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Closure study on measured and modeled optical properties for dry and hydrated laboratory inorganic aerosols with mixtures of dicarboxylic acids

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HIGHLIGHTS

- A lab-based closure study of inorganic salts/dicarboxylic acids was conducted.
- Impacts of POM on aerosols' optical/hygroscopic properties were investigated.
- Closure between measured and modeled aerosol's hygroscopic/optical properties was achieved.

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ABSTRACT

A laboratory-based closure study was completed to compare measured and modeled optical properties and their dependence on controlled relative humidity (RH) for inorganic salts, dicarboxylic acids, and their mixtures. The closure between measured and modeled values of the light scattering coefficients were evaluated by calculating the average relative difference (ARD) values, which revealed agreement within 8.0% for the total scattering (σ_{sp}) and 14.8% for the back scattering (σ_{bsp}) values at dry RH conditions for all test aerosols. These ARD values were less than the total relative uncertainty based on the measurement and modeling approaches, indicating the achievement of closure for σ_{sp} and σ_{bsp}. Optical properties derived from σ_{sp} including: (1) the hygroscopic growth factor, $f_{\sigma_{sp}}$, (2) the backscatter ratio, b, and (3) the Ångström exponent, $å$, were also compared with measured values. The ARD values between corresponding measured and modeled results for these derived optical parameters ranged from 0.1% to 30.8%. The impact of particulate organic matter (POM) on optical and hygroscopic properties of the aerosols tested here was also compared to the aerosol optical and composition measurements that occurred during the New England Air Quality Study-Intercontinental Transport and Chemical Transformation field campaign. Such comparison confirmed that a larger POM mass fraction resulted in less hygroscopicity for both the ambient and the laboratory aerosols. This study evaluated closure between laboratory measurements and model calculations and validated the reliability of the measured and modeled results with the closure analysis. Therefore, Mie-Lorentz model can be used to calculate the optical properties and their dependence on RH for other aerosols with more confidence.

1. Introduction

Atmospheric aerosols influence the radiation balance of the Earth by scattering and absorbing radiation (direct effects) (Yu et al., 2006; Morgan et al., 2010). According to the Fourth Assessment Report (AR4) of Intergovernmental Panel on Climate Change (IPCC), anthropogenic contributions to atmospheric particulate matter (PM) together produce a cooling effect, with a total direct aerosol radiative forcing (DARF) of −0.5 (−0.9 to −0.1) W m^{-2} (IPCC, 2007). However, the level of scientific understanding for DARF is described as "medium-low" according to the AR4. The associated uncertainty on the magnitude of DARF is high mainly because aerosols vary temporally and spatially in their chemical and optical properties. Individual particles contain a large number of chemical constituents and their compositions vary with particle

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size. Particulate organic matter (POM) represents a significant mass fraction (20%–90%) of the sub-μm diameter particulate matter (PM) (Kanakidou et al., 2005). Zhang et al. (2007) reported that POM comprised a major mass fraction (18%–70%, with an average of 45%) of the non-refractory sub-μm diameter particle mass at select locations in the Northern Hemisphere. However, knowledge of the aerosol's POM remains relatively unclear since characterization of POM species is more complex than that of particulate inorganic matter due to the difficulty of sampling and analyzing POM, although measurement techniques have improved with time (Jimenez et al., 2009; Zhang et al., 2011).

Relevant to this study, aerosols containing POM are observed to exhibit different optical and hygroscopic properties than pure inorganic particles, with corresponding implications for visibility and climate (Mazurek et al., 1997; Maria et al., 2004). Some publications have suggested that organics, most of which are sparingly soluble compounds or surfactants, reduce growth in particle size and evaporation rate compared to pure inorganic compounds (Dusek et al., 2010; Shi et al., 2012). In contrast, it has been reported that organic material can either positively or negatively affect the hygroscopicity of inorganic aerosols, depending on the chemical composition and mixing state (Cruz and Pandis, 2000; Choi and Chan, 2002). Tolbert and coworkers have discussed the dependence of the optical properties of the particles that composed of internal mixtures of water-soluble inorganic matter and organic compounds on relative humidity (RH) by performing laboratory experiments to examine the connection between aerosol light extinction, chemical composition and hygroscopicity for those particles: Wise et al. (2003) found that the presence of soluble dicarboxylic acids at the eutonic proportion depressed hygroscopic growth while the presence of low-solubility dicarboxylic acids at the eutonic proportion had no effect on the hygroscopic growth, comparing with pure ammonium sulfate; Garland et al. (2005) suggested that even if insoluble organic substances (e.g., palmitic acid) coat salt particles (e.g., ammonium sulfate) in the atmosphere, there might be relatively little effect on the resulting water uptake and loss; Baynard et al. (2006) presented results for mixtures of sodium chloride and ammonium sulfate with a few dicarboxylic acids and revealed that the RH dependence of aerosol light scattering was most sensitive to aerosol composition and size, while the influence of the mixing state was small; Freedman et al. (2009) found that the real refractive indices of internal mixtures of succinic acid and ammonium sulfate were higher than either of the pure components at the highest organic weight fractions, while for binary internal mixtures of oxalic or adipic acid with ammonium sulfate, the real refractive indices of the mixtures were approximately the same as ammonium sulfate for all organic weight fractions. Additionally, the magnitude of uncertainty in DARF also increases when considering that aerosol optical properties can be affected by the ambient RH (Garland et al., 2007; Fierz-Schmidhauser et al., 2010). Therefore, it is important to characterize the optical and hygroscopic properties of internally mixed PM with more certainty with the completion of laboratory closure studies.

Closure studies have provided improved credibility of results from measurements and models that describe aerosol properties. In particular, closure studies about the optical and hygroscopic properties of PM are of interest to better understand the quality of those results that can then be used to better understand the influence of PM on climate forcing. Kus et al. (2004) evaluated closure for the optical properties of select laboratory generated polydisperse PM at dry and hydrated states. Closure between measured and modeled values of the total light scattering coefficient (σ_{sp}, (m^{-1})), backscatter ratio (b) described by the backscatter coefficient (σ_{bsp}, (m^{-1})) divided by σ_{sp}, and Ångström exponent ($å$) for dry PM was achieved within 0%–5%, 4%–15%, and 3%–17%, respectively. The values of hygroscopic growth factor in terms of σ_{sp} values at a controlled RH value relative to its value at a low reference RH (dry) value, $f_{\sigma_{sp}}(RH, RH_{Ref})$, b, and $å$ at 80% RH agreed within 2%–27%, 1%–14%, 1%–28%, respectively. However, this closure study was limited to inorganic aerosols. Malm et al. (2000a, 2000b, 2003) compared the measured and the modeled optical properties of ambient PM including dry σ_{sp} and $f_{\sigma_{sp}}$ values. They estimated the amount of light scattering at a specific RH associated with individual species using a statistical model and obtained the light scattering efficiency by organic compounds. These results are very useful. However, this approach relies on measurements of σ_{sp} and mass concentrations of ambient aerosol species, not on any assumptions concerning modeled growth or which organic species were hygroscopic.

Choosing appropriate species of PM for laboratory studies can reduce the associated uncertainty and complexity involved in a closure study to better understand the optical and hygroscopic properties of atmospheric aerosols. Common atmospheric inorganic species containing sulfate, nitrates, and ammonium have been characterized (Kus et al., 2004; Hand et al., 2010; Mack et al., 2010). Characterization of organic PM and their mixtures with inorganic material, however, are more complicated due to the challenges that exist to characterize/speciate organic material in ambient PM.

A subset of low molecular weight (C3–C5) dicarboxylic acids were chosen for this study because they contribute 10% or more by mass of water-soluble organic compounds (WSOC) (Miyazaki et al., 2009; Pavuluri et al., 2010) and these WSOC compounds represent the dominant identified compound class (Yu et al., 2005). Hence, the following PM were investigated in this study: (1) inorganic salts including sodium chloride (NaCl) and ammonium sulfate (AS, $(NH_4)_2SO_4$); (2) dicarboxylic acids including glutaric acid (GA, $C_5H_8O_4$), malonic acid (MA, $C_3H_4O_4$), and succinic acid (SA, $C_4H_6O_4$); and (3) the mixtures of these species at select inorganic/organic fractions. GA, MA and SA were specifically chosen because they are abundant dicarboxylic acid and represent soluble (i.e., GA and MA) and sparingly soluble (i.e., SA) organic solutes in water (Choi and Chan, 2002). The physical properties for the test PM in this study are dry density, solubility and dry refractive index (Table 2 as reported in Wang and Rood (2008)).

The primary goal of this research is to evaluate optical and hygroscopic closure for laboratory mixtures of inorganic salts and low molecular weight dicarboxylic acids during carefully controlled scanning RH conditions. Such effort was completed through a closure study that compared measured to modeled light scattering values for laboratory generated particles at dry and controlled increasing and decreasing RH conditions. Measured dry particle size distributions, reagent grade solutes, and thermodynamic data were used with Mie-Lorentz theory to model the optical and hygroscopic growth of these PM. These laboratory results were also compared for consistency to ambient field measurements that occurred along the northeast coast of North America during 2004. With this closure study, the reliability of the measured values and the model "BHMIE" will be validated by comparing measured and calculated relevant optical properties of inorganic/organic mixed aerosols.

2. Methods

2.1. In-situ detection of aerosol optical properties

The extensive optical properties, σ_{sp} and σ_{bsp}, were measured with an RH-scanning nephelometry system (humidograph) operated with increasing and decreasing RH conditions between 30% and 86% (the minimum and maximum RH values varied depending on the actual measuring conditions for each individual RH scan).