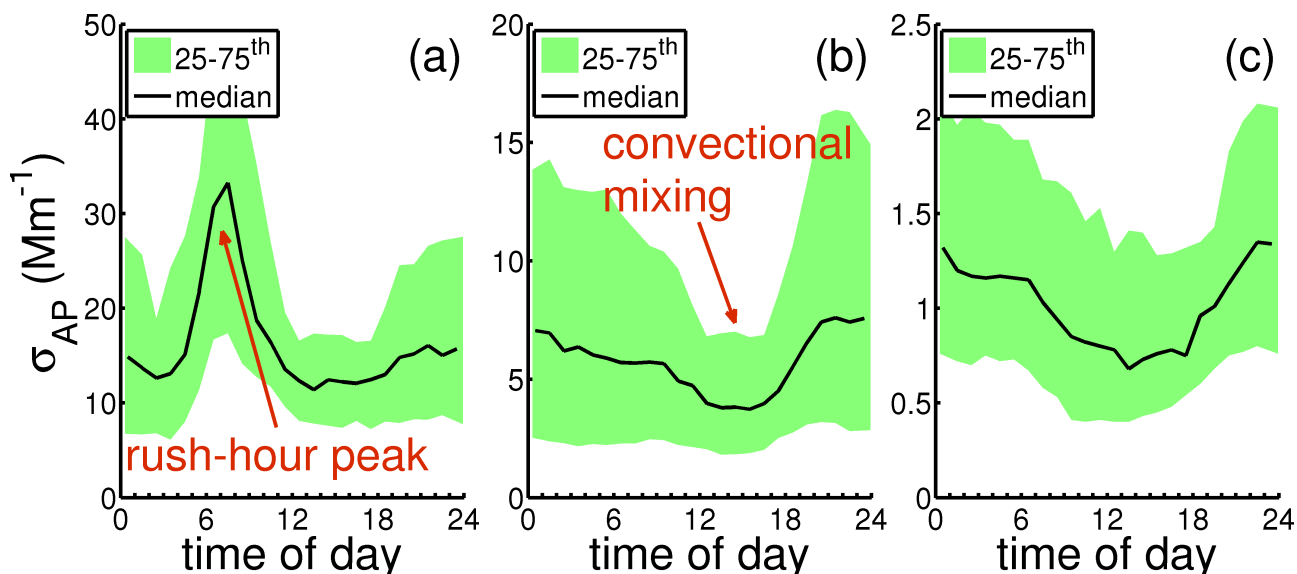


Figure 6: Diurnal behaviour of light absorption coefficients in (a) São Paulo (b) Elandsfontain and (c) Hyytiälä. The green area represents the 25th and 75th percentile range. Note that the y-axis scales differ between the panels.

Small soot particles are volume absorbers (Fig. 4). Therefore, the amount of light absorption by soot is related to the volume of atmospheric soot (Moosmüller et al. 2009). In Hyytiälä, there was a clear diurnal variation in light absorption, with less light absorption during the day, especially during summer, when the mixing layer height is the greatest diluting ground level concentrations the most.

Vehicular emissions that originate from the combustion of fossil fuels have a modal peak mostly below 100 nm in diameter (e.g. Wehner et al. 2004, Karjalainen et al. 2014a). Freshly emitted aerosol particles from vehicles have a high soot content and therefore a low SSA. The refractory component of the aerosol particles investigated in **Paper I**, which to a great extent should comprise soot, had a count mean diameter (CMD) of roughly 70 nm. Here, refractory aerosol particles refer to aerosol particle that can withstand heating to 280°C without being volatilised. Urban areas, which are predominantly affected by traffic should have an SSA that is low and a CMD that is close to that of the fresh traffic-related aerosol particles. When freshly emitted aerosol particles age — through condensation, coagulation and cloud activation involving heterogeneous chemistry — they will grow in size. Growth by other constituents than soot will increase the SSA of the aerosol particles since soot is the most potent light-absorbing species in the atmosphere. Consequently, aerosol particle growth will increase the CMD of the particle population. Moreover, the ageing process of soot will change soot particles from being externally mixed to internally mixed (Moffet and Prather 2009). In **Paper IV**, it was noted that there is a relationship between the CMD and the SSA of the aerosol. The study showed that the CMD range of the aerosol decreased when the SSA of the aerosol decreased.

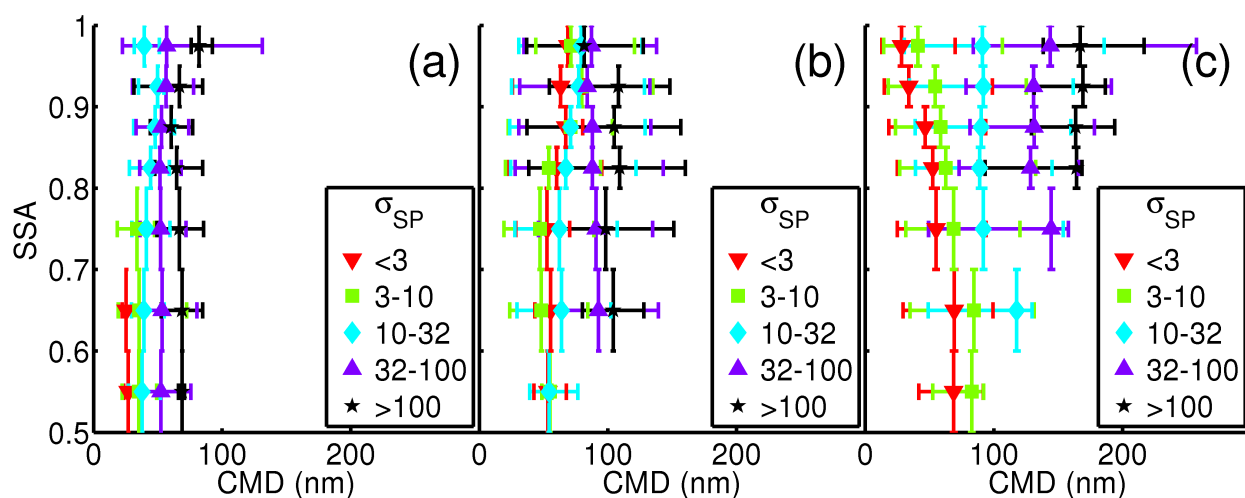


Figure 7 : Single-scattering albedo (SSA) as a function of count mean diameter (CMD) for **(a)** São Paulo, **(b)** Elandsfontain, and **(c)** Hyytiälä (**Paper IV**). The horizontal whiskers indicate the 2.5 and 97.5 percentile range and the vertical whiskers indicate the SSA range. The legend indicates the σ_{SP} range segregation in units of Mm^{-1} .

Figure (7) shows how aerosol particle SSA is related to CMD at different locations. The figure panels (from left to right) are from measurements conducted in São Paulo (urban site), Elandsfontain (industrialised site), and Hyytiälä (background site). In São Paulo, the narrow CMD range is mostly in the CMD range of freshly emitted combustion aerosol. Since Elandsfontain is further away from traffic-related aerosol particle sources, the CMD range is more spread out. For the background station of Hyytiälä, the CMD range is broader still.

In **Paper III**, it was suggested that the SSA of the aerosol particles in São Paulo could be the result of a slow gain in secondary aerosol mass within the city and could be related to the extensive use of bioethanol by the vehicular fleet. The conversion processes from precursor vapours to secondary particulate matter can be long and cumbersome. Bioethanol is chemically different from fossil fuel and blends of gasoline and bioethanol (gasohol) contain different levels of impurities (Agarwal 2007, Karavalakis et al. 2012). Gasohol changes the emissions of the vehicular fleet and has been found to increase aldehyde emissions while reducing NO_x emissions (Graham et al. 2008). Emissions are vehicle-specific and a high ethanol blend does not necessarily lead to low NO_x emissions above a certain mixing ratio of the ethanol blend (Karavalakis et al. 2012). NO_x is an important precursor of secondary photochemical pollutants, such as ozone (O_3) (Jenkin and Clemitshaw 2000). A study by Silva Júnior (2009) concluded that the O_3 concentrations in the city were related to photochemistry and traffic. Moreover, recent research supports the argumentation in

Paper III that increased O₃ levels in São Paulo originate from the photochemical degradation of by-products of bioethanol combustion by the vehicular fleet (Madronich 2014, Salvo and Geiger 2014).

Photochemical smog has been linked to the photochemical degradation of biofuel-related emissions such as aldehydes (Haagen-Smit, 1952; Tanner et al., 1988; Atkinson, 2000). When ethanol is used as vehicle fuel it can crack during combustion to form mainly acetaldehyde and some formaldehyde (Gaffney and Marley 2009). Any reaction that converts nitrogen oxide (NO) to nitrogen dioxide (NO₂) without the involvement of O₃ allows for it to build up (Seinfeld 1989). Such pathways are available either through photodissociation of aldehydes or through their reactions with OH radicals (Seinfeld 1989, Atkinson 2000). Although photochemistry has shown to result in elevated O₃ concentrations and photochemical smog, the aerosol optical properties measured in São Paulo (**Paper III**) do not show a very different SSA in comparison to cities that do not use bioethanol extensively (Fig. 5a). It does not, however, indicate that differences do not exist. One factor that can contribute to a different SSA of the aerosol particles between the cities is the use of heavy duty diesel vehicles and local meteorological conditions such as inversion. The exceptionally low SSA of Granada in Fig. (5a) was measured close to a highway dominated by heavy-duty diesel vehicles during winter months when inversions frequently occur (Lyamani et al. 2008).

A similar set-up to that in **Paper I** would have been needed to determine the size distribution of the refractory component of the aerosol in São Paulo. Such a set-up would also have disclosed the volatility of the particulate OC. However, three modes proved to represent the median size distribution of **Paper III** the best. Research suggest that the nucleation mode is mostly non-refractory (Wehner et al. 2004, Wehner et al. 2009). A fraction of the Aitken mode is likely to contain a substantial fraction of soot and thus be responsible for light absorption by aerosol particles. Particles that have reached the accumulation mode is the result of cloud activation and heterogeneous chemistry subsequent to growth by coagulation and condensation (e.g. Raes et al. 2000). The accumulation mode should, therefore, be internally mixed soot with other constituents. Not all of the vapours that originate from the combustion processes will nucleate immediately when they enter the atmosphere, but evolve in the atmosphere through many chemical reactions (Crutzen and Zimmermann 1991, Jacob 2000, Kroll and Seinfeld 2008). A study of the chemical composition of PM_{2.5} aerosol particles in São Paulo concluded that OC accounted for 42% of the total mass and elemental carbon (EC) 17% measured in two heavily trafficked tunnels in the city (Brito et al. 2013). In **Paper III**, it was found that during new particle formation events only a small fraction of the condensing vapours could be attributed to sulphuric acid, implying that other vapours contributed to the growth and a strong candidate is OC.

4.2 Effects of volatilisation on aerosol optical properties

The mixing state of light-absorbing species impact the amount of light absorption by aerosol particles (Jacobson 2001, Lack and Cappa 2010). When an absorbing core is surrounded by a shell of non-absorbing particulate matter, non-absorbing shell can focus light on the light absorbing core.

Thus, a non-absorbing shell can increase the amount of light absorption of a strongly absorbing core. This phenomenon is called the lensing effect, which gives rise to absorption enhancement in aerosol particles (Lack and Cappa 2010). Laboratory experiments have indicated that the absorption enhancement can be substantial — more than double — depending on the size of the core and the thickness of the shell (Mikhailov et al. 2006). However, there are still substantial differences between laboratory experiments, model simulations and ambient observations (Lack and Cappa 2010, Cappa et al. 2012). Moreover, a shell surrounding an absorbing core can increase the SSA of aerosol particles, again depending on particle size and the thickness of the surrounding shell (Moffet and Prather 2009).

The refractory mode of the aerosol number size distribution associated with vehicle combustion is in the range of 50–80 nm (Fig. (8), Wehner et al. 2004, Wehner 2009). The combustion process in vehicles also produces nucleation-mode particles (e.g. Karjalainen et al. 2014a). These nucleation-mode particles form after combustion already in the tail pipe or immediately after the exhaust cools when it enters the atmosphere (Karjalainen et al. 2014b). The nucleation mode, however, is mostly non-refractory and consists of weakly to non-absorbing species (e.g. Wehner et al. 2004, Rose et al. 2006).

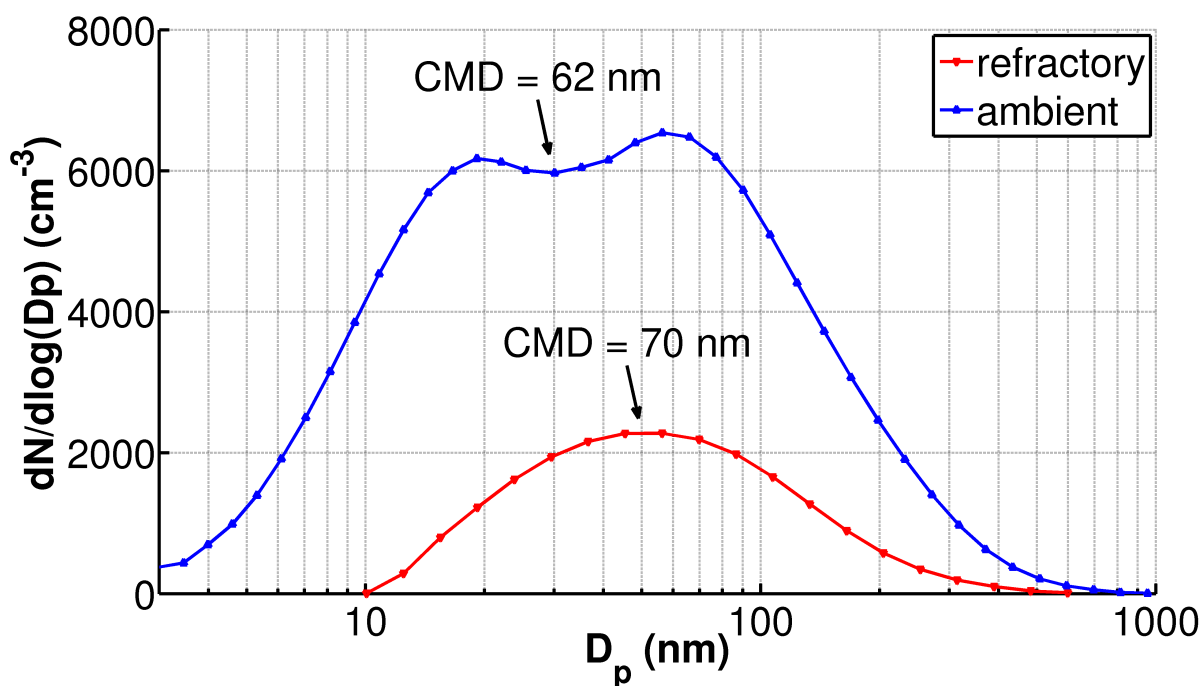


Figure 8 : The average size distribution of the ambient aerosol (initial) and the residual aerosol after heating it to 280°C in Helsinki, Finland. The size distributions are from the measurements of **Paper I**.

It is generally accepted that light scattering by aerosol particles affects the measurement accuracy of filter-based absorption measurements since the optical path of filters changes when aerosol particles deposit onto the filter (Moosmüller et al. 2009). Light-scattering aerosol particles can also increase the reflectivity of the filter, which in turn results in apparent absorption. An approach to minimise

the apparent absorption is to heat the aerosol sample to volatilise the non-refractory components and assume that the residual aerosol is soot alone, thus assuming that the apparent absorption can be neglected. This approach is applied in the COSMOS absorption photometer (Miyazaki et al. 2008).

The use of a thermodenuder to minimise apparent absorption will irreversibly change the optical properties of the sampled aerosol particles (Mikhailov et al. 2006, Moffet and Prather 2009, Lack and Cappa 2010). In the process, the initial amount of light absorption by the ambient aerosol will be lost. Higher temperatures are needed to volatilise low-volatile constituents compared to volatile constituents, whereas inorganic sulphates and nitrates volatilise at lower temperatures (280°C) (Cappa 2010, Tiitta et al. 2010). In **Paper I**, the optical properties of the residual aerosol after thermodenuding were investigated and compared to a non-heated aerosol. A temperature of 280°C was chosen to be high enough to evaporate sulphates and nitrates. At higher temperatures catalysts can oxidise soot and charring of organics can occur which could bias the measurements (Novakov and Corrigan 1995, Wittmaack 2005).

Paper I showed that although 75% of the aerosol volume was removed by a thermodenuder, the residual aerosol had an SSA in the range of 0.4–0.6 and thus exceeding the SSA of pure soot; the SSA of soot is in the range of 0.2–0.3 (Bond and Bergstrom 2006). The results of **Paper I** imply that the refractory aerosol particles were not pure soot. Refractory OC can be one reason why the thermodenuding set-up of **Paper I** did not lower the SSA of the aerosol particles to the SSA of pure soot. An OC/EC analyser (EC stands for elemental carbon) routinely measures OC at temperatures above 300°C. OC/EC analysers measure the volatilisation of evolved carbon (either as CO₂ or CH₄) when the temperature is increased stepwise in pure helium (He) for the determination of OC and subsequently oxygen is introduced in order to oxidise EC (Birch and Cary 1996). In the EUSAAR 2 protocol for OC/EC analysers, the temperature steps for detecting OC are 200, 300, 450 and 650°C and even at the highest temperatures OC can be observed (Cavalli et al. 2010).

During the last day of the short measurement period of **Paper I**, the temperature was varied between 50, 150 and 280°C. A interesting feature of the temperature scans was that not only did the scattering coefficients change with temperature, but so did the measured light absorption coefficients. When the aerosol was heated to 280°C, the light absorption was 64% of what it was when the aerosol had been heated to 50°C. When the aerosol was heated to 150°C, the light absorption was 80% of what it was when the aerosol was heated to 50°C after the Nakayama et al. (2010) penetration depth correction. Since the concentrations during the temperature scans changed, the percentage values were normalised to the light absorption values derived from the Aethalometer. It was thought that the dependence of light absorption coefficients on volatilisation temperature was the result of either a change in the mixing state or a change in the penetration depth of the sampled particles. The change in penetration depth by the aerosol particles due to volatilisation was compensated for as suggested by Nakayama et al. (2010). However, the penetration depth correction has not been verified experimentally (Müller et al. 2014). Whatever the reason, absolute values of light absorption coefficients after using a thermodenuder do not seem to be comparable with values obtained without a thermodenuder.

4.3 Uncertainties related to the interpretation of Ångström exponents

Ambient urban aerosol particles have a higher SSA than aerosol particles that have passed through a thermodenuder (**Paper I**). As previously established, correction functions are an essential part of filter-based absorption measurements. A number of studies have focused on absolute light absorption coefficients derived from measurements of aerosol particles with a range of SSA values (e.g. Bond et al. 1999, Arnott et al. 2005, Sheridan et al. 2005, Virkkula et al. 2005, Müller et al. 2011a). Two widely used correction methods both include subtraction of a fraction of the light scattering by aerosol particles (Bond et al. 1999, Virkkula et al. 2005). However, their performance at multiple wavelengths and the implications for the AAE calculated from these measurements have not been investigated in terms of how the aerosol loading of the filter affects the results. Recent research has shown that there are differences between AAEs calculated from light absorption data derived using different correction algorithms for the Aethalometer (Collaud Coen et al. 2010). In **Paper II**, the AAEs' dependency on filter transmittance and the correction algorithms used for the PSAPs were investigated in more detail.

The study of **Paper II** showed that for the same data-set, different corrections will result in substantially different AAEs. In addition to the most commonly used correction algorithms for the PSAP data, the study also included AAEs using uncorrected absorption coefficients and AAEs calculated using a method that resembles the offline spectral analysis of filter samples (Kirchstetter and Thatcher 2012). **Paper II** also addressed how scattering correction (the term $-s\sigma_{SP}$ in Eq. 11) can bias the AAE. As such, Eq. (11) assumes that a fixed amount of light scattering should be subtracted from the instrument signal after applying the filter transmittance correction function $f(Tr)$. However, in extreme cases this assumption can greatly impact (or even dictate) the AAE. Therefore, the implication of the findings of **Paper II** is that care should be taken when interpreting AAEs calculated using Eq. (11) when the SSA and SAE of the aerosol are high. Furthermore, when interpreting AAEs derived from PSAP measurements one should consider that different corrections can yield different results.

At sites where biomass burning aerosol is predominant, the AAE will be much greater than the AAE at urban sites. Urban air pollution is known to have a AAE that is close to unity whereas biomass burning aerosol particles have an AAE close to 2 (e.g. Kirchstetter et al. 2004, Clarke et al 2007). The AAEs over South Africa were found to be in the range of 1.33–1.90 depending on the PSAP correction algorithm used to derive aerosol light absorption coefficients (**Paper II**). The measurement period comprised almost two years of data and therefore includes biomass burning periods (Eck et al. 2013). The AAE of the east coast of the United States (**Paper II**), influenced by a densely populated area, showed a much lower AAE (0.6–1.2) than what was observed over South Africa, suggesting urban air pollution to be predominant. The AAEs reported in **Paper IV** were calculated from Aethalometer data using the correction algorithm of Arnott et al. (2005), which gave an average AAE of 1.4. As was pointed out in **Paper II**, the correction algorithms can have a substantial impact on the AAE for the PSAP and are also likely to impact the AAEs calculated using different Aethalometer corrections. There are, however, other factors than chemical composition

that affect the spectral dependence of absorption by the aerosol. A non-absorbing shell can change the AAE of absorbing particles substantially (Lack and Cappa 2010): from 1 to 1.6. However, AAEs in the range of 1.0–1.6 do not rule out the presence of brown carbon (BrC), but cannot be determined with great confidence (Gyawali et al. 2009, Lack and Cappa 2010). **Paper II** highlights that there are additional uncertainties when distinguishing urban air pollution from biomass burning aerosols that are related to data post-processing.

For urban aerosol particles, the AAE has been shown to be close to unity for non-coated soot particles. It is also well documented that fresh soot particles have a low SSA (Bond and Bergstrom 2006, Bond et al. 2013, and references therein). Therefore, the AAE range should be narrow when the SSA of the aerosol decreases since soot aerosol particles has a narrower range of AAE values than internally mixed soot-containing aerosol particles. This behaviour was observed at both the rural site in Hyytiälä, Finland (**Paper IV**) and at the industrial region of Elandsfontain in South Africa (**Paper II**). Both studies showed that a high SSA is associated with a wider range of AAE values than when the SSA is low.

The spectral dependence of light scattering can give additional information about the aerosol particles. Scattering Ångström exponents (SAE) are traditionally used as an indicator of the aerosol size distribution of the optically active aerosol particles (e.g. Yoon et al. 2007). The connection between SAE and different weighted mean diameters was investigated in **Paper IV**. The results indicate that the connection between the count mean diameter (CMD) and the SAE did not show the expected dependency of small CMDs yielding high SAE. On the contrary, the study showed that small CMD at the site was associated with small SAE, which is the opposite to the expected behavior. Nucleation-mode particles contribute little to total light scattering by aerosol particles although they can dominate by number concentration (Fig. 3). Moreover, multimodal particle number size distributions cannot unambiguously be related to SAE (Schuster et al. 2006). In **Paper IV**, the weighted scattering mean diameter (ScMD), surface area mean diameter (SMD) and volume mean diameter (VMD) proved to represent the multimodal size distribution at Hyytiälä better than CMDs.

5 Review of papers and the author's contribution

Paper I presented how key aerosol optical properties change with different degrees of volatilisation in an urban environment. The study showed that volatilisation will significantly reduce the SSA of the aerosol, but not necessarily to the SSA of soot as often desired. Furthermore, the study showed that the degree of volatilisation influenced light absorption coefficients. I wrote the main part of the article and did most of the data analysis. I performed the measurements related to the campaign instruments presented in the article.

Paper II showed how the applicability of a PSAP can be extended to either cope with high concentrations or infrequent filter changes by diluting the sample air in conjunction with data post-processing. Furthermore, the study showed that correction functions can affect absorption

Ångström exponents to the same degree as the mixing state of the light absorbing species in the aerosol. I wrote the majority of the article and did most of the data analysis.

Paper III studied the aerosol number size distributions and aerosol optical properties of the metropolitan area of São Paulo in Brazil. The study showed that the submicron aerosol in the city was closely connected to the traffic diurnal cycle. Moreover, the study showed that meteorological conditions impact the aerosol pollutants in the city. The study found that during new particle formation events only a minor fraction of the condensing vapours could be attributed to sulphuric acid. The majority of the work was done by me. I wrote the majority of the article, calibrated, shipped and installed the instruments and subsequently monitored them throughout the campaign, except for the aerosol optical instruments. The majority of the data analysis for the article was also conducted by me.

Paper IV provides an overview of both extensive and intensive aerosol optical properties in a boreal forest in the region of Pirkanmaa in south-western central Finland. The study reports the seasonal and diurnal patterns and investigates the relationship between size distributions at the site and the Ångström exponents associated with them. The study concluded that SAE cannot reliably be used as a proxy for number size distributions at the site. I contributed to the article by calculating light absorption coefficients, took part in the writing process of the article, and helped with interpreting the data.

Paper V presents the seasonal and annual trends of meteorological variables, trace gases and aerosol optical properties. The paper provides a basic analysis of these variables and how they relate to meteorological conditions at the site. The paper concludes that the Elandsfontain site is a polluted continental site, but not as polluted as the cities suffering from the atmospheric brown cloud over Asia. I contributed to the evaluation of the aerosol particle optical properties and to writing and finalising the paper.

6 Conclusions and future outlook

The work in this thesis comprise measurements of aerosol particle optical properties. Much of the thesis is dedicated to aerosol particle light absorption using filter-based absorption measurements. In addition, the characteristics between urban and rural aerosol optical properties are discussed.

Filter-based absorption measurements are a widely used means of determining light absorption by the aerosol. However, sample-filter interactions will result in systematic errors due to multiple scattering in the filter, scattering enhancement by the deposited aerosol and the loading of the filter by the aerosol. One approach to minimise the scattering enhancement of the aerosol in filter-based absorption measurements is to remove the volatile constituents from the particulate phase by heating the aerosol sample. This treatment, however, will irreversibly change the amount of light absorption and scattering by the aerosol. The approach will reduce the need to account for apparent absorption, although additional unknowns are introduced. For an internal mixture of light-absorbing

species, such as soot, volatilisation will reduce particle size and thus change how deeply the particles penetrate into the filter. An alteration of the penetration depth will change the instrument response. Moreover, the volatilisation of non-absorbing species from the particulate phase will change the mixing state of the refractory constituent; which for a submicron aerosol in urban areas mostly consists of soot. **Paper I** showed that light absorption coefficients, as measured by a filter-based absorption instrument, change significantly when aerosol particles pass a thermodenuder. The change was argued to be either due to an increased instrument response due to a change in the penetration depth of the sample or due to a change in mixing state of the aerosol (or both). Nevertheless, absolute values of light absorption coefficients obtained with a thermodenuder ahead of filter-based absorption measurements should not be compared with measurements using non-denuded aerosol. However, such a comparison could provide an optical means to determine the presence of organic carbon (OC) if further developed. Moreover, such a comparison could also provide information about the mixing state of light absorbing particles and the change in absorption Ångström exponents (AAE) due to the aerosol particles mixing state.

Multiwavelength filter-based absorption instruments are a widely used means to determine the AAE of the aerosol. For submicron aerosol, AAEs well above unity are indicative of the presence of OC or brown carbon (BrC). **Paper II** investigated a number of correction algorithms in use for determining the light absorption coefficients obtained using a PSAP. The study concluded that different correction algorithms yield very different AAEs that can lead to conflicting conclusions when trying to distinguish between urban and biomass burning aerosol. **Paper II** pointed out that under certain circumstances the correction of apparent absorption can significantly change the AAE derived from filter-based absorption photometers. Moreover, the correction algorithm used will also significantly affect the estimation of the presence of BrC and how much BrC contributes to light absorption by aerosol particles at short wavelengths. The study showed that the difference can be as big as a factor of three at a wavelength of 467 nm. Preferably, AAEs could be determined from measurements performed in a suspended state.

The need to manually change the filters in a PSAP can be a limiting factor when the instrument is deployed at seldom-visited locations or in highly polluted areas. By diluting the sample air, in addition to data post-processing, this limitation can be overcome and still show a correlation coefficient of 0.9 in comparison to an instrument that automatically changes filters (**Paper II**). Moreover, it was highlighted in the study that the correlation between the PSAP and the MAAP did not deteriorate much for filter transmittances in the range 0.4–0.7 in comparison to 0.7–1.0. The study, therefore, implies that correction functions could be developed for a wider filter transmittance range than 0.7–1.0.

Measurements of light absorption by the aerosol within the city of São Paulo (**Paper III**) showed that light absorption is closely related to the diurnal cycle of the traffic and boundary layer conditions. The average SSA of the São Paulo aerosol was shown to be lower than the values reported for megacities in south-east Asia. However, as suggested in **Paper III**, further studies are required downwind of the city to determine how the SSA evolves to be able to predict the radiative

forcing implications of the city on a regional scale. Through the analysis of new particle formation events, it was found that only a small fraction of the condensable vapours could be attributed to sulphuric acid. The low contribution of sulphuric acid to particle growth is not unexpected since bioethanol does not contain sulphur, and therefore blends of gasoline and bioethanol contain less sulphur than gasoline alone. The study further showed that Beijing and New Delhi in particular have far worse air quality issues than São Paulo (**Paper III**)

At the remote site in Hyytiälä (**Paper IV**), the characteristic peak in light absorption coefficients was not observed since no major city is in proximity to the site. The diurnal behaviour of light absorption by aerosol particles at the site followed the expected pattern of the daily boundary layer evolution, which is strongest during the summer. A greater SSA during the summer was argued to be a result of secondary organic aerosol (SOA) that originates from the surrounding forest. In general, both light absorption and light scattering coefficients were found to be higher in urban areas than at remote locations. The general trend is expected since both wet and dry deposition in addition to dispersion of pollutants will contribute to lower aerosol particle number concentrations at sites that are distant from pollution hot-spots.

The seasonal cycle at Hyytiälä showed the highest scattering and absorption coefficients during winter and lowest absorption and scattering coefficients during summer and autumn, respectively. On the South African Highveld (**Paper V**) a similar trend in light absorption was observed and was also attributed to combustion of fossil fuels in winter and boundary layer mixing in summer. The back-trajectory analysis of **Paper IV** showed that high values of both scattering and absorption were associated with air masses originating south of the Baltic Sea, a region more densely populated than Scandinavia.

In **Paper IV**, it was also noted that the SAE of the aerosol did not always follow the expected behaviour that low SAE is indicative of large particles and vice-versa. A number of weighted mean diameters were investigated. It was found that the count mean diameter (CMD) of the aerosol number size distribution had the opposite behaviour of what was expected. Thus, the study concluded that the closest connection between SAE and a weighted average at that site was the scattering coefficient mean diameter (ScMD) due to the multimodal characteristics of the aerosol.

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