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Technique and theoretical approach for quantifying the hygroscopicity of black-carbon-containing aerosol using a single particle soot photometer

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ABSTRACT

A single particle soot photometer (SP2), an instrument that measures the optical size and refractory black carbon (BC) mass content of individual aerosol particles, was modified to include a compact humidification system, described here. This permits quantification of water uptake by BC-containing particles, an important process that can affect their optical properties and lifetime. A Mie and κ-Köhler theory framework was developed to relate measured humidity-dependent changes in BC aerosol optical size to the hygroscopicity parameter (κ) of the non-BC content in the particles (which is responsible for water uptake by these particles). Laboratory testing of this experimental and theoretical system with both homogeneous non-light-absorbing particles and BC-containing particles was carried out. Agreement between the theoretical predictions and laboratory measurements for the homogenous aerosols validates the experimental methodology. For BC with a 70-nm thick coating of ammonium sulfate, reasonable agreement (equivalent to ~20% in κ) between measurements and theoretical predictions were observed over a span of RH from 70% to 90%. Two SP2s were configured to sample in parallel, one dry and one humidified, permitting continuous monitoring of water uptake by BC-containing aerosol. Operational refinements in SP2 setup to optimize the optical size measurement of BC-containing aerosol, and the consistency between the two SP2s are presented. This system was flown on the NASA DC8 research aircraft during the 2012 DC3 and 2013 SEAC4RS campaigns, providing engineering data included here that demonstrate the system's performance under challenging sampling conditions. Finally, SP2-scattering lookup tables used in the theoretical portions of this work are provided for reference.

1. Introduction

Black carbon (BC), the most strongly light-absorbing component of combustion-generated aerosol, is a significant forcer of global climate (Boucher et al., 2013; Bond et al., 2013) and, at high concentration, a detriment to human health (Highwood

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and Kinnersley, 2005). BC is believed to affect climate in many different ways, including through its direct absorption, its evaporation of clouds (the semi-direct effect), its effect on atmospheric vertical stability, and possibly through its action as a seed particle for cloud condensation or ice nucleation activity (the indirect effect). Contemporary climatological models have trouble predicting BC concentrations and vertical distributions (Koch et al., 2009; Schwarz et al., 2013). This problem is largely attributed, in the upper troposphere and remote atmosphere, to lack of model success in predicting BC removal via wet precipitation (Schwarz et al., 2010; Wang et al., 2014b). In wet precipitation, BC removal may depend strongly on the amount of water-active material internally mixed with the BC mass fraction (which is insoluble in water), as the non-BC fraction will affect particle hygroscopicity. For both dry and wet deposition, BC-containing particle size is an important parameter affecting loss rate (Spackman et al., 2010; Moteki et al., 2012; Wang et al., 2014a), and one that can depend on relative humidity. Depending on the source of the BC, and its co-emitted species, the timescales for accretion of non-BC materials can change, also affecting BC-containing aerosol optical properties and lifetime (Stier et al., 2006).

In addition to potentially affecting BC lifetime, hygroscopic internally mixed material with BC has the potential to influence BC light-absorption, through radiation lensing effects. Redemann et al. (2001) estimate that water uptake by sulfate on BC can nearly double BC light absorption at very high RH (for example near or in clouds). Hence, there is a need for experimental techniques that can quantify water uptake by BC-containing particles, to support improved model prediction capabilities, and to elucidate the impact of this mechanism on BC-containing aerosol optics and size in the atmosphere.

At present there are several effective methods for quantifying the water activity of total ambient aerosol that are not specific to BC-containing particles. These include examination of the shift in aerosol mobility diameter with relative humidity (RH) via hygroscopic tandem differential mobility analyzers (H-TDMA, for a review see Swietlicki et al., 2008); observation of droplet activation by individual particles as a function of water vapor supersaturation (using cloud condensation nuclei counters, e.g., Roberts and Nenes, 2005); and measurement of the relative change in aerosol scattering or extinction at an elevated RH in comparison to a lower reference RH (this is called the scattering or extinction enhancement factor (f(RH)), and has been determined with both cavity ring-down instruments and nephelometers, e.g. Langridge et al., 2011; Zieger et al., 2010). However, as BC typically makes up only a few percent of accumulation-mode aerosol mass, techniques that are not specific to BC-containing particles offer almost no specific information about materials mixed with BC. For this reason, McMeeking et al. (2011) have used a humidified tandem DMA in conjunction with a dry single-particle soot photometer (SP2, Droplet Measurement Technology, Boulder, CO) to resolve humidification impacts on the mobility of BC-containing particles. This approach is promising for ground-based measurements, yet the signal reduction caused by the DMA likely reduces its time resolution too severely for consideration for measurements made from high-speed aircraft.

Here we present a new approach to evaluating water uptake by BC-containing particles using a humidified SP2, with the promise of high temporal resolution that would allow effective deployment on aircraft as well for stationary or low-time resolution sampling. To this end, a compact humidification system has been developed and integrated in an SP2, allowing automated control of sample aerosol RH (discussed in Section 2, with details about instrument optimization).

Determination of the shift in optical size of BC-containing aerosol with RH constrains the aerosol's hygroscopicity. However, to separate the contributions to scattering of the BC and non-BC materials in individual particles, a theoretical approach associating aerosol parameters (including size, index of refraction, and the water hygroscopicity parameter, κ) with scattering signals observed from individual particles in the SP2 has been assembled relying on κ-Köhler (Petters and Kreidenweis, 2007) and Mie theories. Section 3 presents these theories applied both to non-absorbing homogeneous particles and BC-containing particles, while results of laboratory testing are presented in Section 4. The results indicate that these theories perform reasonably well in predicting SP2 observations on known aerosol.

There are two ways to allow comparison of optical sizes measured at different RHs; RH can be varied in time, or two systems can run in parallel with different RH. For high time resolution, the latter is preferred. Hence, we have operated two SP2s, at different RH, in parallel. This combined system, called the “Humidified Dual SP2” (HD-SP2) has flown on the NASA DC8 research aircraft as part of the NSF Deep Convective Clouds and Chemistry Experiment (DC3, 2012) and NASA Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC^{4}RS, 2013) missions. Section 5 discusses the specific issues associated with establishing optical-sizing consistency between two SP2s and presents an assessment of HD-SP2 performance on the aircraft.

A summary of the performance and primary uncertainties in the technique can be found in Section 6.

2. Experimental setup

2.1. The single particle soot photometer

The single particle soot photometer (SP2) has been carefully assessed for its ability to quantify both the BC mass content and total-particle optical size of individual particles (Slowik et al., 2007; Gao et al., 2007; Cross et al., 2010; Laborde et al., 2012). The nomenclature surrounding the term “black carbon” has historically been confused, hence “refractory black carbon” (rBC) is used for the material specifically quantified by the SP2, as recommended by Petzold et al. (2013). rBC is experimentally equivalent to correctly measured “elemental carbon” via the thermal-optical transmittance method (Kondo