Effect of hygroscopic growth on the aerosol light-scattering coefficient:

A review of measurements, techniques and error sources

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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.

Keywords: scattering enhancement, water uptake, hygroscopicity, aerosol light scattering.
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 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, $\text{H}_2\text{SO}_4$, 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, $\text{NaCl}$, or ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, 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.,
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 extinction 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; Zieger et al., 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 minutes. 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 using dew point sensors [Fierz-Schmidhauser et al., 2010a].

Rood et al. [1985] found that the mixing of the dry and moist air with the aerosol stream (as in Pilat and Charlson [1966] and Covert et al. [1972] humidification systems) lead to a brief exposure of the particles to a RH greater than the final RH value measured inside the nephelometer. This made it difficult to accurately resolve the DRH. Another inconvenience of diluting the sample with air at the desired RH was that it reduced the aerosol concentration resulting in a decreased detection signal, problematic in the case of low aerosol concentrations such as might be found in remote or background environments.

In order to avoid dilution of the aerosol sample with dry and moist air, Rood et al. [1985], developed a humidifier in which the sample air was passed through a hollow cylinder with the inside wall covered with nylon mesh and wetted with a H₂SO₄ solution. The wetted wall was gradually heated such that the amount of heat flux through the wall controlled the increasing dew point temperature of the aerosol. The air stream exiting the humidifier was rapidly heated to a peak temperature of 60 °C and then cooled to ambient temperature prior to entering the nephelometer. In the heating section, the RH decreased to
<20% due to the increased temperature. Such a decrease in RH was sufficient to effloresce the previously deliquesced particles, ensuring the particles were on the lower portion of the hysteresis loop. Subsequent cooling increased the aerosol RH to its final value. Particles passing through the cooling chamber experienced a range of RH values depending on the cooler’s temperature. Near the exit of the cooling chamber, the temperature of the aerosol sample returned to room temperature but did not drop below that temperature. Therefore, nowhere in the system had the particles been exposed to a RH greater than that within the nephelometer [Rood et al., 1985]. This prevented particles undergoing deliquescence before reaching the nephelometer and enabled investigation of the hygroscopic behavior of dry particles exposed to increasing RH. Rood et al. [1987] used three nephelometers operated in parallel: one measuring at dry conditions, one measuring at ambient conditions (without conditioning) and the third measuring at enhanced RH after passing through the humidifier described above.

In the set-up of Koloutsou-Vakakis [1996] and Koloutsou-Vakakis et al. [2001] two nephelometers were operated in parallel. One nephelometer measured the scattering coefficient of the ambient aerosol at RH<40% and the second nephelometer scanned through a series of RH values generated by a humidifier placed before the nephelometer. The humidifier was an annular system, in this case consisting of a Teflon membrane supported on a cylindrical stainless steel mesh inside a larger stainless steel tube. Water circulated in the concentric space between the stainless steel tube and the Teflon membrane while the aerosol sample flowed within the mesh. The Teflon membrane allowed transport of water vapor to the aerosol. The amount of water vapor that passed into the aerosol stream was determined by controlling the temperature of the water. This humidifier represented a great improvement with respect to previous designs since it eliminated direct
contact of liquid water with the aerosol flow and avoided the need for dilution to control the RH of the aerosol particles, thus preventing exposure of the aerosol particles to air that is not of the same composition as the ambient air. Currently, the University of Granada, UGR [Titos et al., 2014b] and ESRL-NOAA (Earth System Research Laboratory, National Oceanic and Atmospheric Administration) operate very similar humidifiers; however, in the NOAA humidograph system the nephelometers are operated in series with the humidifier in between [Sheridan et al., 2001; Zhang et al. 2015].

Carrico et al. [2000] further improved the humidification system developed by Koloutsou-Vakakis [1996] by using Peltier thermoelectric coolers. With these coolers, RH>80% was achieved locally upstream of the scanning nephelometer while performing decreasing RH scans within the nephelometer. Thus, this system allowed for investigation of the decreasing RH branch of the hysteresis loop. Similar to Rood et al. [1985], Carrico et al. [1998; 2000] also reported that the highest RH was achieved before the nephelometer in their set-up. To compensate for this effect, Carrico et al. [1998] experimentally measured DRH values for laboratory generated aerosols (NaCl and (NH₄)₂SO₄) and compared their results with literature values. The difference between measured and literature DRH values was attributed to heating within the nephelometer. They determined that heating resulted in a temperature increase of the sample volume of 1.5 ºC. Carrico et al. [1998] used this temperature change to calculate the correct RH within the nephelometer over the entire range of controlled RH measurements and found that the measured and literature DRH values agreed within 2% RH after taking the temperature difference into account.

Day et al. [2000] used a different technique to control the RH of the air sample in their single nephelometer humidograph system. The aerosol sample entered an array of 23
Perma Pure diffusion drying tubes, which were mounted in parallel, after passing through a cyclone that removed particles larger than 2.5 µm in diameter. The diffusion drying tubes consisted of an inner tube of Nafion through which the aerosol sample flowed and an outer tube of stainless steel through which purge air flowed. The RH of the aerosol sample could be increased or decreased depending on the RH of the purge air. After this RH conditioning, the aerosol sample was drawn into a plenum where the RH and temperature of the aerosol sample were continuously monitored and then passed to the nephelometer. This humidification system was able to achieve relative humidity values in the range 5-95%. In order to have accurate measurements of RH, Day et al. [2000] kept the temperature of the aerosol sample nearly constant by housing the array of dryers in an insulated aluminum cylinder that was filled with water. Since the system controls the sample RH without excess heating, it is more likely to have minimized losses of volatile compounds.

Fierz-Schmidhauser et al. [2010a], at the Paul Scherrer Institut (PSI), built a humidification system that was able to identify when aerosol particles were in a metastable state (i.e., in the liquid phase below their DRH). In their system, the aerosol first entered a humidifier, which consisted of a Gore-Tex tube surrounded by a thin water layer in a temperature-controlled metal tube. Following the humidifier, the aerosol entered a dryer that consisted of a single Nafion tube (Perma Pure LLC). The aerosol flowed through the inner part of the tube and was dried by adjusting the flow of dry air on the outside of the Nafion tube. Then, the scattering coefficient was measured by the nephelometer at a controlled RH. A second, parallel nephelometer measured the scattering coefficient at dry conditions. Combined temperature and capacitive RH sensors were used throughout the system and inside the humidified nephelometer to measure air temperature and RH, respectively. In addition, Fierz-Schmidhauser et al. [2010a] installed a dew point sensor
inside the nephelometer to accurately calculate the RH inside the nephelometer. Nevertheless, due to the relatively long time response of the temperature sensor of the dew point mirror (up to several minutes) these RH readings were only applicable during constant RH conditions. During initial laboratory experiments Fierz-Schmidhauser et al. [2010a] observed a temperature difference of about 4.5 °C between the inlet and the sensing volume of the nephelometer at 16.6 lpm caused by the heat of the halogen lamp (75 W) used as the nephelometer light source. Consequently, the RH decreased from ~90% RH at the nephelometer inlet to about 70% RH in the sensing volume. This is a common issue in nephelometers with a halogen lamp light source [e.g. Carrico et al., 1998; Brem et al. 2012]. To reduce this temperature difference, Fierz-Schmidhauser et al. [2010a] placed an air-cooled infrared filter between the lamp and the sensing volume. In addition, on the outside of the sensing volume they placed cooling fins to enlarge the surface and four additional blowers to adjust the nephelometer’s temperature close to room temperature. Similarly, Brem et al. [2012] modified the nephelometer by using a halogen lamp with reduced wattage and by installing a hot mirror in front of the lamp to eliminate thermal radiation. Similar to the Rood et al. [1985] design, in the system of Fierz-Schmidhauser et al. [2010a] the highest RH was achieved before the nephelometer. As a consequence, this allowed for deliquescent particles to exist in two phases if their DRH had been exceeded at any point along the sampling path. These particles remained liquid even if the RH was subsequently lowered on the way to the nephelometer. Thus, in laboratory studies they observed that the deliquescence step change appeared at a lower RH than in the literature. Due to the limited drying capability of the dryer, the ERH could not be observed during their laboratory and ambient measurements [Fierz-Schmidhauser et al., 2010a].
Recently, Ecotech Pty Ltd. has developed a commercial humidified nephelometer tandem system (aerosol conditioning system ACS1000). In the ACS1000 the aerosol flow is split into two paths by an isokinetic flow splitter. The dry sample passes directly into one of the nephelometers to measure the scattering coefficient at dry conditions. The other sample is humidified to a predetermined RH set by the controller and then the scattering coefficient is measured using an additional nephelometer. The humidifier consists of two concentric tubes, the inner one is a Gore-Tex membrane tube surrounded by a thin Milli-Q water layer in a heatable metal tube. The RH can be increased from around 40% up to 90% with an accuracy of ±0.35% according to the manufacturer (http://ecotech.com/wp-content/uploads/2015/02/M010047-ACS-1000-User-Manual-1.0.pdf). The performance of the system using laboratory generated aerosols and its use for ambient measurements have not been addressed in detail in the literature. Zieger et al. [2015] reported a relatively good agreement between the PSI humidograph system described in Fierz-Schmidhauser et al. [2010a] and the Ecotech system during a recent deployment in Finland (see Section 4).

Scanning RH systems such as the ones described above have been widely used for ground-based measurements. Several research groups have also deployed humidification systems for nephelometers on airborne platforms [e.g. Hegg et al., 2008; Sheridan et al., 2012; Pekour et al. 2013]. However, due to variability in the aerosol and time needed to scan through a range of RH, scanning systems are not practical for airborne applications. Thus, airborne measurements are usually performed with fixed humidity systems, where two or three nephelometers measure aerosol scattering at fixed RH levels [Hegg et al., 2002]. Recently, Pekour et al. [2013] developed an airborne humidification system that used three integrating nephelometers to measure the scattering coefficient at three different fixed RH. The system of Pekour et al. [2013] consisted of a number of driers and
humidifiers enabling measurement of $f(RH)$ under hydration or dehydration conditions (always starting with the aerosol in a known state) with a simple system reconfiguration [Pekour et al., 2013; Shinozuka et al., 2013].

3 Humidogram parameterizations

For scanning RH measurements it is possible to develop a fit for the relationship between $f(RH)$ and RH. Many different equations have been used in previous studies. The simplest and most commonly used equation is the one parameter fit equation [e.g., Hänel, 1980; Kotchenruther and Hobbs, 1998; Gassó et al., 2000] initially introduced by Kasten [1969]:

$$f(RH) = (1 - RH/100)^{-\gamma}$$

(Eq. 1)

where $\gamma$ parameterizes the magnitude of the scattering enhancement. Sheridan et al. [2002] used a variation of the equation proposed by Kasten [1969] to include the RH of the reference (dry) nephelometer:

$$f(RH) = \left( \frac{1 - RH/100}{1 - RH_{ref}/100} \right)^{-\gamma}$$

(Eq. 2)

where RH and RH$_{ref}$ are the relative humidity measured inside the humidified and reference nephelometers, respectively.

The two parameter fit equation [e.g., Hänel, 1980; Carrico et al., 2003; Zieger et al., 2011] is similar to Eq. 1, but with an additional parameter, $a$, that represents the intercept at RH=0%:

$$f(RH) = a(1 - RH/100)^{-\gamma}$$

(Eq. 3)
Another variant of the two parameter fit equation is also be found in the literature [Kotchenruther and Hobbs, 1998; Carrico et al., 2003]:

\[ f(RH) = 1 + a(RH/100)^b \]  
(Eq. 4)

Fierz-Schmidhauser et al. [2010b] introduced a modified one parameter equation with the exponent fixed at a value of 7/3 for their measurements at Jungfraujoch:

\[ f(RH) = \left(1 + \frac{RH}{100 - RH}\right)^{7/3} \]  
(Eq. 5)

More complex multi-parameter equations have been proposed in the literature such as the three parameter fit equations used by Sheridan et al. [2001] (Eq. 6) and by Day et al. [2000] (Eq. 7):

\[ f(RH) = a(1 + b(RH/100)^c) \]  
(Eq. 6)

\[ f(RH) = \frac{d + eRH}{1 + hRH} \]  
(Eq. 7)

Polynomial fits have also been used to explore the relationship between \( f(RH) \) and RH. The IMPROVE (Interagency Monitoring of PROtected Visual Environments) network [IMPROVE, 2000], recommends the following best-fit formula for the hygroscopic enhancement of aerosol scattering coefficient as a function of RH:

\[ f(RH) = b_0 + b_1 \left(1 - \frac{RH}{100}\right)^{-1} + b_2 \left(1 - \frac{RH}{100}\right)^{-2} \]  
(Eq. 8)
Koloutsou-Vakakis et al. [2001] also proposed a polynomial fitting of \( f(RH) \) as a function of RH:

\[
f(RH) = 1 + A_1 RH + A_2 RH^2 + A_3 RH^3
\]

(Eq. 9)

Equations 1-9 describe the scattering enhancement due to monotonic hygroscopic growth fairly well. However, these equations do not reproduce the behavior of deliquescent aerosols across the entire humidity range for conditions of either increasing or decreasing RH. Kotchenruther et al. [1999] proposed the use of different fitting equations depending on the observed curve structure of the humidograms. For monotonic curves in which \( f(RH) \) varies smoothly with RH and follows similar pathways on the upper and lower branches of the hysteresis loop they proposed the use of Eq. 4. For deliquescent curves, Kotchenruther et al. [1999] introduced a new equation, Eq. 10, which is a combination of Eqs. 4 and 3 linked by a switch function where \( d \) represents the apparent DRH:

\[
f(RH) = \left[ 1 + a \left( \frac{RH}{100} \right)^b \right] \cdot \left[ 1 - \frac{1}{\pi} \left( \frac{\pi}{2} + \arctan \left( 1 \times 10^{24} \left( \frac{RH}{100} - \frac{d}{100} \right) \right) \right) \right]
\]

(Eq. 10)

Alternatively, Zieger et al. [2010; 2014] proposed fitting the humidogram curve for different RH ranges (e.g., RH<75% and RH>75%) using Eq. 3 to check for hysteresis behavior and deliquescence state by comparing \( \gamma_{RH<75\%} \) and \( \gamma_{RH>75\%} \).

We propose a new parameterization (Eq. 11) in which both sides of the equation are the same (albeit with potentially different constants \( a_i \) and \( \gamma_i \)) following Eq. 3 and are linked by the switch function in the square brackets. With this approach, the parameter \( d \) represents the apparent DRH point and \( \gamma_1 \) and \( \gamma_2 \) represent the scattering enhancement for...
the lower and upper ranges of RH. In addition, this equation provides information about aerosol hygroscopicity: if $\gamma_1 \sim \gamma_2$ then $f(RH)$ increases smoothly with RH while if $\gamma_1 \ll \gamma_2$ there is a sharp increase of $f(RH)$ after the DRH and the aerosol is likely deliquescent.

$$f(RH) = a_1 \left(1 - \frac{RH}{100}\right)^{-\gamma_1} \cdot \left[1 - \frac{1}{\pi} \left(\frac{\pi}{2} + \arctan\left(1 \times 10^{24} \left(\frac{RH}{100} - \frac{d}{100}\right)\right)\right)\right]$$

$$+ a_2 \left(1 - \frac{RH}{100}\right)^{-\gamma_2} \cdot \left[\frac{1}{\pi} \left(\frac{\pi}{2} + \arctan\left(1 \times 10^{24} \left(\frac{RH}{100} - \frac{d}{100}\right)\right)\right)\right]$$

(Eq. 11)

Measurements of $f(RH)$ at 550 nm performed with the University of Granada tandem nephelometer [Titos et al., 2014b] have been used to test the capabilities of the different equations. Figure 1 shows two study cases: case (a) corresponds with measurements of ambient aerosols whilst case (b) corresponds with laboratory measurements of ammonium sulphate. Note that the experimental DRH for ammonium sulphate is shifted to lower RH due to an increase in temperature inside the humidified nephelometer which leads to a decrease in sample RH. The data are fitted using the previous described equations (Eqs. 1 to 11). The $R^2$ and the root mean square error (RMSE) of the fits are also shown in Fig.1.

Case (a) shows a monotonic increase of $f(RH)$ with increasing RH. In this example, all the equations (except Eqs. 1 and 5) show very good agreement with measurements (i.e., $R^2$ values close to 1 and RMSE below 0.1). Case (b) shows the behavior of deliquescent aerosol with a transition in $f(RH)$ at around 70%. Equations 10 and 11 provide the highest $R^2$ and lowest RMSE and are able to reproduce the DRH step while the other equations are not able to satisfactorily reproduce the measurements. Thus, for deliquescent aerosols with negligible enhancement below DRH and a sudden transition at this humidity, Equations 10 and 11 provide the best results (Figure 1b). Eq. 11 has the advantage that the interpretation
of the fit parameters is more straightforward. Here, we have presented an approach for fitting \( f(RH) \) as a function of RH, however, the fit quality should be evaluated to test if the parameterization is suitable for each specific dataset.

[FIGURE 1]

4 Error sources in \( f(RH) \) measurements

Measurements of the scattering enhancement factor are usually performed using custom-made humidifier systems and commercial nephelometers. Differences in the experimental set-ups and measurement procedures may lead to differences in the reported \( f(RH) \) values. Although some published works have investigated the performance of the humidifier systems using laboratory generated ammonium sulphate and/or sodium chloride [e.g., Carrico et al., 2000; Fierz-Schmidhauser et al., 2010a] experimental intercomparisons between different humidifier systems are sparsely performed. Fierz-Schmidhauser et al. [2010a] showed the results of an intercomparison between the Paul Scherrer Institut (PSI) and the DOE/ARM (US Department of Energy Atmospheric Radiation Measurements) tandem humidograph systems. The agreement between \( f(RH) \) values derived from each system varied over the course of the study period but the differences were found to be significant (up to 25\% relative differences in \( f(RH) \)) for specific periods [Fierz-Schmidhauser et al., 2010a]. The authors attributed this difference to distinct RH histories in the two systems (in the PSI system the aerosol sample was exposed to a higher RH before the wet nephelometer than occurred in the DOE/ARM system) so during some periods the instruments were probing different branches of the hysteresis curve. This effect would be especially important for deliquescent aerosols. Other hypotheses for the observed differences were evaporation of semi-volatile substances in the sampling line or in the humidifier, due to different residence times and temperatures [Fierz-Schmidhauser et al.,
2010a]. As mentioned in Section 2, the ACS1000 humidifier system (Ecotech Pty Ltd) was also intercompared with the PSI humidified tandem nephelometer system at Hyytiälä, Finland. Zieger et al. [2015] reported that median f(RH=85%) values determined with both systems agreed within 6% at 525 nm wavelength but larger differences were observed during parts of the campaign. The possible reasons behind these discrepancies were not addressed.

The main sources of error in nephelometer humidographs f(RH) measurements contributing to the overall f(RH) uncertainty as well as to partially explain potential discrepancies between different experimental designs are losses in the humidifier system, insufficient time for reaching the equilibrium RH, and uncertainty in the RH values in the reference and humidified nephelometers, which will be discussed below.

4.1 Losses in the humidification system

Most publications have reported a good agreement between the reference and the humidified nephelometers when measuring scattering coefficients at dry conditions (typically RH<40%), however, these differences ranged from below 2% up to 10% for PM$_{10}$ scattering coefficients at ~550 nm wavelength, depending on the study [e.g. Carrico et al., 2000; Fierz-Schmidhauser et al., 2010a; Titos et al., 2014b]. Usually, the differences were attributed to sampling losses in the humidification system. These losses are higher for PM$_{10}$ than for PM$_{1}$ [e.g., Carrico et al., 2000; Carrico et al., 2003; Titos et al., 2014a], indicating higher losses for larger particles. If the nephelometers are operated in series instead of in parallel, the losses may be even higher. Anderson and Ogren [1998] observed differences around 7% and 1% for PM$_{10}$ and PM$_{1}$ size fractions, respectively, for nephelometers operated in series (without a humidification system).
Another potential issue that could lead to discrepancies in $f(RH)$ comparisons is the evaporation of semi-volatile substances in the sampling lines and in the humidifier depending on the aerosol particle chemical composition, particularly as heating is frequently used to control sample RH at various points in the system. Thus, the temperature of the sampled air should be kept below 40 °C to limit losses of semi-volatile species [Bergin et al., 1997; ten Brink et al., 2000].

Empirical corrections for losses based on the comparison between both the humidified and reference nephelometers at low RH (typically <40%) are commonly applied [e.g., Pan et al., 2009; Fierz-Schmidhauser et al., 2010b; Fierz-Schmidhauser et al., 2010c; Zieger et al., 2011; Titos et al., 2014a; Titos et al., 2014b]. However, a proper correction for such losses is a difficult task even at low RH due to the complex interplay between particle size, water uptake by particles, and different growth rates.

### 4.2 Residence time

Here, the residence time is defined as the average time that the aerosol spends in the humidification system. It is an important parameter because an insufficient residence time may not allow the aerosol particles to reach equilibrium at high RH. It has been shown that some organic/inorganic aerosol mixtures exhibit mass transfer limitations of water and may require residence times of a few seconds for equilibration at RH around 85% while pure inorganic salts equilibrate in less than 1 s [Sjogren et al., 2007; Duplissy et al., 2009]. In the PSI system, for example, the residence time during hydration is around 3 s at high RH while during dehydration this time is shortened to ~1 s [Fierz-Schmidhauser et al., 2010a]. In the NOAA system, the residence time is significantly shorter: ~0.2 s [Fierz-Schmidhauser et al., 2010a]. This difference in the residence time between the PSI and
NOAA systems could be partially responsible of the disagreement observed between the two systems during the intercomparison exercise [Fierz-Schmidhauser et al., 2010a].

4.3 Reference nephelometer RH values

Most authors reference the wet scattering coefficient to that measured below a certain low RH value (typically between 20-40%). To do this, the reference nephelometer is typically kept at RH below 40% (e.g., by gently heating the aerosol sample or by using Nafion dryers), although a constant reference RH in time is difficult to achieve. This approach assumes that there is no scattering enhancement below the reference RH value, which will not be true for many organic and marine influenced aerosol types [e.g., Zieger et al., 2015]. An incorrect assumption of no growth at low RH will result in underestimation of $f(RH)$ values. For this reason, the RH in the reference nephelometer should be kept as low as possible and be reported together with the $f(RH)$ value. Sheridan et al., [2001] calculated $\sigma_{sp}(RH_{ref}=40\%)$ using the lower branch of the $f(RH)$ curve and the derived fitting parameters to account for this effect. Alternatively the hygroscopic scattering enhancement can be studied in terms of the $\gamma$ parameter, which is not affected by the RH in the reference nephelometer, although the interpretation of $\gamma$ is not as intuitive as that of $f(RH)$.

Knowledge of the sample RH upstream of the humidifier is also important in order to know the state of the aerosol. This RH must be low enough to guarantee that it is below the ERH before entering the humidifier so the measured $f(RH)$ is on a known branch of the hysteresis curve. Otherwise, for deliquescent aerosols, the measured $f(RH)$ might correspond with the upper branch of the hysteresis curve. This can be an important issue at humid locations where it is difficult to reduce the sample RH and the aerosol is likely deliquescent.

4.4 Precise measurements of RH in the humidified nephelometer
Precise RH measurements at the point where the scattering is measured are needed in order to obtain accurate estimations of $f(RH)$. For scanning RH measurements, the response time of the RH sensor is an additional factor to consider. For TSI integrating nephelometers, the sample RH sensor has been shown to disagree with more accurate co-located RH sensors. In particular, Fierz-Schmidhauser et al. [2010a] reported that the TSI sensor overestimated RH by 15% at high RH. Titos et al. [2014b] reported a difference of 12% for RH>75% between RH measured with the TSI sensor and a co-located more accurate sensor placed inside the nephelometer chamber. However, without additional evaluation it is difficult to assess whether the TSI sensor is prone to overestimation or if, in these two reported cases, the TSI RH sensors had degraded since installation.

Some experimental designs do not have an additional RH sensor inside the nephelometer cell, but they have a RH sensor either directly upstream or downstream of the humidified nephelometer. This external RH measurement can be used to calculate the RH inside the nephelometer by assuming that the dew point temperature is constant between the nephelometer cell and the external sensor [Carrico et al., 2003; Jefferson, 2011; Titos et al., 2014a]. This assumes that any change in RH between the cell and the external sensor is due solely to temperature differences and no moisture is added or removed from the aerosol sample. This approach requires that the temperature sensor inside the nephelometer have a sufficient time response, is properly calibrated and is representative for the exact temperature at the point where the scattering of the aerosol particles is measured.

To verify the correct operation of the humidifier and to determine the true sample RH, the tandem nephelometer humidograph can be calibrated with laboratory aerosols of known size and composition and, thus, hygroscopicity. A frequent calibration with nebulized salts (e.g. with ammonium sulphate), collocated measured size distributions and
Mie calculations should be performed on a regular basis to ensure a proper measurement of \( f(RH) \). The theoretical \( f(RH) \) can then be derived using Mie theory and compared with the experimental values as shown by Fierz-Schmidhauser et al. [2010a]. Brem et al. [2012] present a detailed description of a laboratory set-up for measuring \( f(RH) \) which includes nephelometer modifications, precise RH determination and optical closure analysis.

5. Uncertainty analysis for \( f(RH) \) measurements

The main factors contributing to the overall uncertainty of the measured \( f(RH) \) are the uncertainty of the particle scattering coefficient measured by each nephelometer, the uncertainty of the RH measured inside the humidified nephelometer and the error of considering a reference RH>0% as dry. Estimations of \( f(RH) \) uncertainty are scarce; Adam et al. [2012] and Zieger et al. [2013] estimated the sensitivity of a Mie model for calculating \( f(RH) \). Zieger et al. [2013] reported a \( f(RH) \) error estimation of around 20%, by propagating the absolute error in RH (1.5-2%) and in the scattering coefficient (10%). In this work, we estimate the uncertainty of \( f(RH) \) using the Monte Carlo technique. The behavior of the instruments has been simulated assuming an absolute error in the RH measurement of 3% (typical error for RH probes, e.g., Vaisala) and a relative error in the scattering coefficient measurement of 9.2% for PM\(_{10}\) particles [Sherman et al., 2015]. The supplementary material of Sherman et al. [2015] provides a detailed assessment of scattering coefficient uncertainty updating previous work by Anderson and Ogren [1998].

To calculate \( f(RH) \) uncertainty, the dry scattering coefficient was selected as a random number between 1 and 200 \( \text{Mm}^{-1} \) where dry refers to RH=0%. This wide range of scattering coefficients was chosen to cover different atmospheric situations and aerosol loads. In order to take into account the measurement uncertainty in the simulated dry scattering coefficient, we introduce a measurement uncertainty of 9.2% [Sherman et al., 2015].
so the simulated final dry scattering coefficient is a random number (following a normal distribution) in the range \([\sigma_{sp} \pm 0.092*\sigma_{sp}]\).

The wet scattering coefficient cannot be simulated as a random number since it depends on the measured dry scattering coefficient. Thus, to simulate a realistic value, we calculated the wet scattering coefficient associated with the previously selected dry scattering coefficient using Eq. 1 and assuming that \(\gamma\) ranges from 0 to 1 in steps of 0.01. The chosen interval for \(\gamma\) covers the gamut from non-hygroscopic aerosol particles (\(\gamma\) equal or close to 0, as can be the case of soot or dust particles) to very hygroscopic particles with \(\gamma\) around 1 (e.g., marine aerosol). The \(\gamma\) parameter should be viewed here as a tool to simulate different aerosol types (from very hygroscopic to hydrophobic aerosols). Finally, we introduce a measurement uncertainty in RH of 3% and assume that the simulated wet scattering coefficient also has an uncertainty 9.2% [Sherman et al., 2015] so the final wet scattering coefficient is a random number (following a normal distribution) in the range \([\sigma_{sp}(RH) \pm 0.092*\sigma_{sp}(RH)]\). Once we have a simulated but realistic pair of scattering coefficients at wet and dry conditions, as they would be measured using two nephelometers, the scattering enhancement factor can be calculated.

This procedure was repeated 500 times using 9 random seeds spanning the entire range of \(\gamma\) and RH on each simulation, leading to a final matrix of around 70 million simulation cases (number of seeds over number of simulations over all RH over all \(\sigma_{sp}(dry)\)). Due to the configuration of the simulations, the number of points included in each bin is randomly distributed, showing no pattern, and is very similar for all the values considered.

The mean, standard deviation and error of \(f(RH)\) were calculated over all the simulations for each RH and \(\gamma\). The \(f(RH)\) error, \(\Delta[f(RH)]\), was estimated as the ratio
between the standard deviation and the mean, multiplied by 100. Figure 2 shows \( f(\text{RH}) \) error as a function of RH and \( \gamma \), calculated considering that the reference RH is 0% (Figure 2a) and that the reference RH is a random number in the range 0-40% (Figure 2b). Estimated errors of \( f(\text{RH}) \) are around 15-20% on average, reaching above 80% at RH of 95% and \( \gamma > 0.9 \). For moderately hygroscopic aerosols (e.g., \( \gamma \sim 0.5 \)), \( f(\text{RH}) \) errors are constrained below 40% even at high RH, which can be regarded as a conservative estimation and is quite large considering there are other factors contributing to \( f(\text{RH}) \) uncertainty (e.g., losses and residence time) that have not been considered in this approach. Assuming the aerosol is dry (no water uptake) at \( \text{RH} \leq 40\% \) might cause an underestimation of up to 25% in \( f(\text{RH}) \) for very hygroscopic aerosols (\( \gamma \sim 1 \)), even at low RH. For moderately hygroscopic aerosols (\( \gamma < 0.5 \)) the relative error is lower than 10-15%.

Zieger et al. [2013] and Adam et al. [2012] present uncertainty estimates using Mie theory which are consistent with the values reported here for moderately hygroscopic aerosols.

### 6 Literature review of ambient measurements of \( f(\text{RH}) \)

In this section we present a literature survey of \( f(\text{RH}) \) measurements performed over the last two decades in very different environments, where a variety of aerosol types predominate. Tables 1-4 report the aerosol light scattering enhancement factors classified according to dominant aerosol types: marine (Table 1), continental (rural and urban) (Table 2), dust (Table 3) and smoke (Table 4). The tables list the measurement location (and study name if appropriate), the study time period, the dominant aerosol type, the size cut, the \( f(\text{RH}) \) value, the RH range used to compute \( f(\text{RH}) \) and the reference. Most measurements were done with a PM\(_{10}\) size cut, although a variety of other size cuts were also used (e.g. PM\(_1\), PM\(_{2.5}\), PM\(_4\)). Because \( f(\text{RH}) \) depends on particle size, the size cut can be an important factor influencing
the magnitude of the measured $f$(RH). The distinction between different aerosol types was usually made by the authors according to air mass trajectories, wind sectors or the predominant chemical composition. Most $f$(RH) values are referenced to a high RH between 80 and 85%, a low RH (<40%) and to a wavelength $\sim$550 nm. Figure 3 summarizes $f$(RH) mean ($\pm$standard deviation) values for PM$_{10}$ size cut, extracted from Tables 1-4.

From Figure 3 and Tables 1-4 it is clear that $f$(RH) values have a strong variability among studies, even for similar aerosol type or conditions. In general, $f$(RH) values are larger for marine sites compared to other environments due to the high hygroscopicity of sea salt particles. $f$(RH) values for marine aerosols (Table 1 and Figure 3) span from values around 1.5 in Sagres [Carrico et al., 2000] to 3.5 in Cabauw for maritime air masses [Zieger et al., 2011]. Most publications report values for both clean marine and polluted marine conditions if applicable; $f$(RH) values tend to be lower for polluted marine situations than for clean conditions. Kotchenruther et al. [1999] reported an opposite behavior, with higher values for polluted than for clean marine conditions, due to enriched sulphate air masses from the anthropogenic sector. Additionally, several marine humidograph studies have obtained $f$(RH) for two size fractions and found that the $f$(RH) values are larger for PM$_1$ than for PM$_{10}$. This behavior as a function of size cut is more evident for clean marine than for polluted marine situations. Sheridan et al. [2002] reported higher $f$(RH) values for PM$_3$ than for PM$_1$, and the difference between $f$(RH) for different size cuts was more marked for clean marine conditions. Zieger et al. [2010] showed that compensating effects between size and hygroscopicity may have a profound effect on $f$(RH); i.e. small and less hygroscopic aerosol can have the same $f$(RH) as large and more hygroscopic aerosol.
Continental aerosol particles, at sites ranging from rural to urban (Table 2) exhibit lower $f$(RH) values than marine sites except for Melpitz and Jungfraujoch which have the largest $f$(RH) values of any of the continental measurements. The rest of the continental sites reported PM$_{10}$ $f$(RH) values below 2 (Figure 3) and exhibit low variability. One hypothesis for the large $f$(RH) values observed in Melpitz and Jungfraujoch is that the reference scattering was measured at a very low RH. Very similar values have been reported for urban aerosols in Granada, Lin’An and Xin’An. Studies reporting $f$(RH) values for clean and polluted conditions showed slightly higher $f$(RH) values for polluted continental aerosols [Yan et al., 2009; Chen et al., 2014]. Airborne measurements over a continental site showed decreasing $f$(RH) values with height during an extended aircraft campaign, with values around 2 in the planetary boundary layer and values lower than 2 in the free troposphere [Sheridan et al., 2012].

Dust particles are reported to be one of the atmospheric aerosol constituents with the lowest hygroscopicity. According to the studies reviewed in Table 3, $f$(RH) values for dust dominated situations ranged from 1.1 to 2.1. The largest values were reported during ACE-Asia campaign [Kim et al., 2006; Carrico et al., 2003] where marine aerosol may have also been mixed in, leading to an increase scattering enhancement.

Table 4 lists $f$(RH) values for biomass burning and volcanic aerosols. Those from volcanic emissions exhibit the largest $f$(RH) with values above 2.5 [Carrico et al., 2003]. The lowest $f$(RH) was found for biomass burning aerosols in PM$_4$ [Kotchenruther and Hobbs, 1998]. $f$(RH) values reported by Carrico et al. [2003] for dust dominated situations (Table 3) and for volcanic ash (Table 4) were on the upper range of the values reported in the literature for these aerosol types. According to Carrico et al. [2003], the volcanic-dominated air masses featured high SO$_2$ and sub-micrometer SO$_4^{2-}$ concentrations, the latter
being a mixture of $\text{H}_2\text{SO}_4$ and $\text{NH}_4\text{HSO}_4$ [Huebert et al., 2003]. In addition, the Carrico et al. [2003] measurements were carried out onboard a cruise, which might contribute also to the high $f(\text{RH})$ values observed, due to the potential influence of marine aerosols. Gras et al. [1999] showed different $f(\text{RH})$ factors for smoke from north Australian savannah fires compared to peat fires in Indonesia and suggested that fuel composition played an important role in the smoke $f(\text{RH})$ values. This is supported by laboratory study results presented by Hand et al. [2010] and Day et al. [2006]. Hand et al. [2010] measured $f(\text{RH})$ for fresh biomass burning using different type fuels in the laboratory and found that $f(\text{RH})$ ranged from 0.99±0.08 to 1.81±0.08 at 80–85% RH depending on fuel type. Hand et al. [2010] also showed that fuels with higher inorganic mass fractions and soot internally and externally mixed with inorganic species resulted in higher $f(\text{RH})$ values. In contrast, they found that relatively pure soot particles resulted in only minimal scattering enhancement with RH. The laboratory study of Day et al. [2006] reported that not only the fuel, but also the age of the resulting smoke influences the hygroscopic scattering enhancement, with minute-old smoke tending to be more hygroscopic than hour-old smoke. Magi and Hobbs [2003] showed a similar trend of decreasing $f(\text{RH})$ with the smoke age for ambient measurements in Africa. The large range of $f(\text{RH})$ values for biomass burning aerosols found in the literature can be attributed to the range of RH values for which $f(\text{RH})$ is reported, the variety of fuel types and burning conditions, chemical composition of the smoke and the degree of aging and processing in the atmosphere. Reid et al. [2005] reviewed intensive properties of biomass burning aerosols, including aerosol hygroscopic scattering enhancement and suggested that differences between $f(\text{RH})$ values reported in the literature could be partially attributed to hysteresis effects too. For example, Kotchenruther
and Hobbs [1998] cases were taken in a very humid Brazilian environment and the particles may not have fully dried out at 30% RH, leading to lower reported f(RH) values.

[FIGURE 3]

[TABLES 1-4]

7 Predictions of f(RH) using ancillary information

Since f(RH) measurements are relatively scarce worldwide, spatial and temporal coverage of optical aerosol hygroscopicity would be enhanced if other aerosol parameters could be used as proxies to estimate f(RH). Toward this goal, many authors have investigated the relationship between f(RH) and/or γ and the aerosol chemical composition [e.g. Quinn et al., 2005; Baynard et al., 2006; Titos et al., 2014b; Zhang et al., 2015; Zieger et al., 2014; Zieger et al., 2015] and between f(RH) and/or γ and other aerosol optical parameters such as the single scattering albedo, SSA [e.g., Titos et al., 2014a], the scattering Ångström exponent, SAE [e.g., Nessler et al., 2005], or the submicrometer scattering fraction, Rsp [e.g., Sheridan et al., 2001; Doherty et al., 2005].

Based on humidograph and chemical composition measurements for three different field campaigns, Quinn et al. [2005] proposed a linear parameterization based on the mass fraction (F₀) of organic matter and sulphate to estimate γ (Table 5). Malm et al. [2005] also observed a clear tendency of decreasing f(RH) for increasing the organic carbon content. Wang et al. [2007] showed that f(RH=82%) decreased linearly with F₀ (Table 5), with a decrease of 39% in f(RH=82%) as F₀ increased from 0–0.25 to 0.75–1.0. A linear relationship between f(RH=85%) and the organic matter fraction at an urban environment was obtained by Titos et al. [2014b]. However, Titos et al. [2014b] found that their linear relationship was not valid during a dust dominated event, although the number of samples
was too limited to draw strong conclusions. Zhang et al. [2015] also used a similar approach as that described by Quinn et al. [2005] for data from Yangtze River Delta (China), but did not find a strong linear relationship (R² = 0.14, see Table 5). Including nitrate into the organic mass fraction calculation significantly improved their results (R²=0.68). Zhang et al. [2015] further improved the hygroscopicity parameterization by incorporating additional species (NH₄⁺, Cl⁻ and equivalent black carbon, EBC); they presented this improved parameterization in terms of f(RH=85%) instead of γ. Like Zhang et al. [2015], Zieger et al. [2014; 2015] included, in addition to SO₄²⁻, the contribution of NO₃⁻, NH₄⁺ and EBC into the calculation of the organic mass fraction. Using data from two different sites (Hyytiälä and Melpitz), Zieger et al. [2015] showed that the two data sets did not show the same joint linear trend when using SO₄²⁻ to determine F₀ but the data sets were consistent when the contribution of NO₃⁻, NH₄⁺ and EBC was included. Although all studies point to a clear relationship between aerosol scattering enhancement and the organic/inorganic mass fraction, the results from Zhang et al. [2015] and Zieger et al. [2015] suggest that to obtain reliable estimations of γ or f(RH=85%) a complete chemical characterization is needed. It is also important to note that these studies used submicron chemical composition data and the coarse mode was not considered in the parameterizations.

**[TABLE 5]**

High frequency chemical composition measurements occur primarily on a campaign type basis and are fairly rare. Thus, it is useful to consider whether other aerosol parameters, for example, aerosol optical properties, can be used to parameterize f(RH). Sheridan et al. [2001] showed distinct populations of f(RH) as a function of aerosol SSA and Rₛₚ in the Southern Great Plains, OK (USA). f(RH=85%) values were lower for SSA <
0.8 (median value of 1.55) and Rsp < 0.6 (median 1.59) compared with a median value of 1.83 for all the data [Sheridan et al. 2001]. Doherty et al. [2005] also showed that during ACE-ASIA \( f(\text{RH}=85\%) \) decreases as Rsp decreases. Doherty et al. [2005] obtained a mean \( f(\text{RH}=85\%) \) of 2.33 for Rsp > 0.80, 2.17 for 0.45 < Rsp < 0.80 and 1.76 for Rsp < 0.45, which suggested that the higher the contribution of submicrometer particles to the scattering coefficient the higher the scattering enhancement. Nessler et al. [2005] proposed a polynomial parameterization of \( f(\text{RH}) \) as a function of the SAE at Jungfraujoch, assuming that the coarse mode was mainly dust and it was non-hygroscopic. At a continentally-influenced marine site, Titos et al. [2014a] observed a clear tendency of increasing \( \gamma \) for decreasing SAE and increasing SSA (larger and more scattering particles had higher scattering enhancement) and proposed a parameterization of \( \gamma \) as a function of the dry SSA valid for marine sites with anthropogenic influence. The potential of these parameterizations lies in their simplicity, as the aerosol scattering enhancement can be estimated by a single parameter such as the dry single scattering albedo, which can be obtained at a wide variety of global sites.

There are limitations to simple parameterizations – for example, in the study of Titos et al. [2014a] the coarse mode was dominated by sea salt particles while the concentration of other species that typically accumulate in the coarse fraction (e.g., dust) was negligible. A SSA/\( f(\text{RH}) \) parameterization would fail when both types of aerosols were present, as pure dust aerosols do not experience significant hygroscopic growth, but the SSA (and SAE) of dust aerosol can be similar to that of sea salt.

8 Final remarks and recommendations

The enhancement of aerosol light-scattering as a function of RH is an important factor in aerosol climate forcing calculations. This article reviews nephelometry measurements of
aerosol hygroscopicity over the last 50 years, including system design, data treatment and results. The following remarks and recommendations can be derived from this review:

System design aspects:

- Control of RH using dilution of the aerosol sample with moist air limits the signal and leads to difficulty in resolving the DRH due to discrepancies between maximum RH experienced by the aerosol and measured RH. Use of an annular water vapor permeable membrane to humidify the air sample eliminates the signal degradation caused by dilution; however this technique can still result in exposure of the aerosol sample to higher RH values than measured inside the nephelometer.

- For nephelometers with a halogen lamp light source, the temperature difference between the inlet and the sensing volume can be reduced by modifying the nephelometer [Fierz-Schmidhauser et al., 2010a; Brem et al., 2012].

- Comparisons between humidified tandem nephelometer systems are scarce. The reasons behind the discrepancies observed are not fully known. Intercomparisons between humidograph systems are needed to improve measurement understanding and better define the historic $f(RH)$ measurement record.

- We strongly support the recommendations made by Zieger et al., [2013] to calibrate humidograph systems with salts of known hygroscopicity and to perform optical closure studies to assure an optimal functioning of the tandem nephelometer humidograph system. The procedure described by Brem et al. [2012] can be used as reference.

Data treatment:
A review of the fit equations relating $f(RH)$ to RH used in previous publications has been presented. The two parameter fit equations are easy to apply and provide good agreement for monotonic $f(RH)$ increases but perform poorly for deliquescent aerosols. We propose a new equation which relies on fitting scanning humidograph data over several RH ranges to evaluate hygroscopicity and identify the presence of deliquescent aerosol.

Error sources:

- Differences between nephelometers when measuring at low RH have been commonly attributed to sampling losses in the humidifier. The agreement between the nephelometers should be reported and considered when calculating $f(RH)$.

- Precise, fast-response and calibrated T/RH sensors, especially in the sensing volume of the nephelometer, are needed. Additional sensors located up- and down-stream of the humidifier are also necessary to know the RH to which the aerosol has been exposed.

- Sample residence times inside the humidification system may affect observations of hygroscopic growth as some aerosol types require longer to equilibrate to the RH to which they are exposed.

- A Monte Carlo uncertainty study has shown that the more hygroscopic the aerosol the higher the uncertainty in $f(RH)$. The uncertainty also increases as RH increases, especially for RH>$80\%$. The assumption that scattering enhancement does not occur below some reference RH value may lead to underestimation of the scattering enhancement (up to 25%).
Measurement uncertainties are expected to be higher than those reported here if other issues such as losses in the humidifier system, insufficient residence times or uncalibrated RH sensors, for example, are also considered. We have established a lower limit for the uncertainty in $f(RH)$ of around 30-40%.

Ambient measurement review:

- The review of $f(RH)$ values from the literature reveals a large variability of $f(RH)$ across measurement sites and aerosol types. In general, the highest $f(RH)$ values were measured in clean marine environments, with pollution having a major influence on $f(RH)$ values at those sites (pollution typically decreased the $f(RH)$ of marine aerosol). Dust aerosol tended to have the lowest reported hygroscopicity of any of the aerosol types studied.
- Taking into account the differences in the instrumentation, methodology, size cut and the uncertainties, the comparison of $f(RH)$ values among studies is not straightforward. For this reason, it is important that authors include detailed information about the instrumentation and the data treatment in order to enable a direct comparison with other studies and to reduce uncertainties.
- There is a clear relationship between $f(RH)$ and the organic/inorganic mass fraction. However, to obtain reliable estimations of $\gamma$ or $f(RH=85\%)$ a complete chemical characterization may be needed – considering sulphate and organic matter alone may not be sufficient.
- Optical variables such as the single scattering albedo and the scattering Ångström exponent have been used as proxies for $f(RH)$. These simple parameterization
schemes are valuable for specific sites and/or aerosol types but have not been shown to be general applicable.

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Table captions

Table 1: Aerosol light scattering enhancement factors for marine locations. The table lists
the measurement site (study name if appropriate), the study time period, the dominant
situation (if reported), the size cut, the \( f(\text{RH}) \) value, the RH range used to compute \( f(\text{RH}) \)
and the reference. Measurements were performed onboard: *aircraft or **cruise. \( f(\text{RH}_{\text{meas}}) \)
refers to mean±SD, unless noted (†median, range of values are given between brackets).

Table 2: Same as Table 1 but for continental (rural and urban) locations.

Table 3: Same as Table 1 but for situations dominated by dust particles.

Table 4: Same as Table 1 but for situations dominated by smoke.

Table 5: Parameterizations of aerosol hygroscopicity, \( \gamma \) or \( f(\text{RH}=85\%) \), as a function of the
organic mass fraction, \( F_0 \). OM = Organic Matter, \( \text{SO}_4^{2-} = \) sulphate, \( \text{NO}_3^- = \) nitrate, \( \text{NH}_4^+ = \)
ammonia, EBC = Equivalent Black Carbon, \( R^2 = \) coefficient of determination.

Figure captions

Figure 1: Humidogram examples fitted using Eq. 1-11 and corresponding coefficient of
determination, \( R^2 \), and root mean squared error, RMSE, for each fit and case. Measured
data represent increasing RH scans and \( f(\text{RH}) \) refers to 550 nm wavelength. (a) Ambient
aerosol in Granada, Spain (b) Laboratory generated ammonium sulphate.

Figure 2: Simulated \( f(\text{RH}) \) error (color scale) as a function of relative humidity, RH, and the
hygroscopic parameter \( \gamma \), for a reference RH of 0\% (a) and a random reference RH in the
range 0-40\% (b).

Figure 3: Mean values of \( f(\text{RH}=80-85\%) \) from Tables 1-4 for PM\(_{10}\) aerosol. The error-bars
represent standard deviation if reported. For the marine and rural/urban sites, the dark blue
and yellowish bars respectively refer to polluted conditions.