Review article

Effect of hygroscopic growth on the aerosol light-scattering coefficient: A review of measurements, techniques and error sources

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HIGHLIGHTS

- Uncertainty in f(RH) is 20–40% for moderately hygroscopic aerosols.
- Assumption of no growth at RH<40% contribute to higher uncertainty.
- High variability in measured f(RH) values.
- Highest f(RH) values in clean marine environments.

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ABSTRACT

Knowledge of the scattering enhancement factor, f(RH), is important for an accurate description of direct aerosol radiative forcing. This factor is defined as the ratio between the scattering coefficient at enhanced relative humidity, RH, to a reference (dry) scattering coefficient. Here, we review the different experimental designs used to measure the scattering coefficient at dry and humidified conditions as well as the procedures followed to analyze the measurements. Several empirical parameterizations for the relationship between f(RH) and RH have been proposed in the literature. These parameterizations have been reviewed and tested using experimental data representative of different hygroscopic growth behavior and a new parameterization is presented. The potential sources of error in f(RH) are discussed. A Monte Carlo method is used to investigate the overall measurement uncertainty, which is found to be around 20–40% for moderately hygroscopic aerosols. The main factors contributing to this uncertainty are the uncertainty in RH measurement, the dry reference state and the nephelometer uncertainty. A literature survey of nephelometry-based f(RH) measurements is presented as a function of aerosol type. In general, the highest f(RH) values were measured in clean marine environments, with pollution having a major influence on f(RH). Dust aerosol tended to have the lowest reported hygroscopicity of any of the aerosol types studied. Major open questions and suggestions for future research priorities are outlined.

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1. Introduction

Atmospheric aerosols are able to scatter and absorb solar radiation. The magnitude of the radiative impact of these aerosol optical properties depends on size and composition of the particles as well as on the atmospheric conditions such as relative humidity (RH) and sun angle. Uncertainties in aerosol optical properties contribute to uncertainties in climate forcing and visibility estimates. Considerable research has taken place in the last several decades to investigate the role of atmospheric aerosol particles on

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the Earth's radiative balance and, additionally, has motivated regulatory efforts to mitigate their contribution to degradation of visibility and air quality.

The scattering enhancement factor, $f(RH)$, describes the dependence of the aerosol light-scattering coefficient, $\sigma_{sp}(\lambda)$, on relative humidity, RH. $f(RH)$ is calculated as the ratio of the scattering coefficient at a certain RH to the corresponding dry (or reference) scattering coefficient. The scattering enhancement factor, which is the focus of this review, is dependent on the aerosol chemistry and size distribution (e.g., Zieger et al., 2013). Depending on their size and composition, aerosol particles can take up water, which increases their size relative to their dry equivalents, leading them to scatter more light because of the increase in the particle cross section. Particle composition is important because it determines the refractive index and the hygroscopic nature of the particles. In addition to a change in size, wet particles will have different refractive indices and angular scattering properties than their dry counterparts.

Aerosol particles can be characterized as a function of their hygroscopicity. Some pure aerosol species like soot or mineral dust are insoluble and do not grow significantly in diameter with increasing RH (e.g. Weingartner et al., 1997; Sjogren et al., 2007). In contrast, other aerosol species like sulfuric acid, H_2SO_4, and some organics are soluble and do take up water. These particles are hygroscopic and they grow or shrink smoothly as the RH increases or decreases. A third type of hygroscopic growth is exhibited by deliquescent aerosols like sodium chloride, NaCl, or ammonium sulphate, $(NH_4)_2SO_4$, which experience a sudden phase transition from solid to liquid at a defined RH. The RH at which the phase transition occurs is called the deliquescence relative humidity (DRH); DRH is a characteristic of the specific chemical compound (Orr et al., 1958). Once the RH is above the DRH and the particle is mainly liquid, exposing the particle to decreasing RH does not result in recrystallization at the DRH; rather, crystallization occurs at a RH below the DRH. The RH at which recrystallization occurs is called the efflorescence relative humidity (ERH). Because the DRH and ERH are different, deliquescent aerosols can exist in two different phases at the same RH when that RH is greater than ERH but less than DRH. The curve describing the deliquescent aerosol state as a function of RH is termed the hysteresis loop (Orr et al., 1958). The RH history of an air parcel along with the knowledge of the composition and size of aerosol particles within that parcel are important because they define what fraction of the atmospheric aerosol is present as liquid droplets. The liquid fraction scatters much more light than its corresponding solid fraction (e.g. Toon et al., 1976; Sloane, 1984).

In-situ measurements of aerosol scattering coefficients are usually performed at RH below 30–40% (WMO/GAW, 2003). This means that the in-situ aerosol scattering measurements are not representative of ambient conditions. Therefore, knowledge of the scattering enhancement due to water uptake is necessary to transform dry measurements into more relevant ambient measurements. This is important for comparison and validation of remote sensing with in-situ measurements (e.g., Andrews et al., 2004; Zieger et al., 2011, 2012; Estéve et al., 2012; Sheridan et al., 2012; Tesche et al., 2014), and for calculation of the direct aerosol radiative forcing (e.g., Pilinis et al., 1995; IPCC, 2013). Currently, aerosol-cloud interactions represent one of the largest uncertainties in estimating the effects of aerosol on radiative forcing (IPCC, 2013). One key parameter for this estimate is to determine what fraction of aerosol particles can act as cloud condensation nuclei (CCN) and form cloud droplets. Several parameterizations have been proposed in the literature to estimate CCN from ancillary information; i.e. aerosol optical properties (Jefferson, 2010), chemical composition (Ervens et al., 2010) or scattering enhancement factor (Ervens et al., 2007). Ervens et al. (2007) reported reliable predictions of CCN number concentration using $f(RH)$ for supersaturations higher than 0.3%, and a poor agreement between measured and predicted CCN for low supersaturations.

$f(RH)$ can be obtained from nephelometry measurements made at different RH conditions (e.g. Covert et al., 1972) or from visibility measurements at ambient RH and dry scattering measurements (e.g. Liu et al., 2008). Gordon et al. (2015) presented a novel open-path aerosol extinction cavity ringdown spectrometer which allows determining the extinction enhancement factor at high relative humidity (RH>90%). Recent studies have reported backscattering enhancement factors determined with remote-sensing techniques, such as combined lidar and radiosounding RH measurements (e.g. Granados-Muñoz et al., 2015; Fernández et al., 2015). Alternatively, estimates of $f(RH)$ can be computed by applying Mie theory to aerosol size distributions with assumptions about chemical properties and measured growth factors (e.g., Adam et al., 2012; Zieger et al., 2013). The drawback of using HTDMA (Humidified Tandem Differential Mobility Analyzer) size distribution data to estimate $f(RH)$ is that the coarse mode is not considered and coarse mode aerosol (e.g. sea salt) can have a significant effect on scattering enhancement factors (Zieger et al., 2011, 2014).

In this work, we will focus on aerosol scattering enhancement factors determined using nephelometry techniques which have been in use since the 1960s. A detailed description of various humidified nephelometer system design is presented. The possible sources of discrepancy in $f(RH)$ among studies are discussed and the uncertainty of $f(RH)$ measurements is estimated. In addition, we perform a survey of aerosol scattering enhancement factors for various aerosol types that were measured under a variety of atmospheric conditions, from pristine environments to urban regions around the globe.

2. History and development of humidified nephelometers

There have been many types of humidograph systems deployed over the years. Here, we describe some of the key variations, including number of nephelometers, flow path through nephelometers and method of conditioning aerosol sample to vary RH, among others. Where relevant, limitations of each system and/or the specific experimental conditions affecting determination/uncertainty of $f(RH)$ are noted.

The first humidified nephelometer was built by Pilat and Charlson (1966). This device was used to measure the RH dependency of light scattering by polydisperse NaCl particles in the laboratory. The aerosol sample was heated to 50 °C and then mixed with a stream of moist air and a stream of dry air. By changing the flow rates of both streams the desired humidity was achieved.

Another humidification system for a nephelometer was developed by Covert et al. (1972). As in the device of Pilat and Charlson (1966), the variation of the RH of the aerosol sample was achieved by addition of a controlled, warm and moist air stream. This air stream was then introduced in a mixing chamber under highly turbulent flow conditions in order to achieve a uniform RH aerosol sample. After the mixing chamber, the aerosol passed through a series of chambers of different volumes to allow growth to equilibrium sizes at a given RH, before the scattering coefficient was measured with a nephelometer. The RH in the nephelometer was calculated from a temperature and dew point sensor located in the scattering chamber. The system of Covert et al. (1972) was able to change the RH from 20 to 90% in 4 min. This short scan time is appropriate in order to sample homogeneous atmospheric aerosol, especially when using only one nephelometer. However, for such large changes in RH in such a small time, the RH sensors need to have a very fast time response, which is difficult to achieve even