

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

2 **A review of measurements, techniques and error sources**

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28 **Abstract**

29 Knowledge of the scattering enhancement factor, $f(\text{RH})$, is important for an accurate
30 description of direct aerosol radiative forcing. This factor is defined as the ratio between the
31 scattering coefficient at enhanced relative humidity, RH, to a reference (dry) scattering
32 coefficient. Here, we review the different experimental designs used to measure the
33 scattering coefficient at dry and humidified conditions as well as the procedures followed to
34 analyze the measurements. Several empirical parameterizations for the relationship between
35 $f(\text{RH})$ and RH have been proposed in the literature. These parameterizations have been
36 reviewed and tested using experimental data representative of different hygroscopic growth
37 behavior and a new parameterization is presented. The potential sources of error in $f(\text{RH})$
38 are discussed. A Monte Carlo method is used to investigate the overall measurement
39 uncertainty, which is found to be around 20-40% for moderately hygroscopic aerosols. The
40 main factors contributing to this uncertainty are the uncertainty in RH measurement, the dry
41 reference state and the nephelometer uncertainty. A literature survey of nephelometry-
42 based $f(\text{RH})$ measurements is presented as a function of aerosol type. In general, the highest
43 $f(\text{RH})$ values were measured in clean marine environments, with pollution having a major
44 influence on $f(\text{RH})$. Dust aerosol tended to have the lowest reported hygroscopicity of any
45 of the aerosol types studied. Major open questions and suggestions for future research
46 priorities are outlined.

47

48 **Keywords:** scattering enhancement, water uptake, hygroscopicity, aerosol light scattering.

49

50 1 Introduction

51 Atmospheric aerosols are able to scatter and absorb solar radiation. The magnitude of the
52 radiative impact of these aerosol optical properties depends on size and composition of the
53 particles as well as on the atmospheric conditions such as relative humidity (RH) and sun
54 angle. Uncertainties in aerosol optical properties contribute to uncertainties in climate
55 forcing and visibility estimates. Considerable research has taken place in the last several
56 decades to investigate the role of atmospheric aerosol particles on the Earth's radiative
57 balance and, additionally, has motivated regulatory efforts to mitigate their contribution to
58 degradation of visibility and air quality.

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

70 Aerosol particles can be characterized as a function of their hygroscopicity. Some
71 pure aerosol species like soot or mineral dust are insoluble and do not grow significantly in
72 diameter with increasing RH [e.g. *Weingartner et al.*, 1997; *Sjogren et al.*, 2007]. In

73 contrast, other aerosol species like sulfuric acid, H_2SO_4 , and some organics are soluble and
74 do take up water. These particles are hygroscopic and they grow or shrink smoothly as the
75 RH increases or decreases. A third type of hygroscopic growth is exhibited by deliquescent
76 aerosols like sodium chloride, NaCl , or ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, which experience
77 a sudden phase transition from solid to liquid at a defined RH. The RH at which the phase
78 transition occurs is called the deliquescence relative humidity (DRH); DRH is a
79 characteristic of the specific chemical compound [Orr *et al.*, 1958]. Once the RH is above
80 the DRH and the particle is mainly liquid, exposing the particle to decreasing RH does not
81 result in recrystallization at the DRH; rather, crystallization occurs at a RH below the DRH.
82 The RH at which recrystallization occurs is called the efflorescence relative humidity
83 (ERH). Because the DRH and ERH are different, deliquescent aerosols can exist in two
84 different phases at the same RH when that RH is greater than ERH but less than DRH. The
85 curve describing the deliquescent aerosol state as a function of RH is termed the hysteresis
86 loop [Orr *et al.*, 1958]. The RH history of an air parcel along with the knowledge of the
87 composition and size of aerosol particles within that parcel are important because they
88 define what fraction of the atmospheric aerosol is present as liquid droplets. The liquid
89 fraction scatters much more light than its corresponding solid fraction [e.g. Toon *et al.*,
90 1976; Sloane, 1984].

91 In-situ measurements of aerosol scattering coefficients are usually performed at RH
92 below 30-40% [WMO/GAW, 2003]. This means that the in-situ aerosol scattering
93 measurements are not representative of ambient conditions. Therefore, knowledge of the
94 scattering enhancement due to water uptake is necessary to transform dry measurements
95 into more relevant ambient measurements. This is important for comparison and validation
96 of remote sensing with in-situ measurements [e.g., Andrews *et al.*, 2004; Zieger *et al.*,

97 2011; Zieger *et al.*, 2012; Estéve *et al.*, 2012; Sheridan *et al.*, 2012; Tesche *et al.*, 2014],
98 and for calculation of the direct aerosol radiative forcing [e.g., Pilinis *et al.*, 1995; IPCC,
99 2013]. Currently, aerosol-cloud interactions represent one of the largest uncertainties in
100 estimating the effects of aerosol on radiative forcing [IPCC, 2013]. One key parameter for
101 this estimate is to determine what fraction of aerosol particles can act as cloud condensation
102 nuclei (CCN) and form cloud droplets. Several parameterizations have been proposed in the
103 literature to estimate CCN from ancillary information; i.e. aerosol optical properties
104 [Jefferson, 2010], chemical composition [Ervens *et al.*, 2010] or scattering enhancement
105 factor [Ervens *et al.*, 2007]. Ervens *et al.* [2007] reported reliable predictions of CCN
106 number concentration using $f(\text{RH})$ for supersaturations higher than 0.3%, and a poor
107 agreement between measured and predicted CCN for low supersaturations.

108 $f(\text{RH})$ can be obtained from nephelometry measurements made at different RH
109 conditions [e.g. Covert *et al.*, 1972] or from visibility measurements at ambient RH and dry
110 scattering measurements [e.g. Liu *et al.*, 2008]. Gordon *et al.* [2015] presented a novel
111 open-path aerosol extinction cavity ringdown spectrometer which allows determining the
112 extinction enhancement factor at high relative humidity (RH>90%). Recent studies have
113 reported backscattering enhancement factors determined with remote-sensing techniques,
114 such as combined lidar and radiosounding RH measurements [e.g. Granados-Muñoz *et al.*,
115 2015; Fernández *et al.*, 2015]. Alternatively, estimates of $f(\text{RH})$ can be computed by
116 applying Mie theory to aerosol size distributions with assumptions about chemical
117 properties and measured growth factors [e.g., Adam *et al.*, 2012; Zieger *et al.*, 2013]. The
118 drawback of using HTDMA (Humidified Tandem Differential Mobility Analyzer) size
119 distribution data to estimate $f(\text{RH})$ is that the coarse mode is not considered and coarse

120 mode aerosol (e.g. sea salt) can have a significant effect on scattering enhancement factors
121 [*Zieger et al.*, 2011; *Zieger et al.*, 2014].

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

129 **2 History and development of humidified nephelometers**

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

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

140 Another humidification system for a nephelometer was developed by *Covert et al.*
141 [1972]. As in the device of *Pilat and Charlson* [1966], the variation of the RH of the
142 aerosol sample was achieved by addition of a controlled, warm and moist air stream. This
143 air stream was then introduced in a mixing chamber under highly turbulent flow conditions

144 in order to achieve a uniform RH aerosol sample. After the mixing chamber, the aerosol
145 passed through a series of chambers of different volumes to allow growth to equilibrium
146 sizes at a given RH, before the scattering coefficient was measured with a nephelometer.
147 The RH in the nephelometer was calculated from a temperature and dew point sensor
148 located in the scattering chamber. The system of *Covert et al.* [1972] was able to change the
149 RH from 20 to 90% in 4 minutes. This short scan time is appropriate in order to sample
150 homogeneous atmospheric aerosol, especially when using only one nephelometer.
151 However, for such large changes in RH in such a small time, the RH sensors need to have a
152 very fast time response, which is difficult to achieve even using dew point sensors [*Fierz-*
153 *Schmidhauser et al.*, 2010a].

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

161 In order to avoid dilution of the aerosol sample with dry and moist air, *Rood et al.*
162 [1985], developed a humidifier in which the sample air was passed through a hollow
163 cylinder with the inside wall covered with nylon mesh and wetted with a H₂SO₄ solution.
164 The wetted wall was gradually heated such that the amount of heat flux through the wall
165 controlled the increasing dew point temperature of the aerosol. The air stream exiting the
166 humidifier was rapidly heated to a peak temperature of 60 °C and then cooled to ambient
167 temperature prior to entering the nephelometer. In the heating section, the RH decreased to

168 <20% due to the increased temperature. Such a decrease in RH was sufficient to effloresce
169 the previously deliquesced particles, ensuring the particles were on the lower portion of the
170 hysteresis loop. Subsequent cooling increased the aerosol RH to its final value. Particles
171 passing through the cooling chamber experienced a range of RH values depending on the
172 cooler's temperature. Near the exit of the cooling chamber, the temperature of the aerosol
173 sample returned to room temperature but did not drop below that temperature. Therefore,
174 nowhere in the system had the particles been exposed to a RH greater than that within the
175 nephelometer [Rood *et al.*, 1985]. This prevented particles undergoing deliquescence before
176 reaching the nephelometer and enabled investigation of the hygroscopic behavior of dry
177 particles exposed to increasing RH. Rood *et al.* [1987] used three nephelometers operated
178 in parallel: one measuring at dry conditions, one measuring at ambient conditions (without
179 conditioning) and the third measuring at enhanced RH after passing through the humidifier
180 described above.

181 In the set-up of *Koloutsou-Vakakis* [1996] and *Koloutsou-Vakakis et al.* [2001] two
182 nephelometers were operated in parallel. One nephelometer measured the scattering
183 coefficient of the ambient aerosol at RH<40% and the second nephelometer scanned
184 through a series of RH values generated by a humidifier placed before the nephelometer.
185 The humidifier was an annular system, in this case consisting of a Teflon membrane
186 supported on a cylindrical stainless steel mesh inside a larger stainless steel tube. Water
187 circulated in the concentric space between the stainless steel tube and the Teflon membrane
188 while the aerosol sample flowed within the mesh. The Teflon membrane allowed transport
189 of water vapor to the aerosol. The amount of water vapor that passed into the aerosol
190 stream was determined by controlling the temperature of the water. This humidifier
191 represented a great improvement with respect to previous designs since it eliminated direct

192 contact of liquid water with the aerosol flow and avoided the need for dilution to control the
193 RH of the aerosol particles, thus preventing exposure of the aerosol particles to air that is
194 not of the same composition as the ambient air. Currently, the University of Granada, UGR
195 [Titos *et al.*, 2014b] and ESRL-NOAA (Earth System Research Laboratory, National
196 Oceanic and Atmospheric Administration) operate very similar humidifiers; however, in
197 the NOAA humidograph system the nephelometers are operated in series with the
198 humidifier in between [Sheridan *et al.*, 2001; Zhang *et al.* 2015].

199 *Carrico et al.* [2000] further improved the humidification system developed by
200 *Koloutsou-Vakakis* [1996] by using Peltier thermoelectric coolers. With these coolers,
201 $RH > 80\%$ was achieved locally upstream of the scanning nephelometer while performing
202 decreasing RH scans within the nephelometer. Thus, this system allowed for investigation
203 of the decreasing RH branch of the hysteresis loop. Similar to *Rood et al.* [1985], *Carrico*
204 *et al.* [1998; 2000] also reported that the highest RH was achieved before the nephelometer
205 in their set-up. To compensate for this effect, *Carrico et al.* [1998] experimentally
206 measured DRH values for laboratory generated aerosols (NaCl and $(NH_4)_2SO_4$) and
207 compared their results with literature values. The difference between measured and
208 literature DRH values was attributed to heating within the nephelometer. They determined
209 that heating resulted in a temperature increase of the sample volume of 1.5 °C. *Carrico et*
210 *al.* [1998] used this temperature change to calculate the correct RH within the nephelometer
211 over the entire range of controlled RH measurements and found that the measured and
212 literature DRH values agreed within 2% RH after taking the temperature difference into
213 account.

214 *Day et al.* [2000] used a different technique to control the RH of the air sample in
215 their single nephelometer humidograph system. The aerosol sample entered an array of 23

216 Perma Pure diffusion drying tubes, which were mounted in parallel, after passing through a
217 cyclone that removed particles larger than 2.5 μm in diameter. The diffusion drying tubes
218 consisted of an inner tube of Nafion through which the aerosol sample flowed and an outer
219 tube of stainless steel through which purge air flowed. The RH of the aerosol sample could
220 be increased or decreased depending on the RH of the purge air. After this RH
221 conditioning, the aerosol sample was drawn into a plenum where the RH and temperature
222 of the aerosol sample were continuously monitored and then passed to the nephelometer.
223 This humidification system was able to achieve relative humidity values in the range 5-
224 95%. In order to have accurate measurements of RH, *Day et al.* [2000] kept the temperature
225 of the aerosol sample nearly constant by housing the array of dryers in an insulated
226 aluminum cylinder that was filled with water. Since the system controls the sample RH
227 without excess heating, it is more likely to have minimized losses of volatile compounds.

228 *Fierz-Schmidhauser et al.* [2010a], at the Paul Scherrer Institut (PSI), built a
229 humidification system that was able to identify when aerosol particles were in a metastable
230 state (i.e., in the liquid phase below their DRH). In their system, the aerosol first entered a
231 humidifier, which consisted of a Gore-Tex tube surrounded by a thin water layer in a
232 temperature-controlled metal tube. Following the humidifier, the aerosol entered a dryer
233 that consisted of a single Nafion tube (Perma Pure LLC). The aerosol flowed through the
234 inner part of the tube and was dried by adjusting the flow of dry air on the outside of the
235 Nafion tube. Then, the scattering coefficient was measured by the nephelometer at a
236 controlled RH. A second, parallel nephelometer measured the scattering coefficient at dry
237 conditions. Combined temperature and capacitive RH sensors were used throughout the
238 system and inside the humidified nephelometer to measure air temperature and RH,
239 respectively. In addition, *Fierz-Schmidhauser et al.* [2010a] installed a dew point sensor

240 inside the nephelometer to accurately calculate the RH inside the nephelometer.
241 Nevertheless, due to the relatively long time response of the temperature sensor of the dew
242 point mirror (up to several minutes) these RH readings were only applicable during
243 constant RH conditions. During initial laboratory experiments *Fierz-Schmidhauser et al.*
244 [2010a] observed a temperature difference of about 4.5 °C between the inlet and the sensing
245 volume of the nephelometer at 16.6 lpm caused by the heat of the halogen lamp (75 W)
246 used as the nephelometer light source. Consequently, the RH decreased from ~90% RH at
247 the nephelometer inlet to about 70% RH in the sensing volume. This is a common issue in
248 nephelometers with a halogen lamp light source [e.g. *Carrico et al.*, 1998; *Brem et al.*
249 2012]. To reduce this temperature difference, *Fierz-Schmidhauser et al.* [2010a] placed an
250 air-cooled infrared filter between the lamp and the sensing volume. In addition, on the
251 outside of the sensing volume they placed cooling fins to enlarge the surface and four
252 additional blowers to adjust the nephelometer's temperature close to room temperature.
253 Similarly, *Brem et al.* [2012] modified the nephelometer by using a halogen lamp with
254 reduced wattage and by installing a hot mirror in front of the lamp to eliminate thermal
255 radiation. Similar to the *Rood et al.* [1985] design, in the system of *Fierz-Schmidhauser et*
256 *al.* [2010a] the highest RH was achieved before the nephelometer. As a consequence, this
257 allowed for deliquescent particles to exist in two phases if their DRH had been exceeded at
258 any point along the sampling path. These particles remained liquid even if the RH was
259 subsequently lowered on the way to the nephelometer. Thus, in laboratory studies they
260 observed that the deliquescence step change appeared at a lower RH than in the literature.
261 Due to the limited drying capability of the dryer, the ERH could not be observed during
262 their laboratory and ambient measurements [*Fierz-Schmidhauser et al.*, 2010a].

263 Recently, Ecotech Pty Ltd. has developed a commercial humidified nephelometer
264 tandem system (aerosol conditioning system ACS1000). In the ACS1000 the aerosol flow
265 is split into two paths by an isokinetic flow splitter. The dry sample passes directly into one
266 of the nephelometers to measure the scattering coefficient at dry conditions. The other
267 sample is humidified to a predetermined RH set by the controller and then the scattering
268 coefficient is measured using an additional nephelometer. The humidifier consists of two
269 concentric tubes, the inner one is a Gore-Tex membrane tube surrounded by a thin Milli-Q
270 water layer in a heatable metal tube. The RH can be increased from around 40% up to 90%
271 with an accuracy of $\pm 0.35\%$ according to the manufacturer ([http://ecotech.com/wp-](http://ecotech.com/wp-content/uploads/2015/02/M010047-ACS-1000-User-Manual-1.0.pdf)
272 [content/uploads/2015/02/M010047-ACS-1000-User-Manual-1.0.pdf](http://ecotech.com/wp-content/uploads/2015/02/M010047-ACS-1000-User-Manual-1.0.pdf)). The performance of
273 the system using laboratory generated aerosols and its use for ambient measurements have
274 not been addressed in detail in the literature. *Zieger et al.* [2015] reported a relatively good
275 agreement between the PSI humidograph system described in *Fierz-Schmidhauser et al.*
276 [2010a] and the Ecotech system during a recent deployment in Finland (see Section 4).

277 Scanning RH systems such as the ones described above have been widely used for
278 ground-based measurements. Several research groups have also deployed humidification
279 systems for nephelometers on airborne platforms [e.g. *Hegg et al.*, 2008; *Sheridan et al.*,
280 2012; *Pekour et al.* 2013]. However, due to variability in the aerosol and time needed to
281 scan through a range of RH, scanning systems are not practical for airborne applications.
282 Thus, airborne measurements are usually performed with fixed humidity systems, where
283 two or three nephelometers measure aerosol scattering at fixed RH levels [*Hegg et al.*,
284 2002]. Recently, *Pekour et al.* [2013] developed an airborne humidification system that
285 used three integrating nephelometers to measure the scattering coefficient at three different
286 fixed RH. The system of *Pekour et al.* [2013] consisted of a number of driers and

287 humidifiers enabling measurement of $f(\text{RH})$ under hydration or dehydration conditions
288 (always starting with the aerosol in a known state) with a simple system reconfiguration
289 [Pekour *et al.*, 2013; Shinozuka *et al.*, 2013].

290 **3 Humidogram parameterizations**

291 For scanning RH measurements it is possible to develop a fit for the relationship between
292 $f(\text{RH})$ and RH. Many different equations have been used in previous studies. The simplest
293 and most commonly used equation is the one parameter fit equation [e.g., Hänel, 1980;
294 Kotchenruther and Hobbs, 1998; Gassó *et al.*, 2000] initially introduced by Kasten [1969]:

$$295 \quad f(\text{RH}) = (1 - \text{RH}/100)^{-\gamma}$$

296 (Eq. 1)

297 where γ parameterizes the magnitude of the scattering enhancement. Sheridan *et al.* [2002]
298 used a variation of the equation proposed by Kasten [1969] to include the RH of the
299 reference (dry) nephelometer:

$$300 \quad f(\text{RH}) = \left(\frac{1 - \text{RH}/100}{1 - \text{RH}_{\text{ref}}/100} \right)^{-\gamma}$$

301 (Eq. 2)

302 where RH and RH_{ref} are the relative humidity measured inside the humidified and reference
303 nephelometers, respectively.

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

$$307 \quad f(\text{RH}) = a(1 - \text{RH}/100)^{-\gamma}$$

308 (Eq. 3)

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

$$311 \quad f(RH) = 1 + a(RH/100)^b$$

312 (Eq. 4)

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

$$315 \quad f(RH) = \left(1 + \frac{RH}{100 - RH}\right)^{7/3}$$

316 (Eq. 5)

317 More complex multi-parameter equations have been proposed in the literature such
318 as the three parameter fit equations used by *Sheridan et al.* [2001] (Eq. 6) and by *Day et al.*
319 [2000] (Eq. 7):

$$320 \quad f(RH) = a(1 + b(RH/100)^c)$$

321 (Eq. 6)

$$322 \quad f(RH) = \frac{d + eRH}{1 + hRH}$$

323 (Eq. 7)

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

$$329 \quad f(RH) = b_0 + b_1 \left(1 - \frac{RH}{100}\right)^{-1} + b_2 \left(1 - \frac{RH}{100}\right)^{-2}$$

328 (Eq. 8)

330 *Koloutsou-Vakakis et al.* [2001] also proposed a polynomial fitting of $f(RH)$ as a
 331 function of RH:

$$332 \quad f(RH) = 1 + A_1RH + A_2RH^2 + A_3RH^3$$

333 (Eq. 9)

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

$$343 \quad f(RH) = \left[1 + a \left(\frac{RH}{100} \right)^b \right] \cdot \left[1 - \frac{1}{\pi} \left(\frac{\pi}{2} + \arctan \left(1 \times 10^{24} \left\langle \frac{RH}{100} - \frac{d}{100} \right\rangle \right) \right) \right]$$

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

(Eq. 10)

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

347 We propose a new parameterization (Eq. 11) in which both sides of the equation are
 348 the same (albeit with potentially different constants a_i and γ_i) following Eq. 3 and are linked
 349 by the switch function in the square brackets. With this approach, the parameter d
 350 represents the apparent DRH point and γ_1 and γ_2 represent the scattering enhancement for

351 the lower and upper ranges of RH. In addition, this equation provides information about
 352 aerosol hygroscopicity: if $\gamma_1 \sim \gamma_2$ then $f(\text{RH})$ increases smoothly with RH while if $\gamma_1 \ll \gamma_2$
 353 there is a sharp increase of $f(\text{RH})$ after the DRH and the aerosol is likely deliquescent.

$$\begin{aligned}
 354 \quad f(\text{RH}) = & a_1 \left(1 - \frac{\text{RH}}{100}\right)^{-\gamma_1} \cdot \left[1 - \frac{1}{\pi} \left(\frac{\pi}{2} + \arctan\left(1 \times 10^{24} \left\langle \frac{\text{RH}}{100} - \frac{d}{100} \right\rangle\right)\right)\right] \\
 & + a_2 \left(1 - \frac{\text{RH}}{100}\right)^{-\gamma_2} \cdot \left[\frac{1}{\pi} \left(\frac{\pi}{2} + \arctan\left(1 \times 10^{24} \left\langle \frac{\text{RH}}{100} - \frac{d}{100} \right\rangle\right)\right)\right]
 \end{aligned} \tag{Eq. 11}$$

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

364 Case (a) shows a monotonic increase of $f(\text{RH})$ with increasing RH. In this example,
 365 all the equations (except Eqs. 1 and 5) show very good agreement with measurements (i.e.,
 366 R^2 values close to 1 and RMSE below 0.1). Case (b) shows the behavior of deliquescent
 367 aerosol with a transition in $f(\text{RH})$ at around 70%. Equations 10 and 11 provide the highest
 368 R^2 and lowest RMSE and are able to reproduce the DRH step while the other equations are
 369 not able to satisfactorily reproduce the measurements. Thus, for deliquescent aerosols with
 370 negligible enhancement below DRH and a sudden transition at this humidity, Equations 10
 371 and 11 provide the best results (Figure 1b). Eq. 11 has the advantage that the interpretation

372 of the fit parameters is more straightforward. Here, we have presented an approach for
373 fitting $f(\text{RH})$ as a function of RH, however, the fit quality should be evaluated to test if the
374 parameterization is suitable for each specific dataset.

375 [FIGURE 1]

376 **4 Error sources in $f(\text{RH})$ measurements**

377 Measurements of the scattering enhancement factor are usually performed using custom-
378 made humidifier systems and commercial nephelometers. Differences in the experimental
379 set-ups and measurement procedures may lead to differences in the reported $f(\text{RH})$ values.
380 Although some published works have investigated the performance of the humidifier
381 systems using laboratory generated ammonium sulphate and/or sodium chloride [e.g.,
382 *Carrico et al.*, 2000; *Fierz-Schmidhauser et al.*, 2010a] experimental intercomparisons
383 between different humidifier systems are sparsely performed. *Fierz-Schmidhauser et al.*
384 [2010a] showed the results of an intercomparison between the Paul Scherrer Institut (PSI)
385 and the DOE/ARM (US Department of Energy Atmospheric Radiation Measurements)
386 tandem humidograph systems. The agreement between $f(\text{RH})$ values derived from each
387 system varied over the course of the study period but the differences were found to be
388 significant (up to 25% relative differences in $f(\text{RH})$) for specific periods [*Fierz-*
389 *Schmidhauser et al.*, 2010a]. The authors attributed this difference to distinct RH histories
390 in the two systems (in the PSI system the aerosol sample was exposed to a higher RH
391 before the wet nephelometer than occurred in the DOE/ARM system) so during some
392 periods the instruments were probing different branches of the hysteresis curve. This effect
393 would be especially important for deliquescent aerosols. Other hypotheses for the observed
394 differences were evaporation of semi-volatile substances in the sampling line or in the
395 humidifier, due to different residence times and temperatures [*Fierz-Schmidhauser et al.*,

396 2010a]. As mentioned in Section 2, the ACS1000 humidifier system (Ecotech Pty Ltd) was
397 also intercompared with the PSI humidified tandem nephelometer system at Hyytiälä,
398 Finland. *Zieger et al.* [2015] reported that median $f(\text{RH}=85\%)$ values determined with both
399 systems agreed within 6% at 525 nm wavelength but larger differences were observed
400 during parts of the campaign. The possible reasons behind these discrepancies were not
401 addressed.

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

407 **4.1 Losses in the humidification system**

408 Most publications have reported a good agreement between the reference and the
409 humidified nephelometers when measuring scattering coefficients at dry conditions
410 (typically $\text{RH} < 40\%$), however, these differences ranged from below 2% up to 10% for
411 PM_{10} scattering coefficients at ~ 550 nm wavelength, depending on the study [e.g. *Carrico*
412 *et al.*, 2000; *Fierz-Schmidhauser et al.*, 2010a; *Titos et al.*, 2014b]. Usually, the differences
413 were attributed to sampling losses in the humidification system. These losses are higher for
414 PM_{10} than for PM_1 [e.g., *Carrico et al.*, 2000; *Carrico et al.*, 2003; *Titos et al.*, 2014a],
415 indicating higher losses for larger particles. If the nephelometers are operated in series
416 instead of in parallel, the losses may be even higher. *Anderson and Ogren* [1998] observed
417 differences around 7% and 1% for PM_{10} and PM_1 size fractions, respectively, for
418 nephelometers operated in series (without a humidification system).

419 Another potential issue that could lead to discrepancies in $f(\text{RH})$ comparisons is the
420 evaporation of semi-volatile substances in the sampling lines and in the humidifier
421 depending on the aerosol particle chemical composition, particularly as heating is
422 frequently used to control sample RH at various points in the system. Thus, the temperature
423 of the sampled air should be kept below 40 °C to limit losses of semi-volatile species
424 [Bergin *et al.*, 1997; ten Brink *et al.*, 2000].

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

431 **4.2 Residence time**

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

442 NOAA systems could be partially responsible of the disagreement observed between the
443 two systems during the intercomparison exercise [*Fierz-Schmidhauser et al.*, 2010a].

444 **4.3 Reference nephelometer RH values**

445 Most authors reference the wet scattering coefficient to that measured below a certain low
446 RH value (typically between 20-40%). To do this, the reference nephelometer is typically
447 kept at RH below 40% (e.g., by gently heating the aerosol sample or by using Nafion
448 dryers), although a constant reference RH in time is difficult to achieve. This approach
449 assumes that there is no scattering enhancement below the reference RH value, which will
450 not be true for many organic and marine influenced aerosol types [e.g., *Zieger et al.*, 2015].
451 An incorrect assumption of no growth at low RH will result in underestimation of $f(\text{RH})$
452 values. For this reason, the RH in the reference nephelometer should be kept as low as
453 possible and be reported together with the $f(\text{RH})$ value. *Sheridan et al.*, [2001] calculated
454 $\sigma_{\text{sp}}(\text{RH}_{\text{ref}}=40\%)$ using the lower branch of the $f(\text{RH})$ curve and the derived fitting
455 parameters to account for this effect. Alternatively the hygroscopic scattering enhancement
456 can be studied in terms of the γ parameter, which is not affected by the RH in the reference
457 nephelometer, although the interpretation of γ is not as intuitive as that of $f(\text{RH})$.

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

465 **4.4 Precise measurements of RH in the humidified nephelometer**

466 Precise RH measurements at the point where the scattering is measured are needed in order
467 to obtain accurate estimations of $f(\text{RH})$. For scanning RH measurements, the response time
468 of the RH sensor is an additional factor to consider. For TSI integrating nephelometers, the
469 sample RH sensor has been shown to disagree with more accurate co-located RH sensors.
470 In particular, *Fierz-Schmidhauser et al.* [2010a] reported that the TSI sensor
471 overestimated RH by 15% at high RH. *Titos et al.* [2014b] reported a difference of 12% for
472 $\text{RH} > 75\%$ between RH measured with the TSI sensor and a co-located more accurate sensor
473 placed inside the nephelometer chamber. However, without additional evaluation it is
474 difficult to assess whether the TSI sensor is prone to overestimation or if, in these two
475 reported cases, the TSI RH sensors had degraded since installation.

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

486 To verify the correct operation of the humidifier and to determine the true sample
487 RH, the tandem nephelometer humidograph can be calibrated with laboratory aerosols of
488 known size and composition and, thus, hygroscopicity. A frequent calibration with
489 nebulized salts (e.g. with ammonium sulphate), collocated measured size distributions and

490 Mie calculations should be performed on a regular basis to ensure a proper measurement of
491 $f(\text{RH})$. The theoretical $f(\text{RH})$ can then be derived using Mie theory and compared with the
492 experimental values as shown by *Fierz-Schmidhauser et al.* [2010a]. *Brem et al.* [2012]
493 present a detailed description of a laboratory set-up for measuring $f(\text{RH})$ which includes
494 nephelometer modifications, precise RH determination and optical closure analysis.

495 **5. Uncertainty analysis for $f(\text{RH})$ measurements**

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

509 To calculate $f(\text{RH})$ uncertainty, the dry scattering coefficient was selected as a
510 random number between 1 and 200 Mm^{-1} where dry refers to $\text{RH} = 0\%$. This wide range of
511 scattering coefficients was chosen to cover different atmospheric situations and aerosol
512 loads. In order to take into account the measurement uncertainty in the simulated dry
513 scattering coefficient, we introduce a measurement uncertainty of 9.2% [*Sherman et al.*,

514 2015] so the simulated final dry scattering coefficient is a random number (following a
515 normal distribution) in the range $[\sigma_{sp} \pm 0.092 * \sigma_{sp}]$.

516 The wet scattering coefficient cannot be simulated as a random number since it
517 depends on the measured dry scattering coefficient. Thus, to simulate a realistic value, we
518 calculated the wet scattering coefficient associated with the previously selected dry
519 scattering coefficient using Eq. 1 and assuming that γ ranges from 0 to 1 in steps of 0.01.
520 The chosen interval for γ covers the gamut from non-hygroscopic aerosol particles (γ equal
521 or close to 0, as can be the case of soot or dust particles) to very hygroscopic particles with
522 γ around 1 (e.g., marine aerosol). The γ parameter should be viewed here as a tool to
523 simulate different aerosol types (from very hygroscopic to hydrophobic aerosols). Finally,
524 we introduce a measurement uncertainty in RH of 3% and assume that the simulated wet
525 scattering coefficient also has an uncertainty 9.2% [Sherman *et al.*, 2015] so the final wet
526 scattering coefficient is a random number (following a normal distribution) in the range
527 $[\sigma_{sp}(RH) \pm 0.092 * \sigma_{sp}(RH)]$. Once we have a simulated but realistic pair of scattering
528 coefficients at wet and dry conditions, as they would be measured using two
529 nephelometers, the scattering enhancement factor can be calculated.

530 This procedure was repeated 500 times using 9 random seeds spanning the entire
531 range of γ and RH on each simulation, leading to a final matrix of around 70 million
532 simulation cases (number of seeds over number of simulations over all RH over all
533 $\sigma_{sp}(\text{dry})$). Due to the configuration of the simulations, the number of points included in each
534 bin is randomly distributed, showing no pattern, and is very similar for all the values
535 considered.

536 The mean, standard deviation and error of $f(\text{RH})$ were calculated over all the
537 simulations for each RH and γ . The $f(\text{RH})$ error, $\Delta[f(\text{RH})]$, was estimated as the ratio

538 between the standard deviation and the mean, multiplied by 100. Figure 2 shows $f(\text{RH})$
539 error as a function of RH and γ , calculated considering that the reference RH is 0% (Figure
540 2a) and that the reference RH is a random number in the range 0-40% (Figure 2b).
541 Estimated errors of $f(\text{RH})$ are around 15-20% on average, reaching above 80% at RH of
542 95% and $\gamma > 0.9$. For moderately hygroscopic aerosols (e.g., $\gamma \sim 0.5$), $f(\text{RH})$ errors are
543 constrained below 40% even at high RH, which can be regarded as a conservative
544 estimation and is quite large considering there are other factors contributing to $f(\text{RH})$
545 uncertainty (e.g., losses and residence time) that have not been considered in this approach.
546 Assuming the aerosol is dry (no water uptake) at $\text{RH} \leq 40\%$ might cause an
547 underestimation of up to 25% in $f(\text{RH})$ for very hygroscopic aerosols ($\gamma \sim 1$), even at low
548 RH. For moderately hygroscopic aerosols ($\gamma < 0.5$) the relative error is lower than 10-15%.
549 *Zieger et al.* [2013] and *Adam et al.* [2012] present uncertainty estimates using Mie theory
550 which are consistent with the values reported here for moderately hygroscopic aerosols.

551 [FIGURE 2]

552 553 **6 Literature review of ambient measurements of $f(\text{RH})$**

554 In this section we present a literature survey of $f(\text{RH})$ measurements performed over the last
555 two decades in very different environments, where a variety of aerosol types predominate.
556 Tables 1-4 report the aerosol light scattering enhancement factors classified according to
557 dominant aerosol types: marine (Table 1), continental (rural and urban) (Table 2), dust
558 (Table 3) and smoke (Table 4). The tables list the measurement location (and study name if
559 appropriate), the study time period, the dominant aerosol type, the size cut, the $f(\text{RH})$ value,
560 the RH range used to compute $f(\text{RH})$ and the reference. Most measurements were done with
561 a PM_{10} size cut, although a variety of other size cuts were also used (e.g. PM_1 , $\text{PM}_{2.5}$, PM_4).
562 Because $f(\text{RH})$ depends on particle size, the size cut can be an important factor influencing

563 the magnitude of the measured $f(\text{RH})$. The distinction between different aerosol types was
564 usually made by the authors according to air mass trajectories, wind sectors or the
565 predominant chemical composition. Most $f(\text{RH})$ values are referenced to a high RH
566 between 80 and 85%, a low RH (<40%) and to a wavelength ~ 550 nm. Figure 3
567 summarizes $f(\text{RH})$ mean (\pm standard deviation) values for PM_{10} size cut, extracted from
568 Tables 1-4.

569 From Figure 3 and Tables 1-4 it is clear that $f(\text{RH})$ values have a strong variability
570 among studies, even for similar aerosol type or conditions. In general, $f(\text{RH})$ values are
571 larger for marine sites compared to other environments due to the high hygroscopicity of
572 sea salt particles. $f(\text{RH})$ values for marine aerosols (Table 1 and Figure 3) span from values
573 around 1.5 in Sagres [*Carrico et al.*, 2000] to 3.5 in Cabauw for maritime air masses
574 [*Zieger et al.*, 2011]. Most publications report values for both clean marine and polluted
575 marine conditions if applicable; $f(\text{RH})$ values tend to be lower for polluted marine
576 situations than for clean conditions. *Kotchenruther et al.* [1999] reported an opposite
577 behavior, with higher values for polluted than for clean marine conditions, due to enriched
578 sulphate air masses from the anthropogenic sector. Additionally, several marine
579 humidograph studies have obtained $f(\text{RH})$ for two size fractions and found that the $f(\text{RH})$
580 values are larger for PM_1 than for PM_{10} . This behavior as a function of size cut is more
581 evident for clean marine than for polluted marine situations. *Sheridan et al.* [2002] reported
582 higher $f(\text{RH})$ values for PM_3 than for PM_1 , and the difference between $f(\text{RH})$ for different
583 size cuts was more marked for clean marine conditions. *Zieger et al.* [2010] showed that
584 compensating effects between size and hygroscopicity may have a profound effect on
585 $f(\text{RH})$; i.e. small and less hygroscopic aerosol can have the same $f(\text{RH})$ as large and more
586 hygroscopic aerosol.

587 Continental aerosol particles, at sites ranging from rural to urban (Table 2) exhibit
588 lower $f(\text{RH})$ values than marine sites except for Melpitz and Jungfraujoch which have the
589 largest $f(\text{RH})$ values of any of the continental measurements. The rest of the continental
590 sites reported PM_{10} $f(\text{RH})$ values below 2 (Figure 3) and exhibit low variability. One
591 hypothesis for the large $f(\text{RH})$ values observed in Melpitz and Jungfraujoch is that the
592 reference scattering was measured at a very low RH. Very similar values have been
593 reported for urban aerosols in Granada, Lin'An and Xin'An. Studies reporting $f(\text{RH})$ values
594 for clean and polluted conditions showed slightly higher $f(\text{RH})$ values for polluted
595 continental aerosols [Yan *et al.*, 2009; Chen *et al.*, 2014]. Airborne measurements over a
596 continental site showed decreasing $f(\text{RH})$ values with height during an extended aircraft
597 campaign, with values around 2 in the planetary boundary layer and values lower than 2 in
598 the free troposphere [Sheridan *et al.*, 2012].

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

604 Table 4 lists $f(\text{RH})$ values for biomass burning and volcanic aerosols. Those from
605 volcanic emissions exhibit the largest $f(\text{RH})$ with values above 2.5 [Carrico *et al.*, 2003].
606 The lowest $f(\text{RH})$ was found for biomass burning aerosols in PM_4 [Kotchenruther and
607 Hobbs, 1998]. $f(\text{RH})$ values reported by Carrico *et al.* [2003] for dust dominated situations
608 (Table 3) and for volcanic ash (Table 4) were on the upper range of the values reported in
609 the literature for these aerosol types. According to Carrico *et al.* [2003], the volcanic-
610 dominated air masses featured high SO_2 and sub-micrometer SO_4^{2-} concentrations, the latter

611 being a mixture of H_2SO_4 and NH_4HSO_4 [Huebert *et al.*, 2003]. In addition, the Carrico *et*
612 *al.* [2003] measurements were carried out onboard a cruise, which might contribute also to
613 the high $f(\text{RH})$ values observed, due to the potential influence of marine aerosols. Gras *et*
614 *al.* [1999] showed different $f(\text{RH})$ factors for smoke from north Australian savannah fires
615 compared to peat fires in Indonesia and suggested that fuel composition played an
616 important role in the smoke $f(\text{RH})$ values. This is supported by laboratory study results
617 presented by Hand *et al.* [2010] and Day *et al.* [2006]. Hand *et al.* [2010] measured $f(\text{RH})$
618 for fresh biomass burning using different type fuels in the laboratory and found that $f(\text{RH})$
619 ranged from 0.99 ± 0.08 to 1.81 ± 0.08 at 80–85% RH depending on fuel type. Hand *et al.*
620 [2010] also showed that fuels with higher inorganic mass fractions and soot internally and
621 externally mixed with inorganic species resulted in higher $f(\text{RH})$ values. In contrast, they
622 found that relatively pure soot particles resulted in only minimal scattering enhancement
623 with RH. The laboratory study of Day *et al.* [2006] reported that not only the fuel, but also
624 the age of the resulting smoke influences the hygroscopic scattering enhancement, with
625 minute-old smoke tending to be more hygroscopic than hour-old smoke. Magi and Hobbs
626 [2003] showed a similar trend of decreasing $f(\text{RH})$ with the smoke age for ambient
627 measurements in Africa. The large range of $f(\text{RH})$ values for biomass burning aerosols
628 found in the literature can be attributed to the range of RH values for which $f(\text{RH})$ is
629 reported, the variety of fuel types and burning conditions, chemical composition of the
630 smoke and the degree of aging and processing in the atmosphere. Reid *et al.* [2005]
631 reviewed intensive properties of biomass burning aerosols, including aerosol hygroscopic
632 scattering enhancement and suggested that differences between $f(\text{RH})$ values reported in the
633 literature could be partially attributed to hysteresis effects too. For example, Kotchenruther

634 *and Hobbs [1998]* cases were taken in a very humid Brazilian environment and the particles
635 may not have fully dried out at 30% RH, leading to lower reported $f(\text{RH})$ values.

636 **[FIGURE 3]**

637
638 **[TABLES 1-4]**

639

640 **7 Predictions of $f(\text{RH})$ using ancillary information**

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

650 Based on humidograph and chemical composition measurements for three different
651 field campaigns, *Quinn et al.* [2005] proposed a linear parameterization based on the mass
652 fraction (F_0) of organic matter and sulphate to estimate γ (Table 5). *Malm et al.* [2005] also
653 observed a clear tendency of decreasing $f(\text{RH})$ for increasing the organic carbon content.
654 *Wang et al.* [2007] showed that $f(\text{RH}=82\%)$ decreased linearly with F_0 (Table 5), with a
655 decrease of 39% in $f(\text{RH}=82\%)$ as F_0 increased from 0–0.25 to 0.75–1.0. A linear
656 relationship between $f(\text{RH}=85\%)$ and the organic matter fraction at an urban environment
657 was obtained by *Titos et al.* [2014b]. However, *Titos et al.* [2014b] found that their linear
658 relationship was not valid during a dust dominated event, although the number of samples

659 was too limited to draw strong conclusions. *Zhang et al.* [2015] also used a similar
660 approach as that described by *Quinn et al.* [2005] for data from Yangtze River Delta
661 (China), but did not find a strong linear relationship ($R^2 = 0.14$, see Table 5). Including
662 nitrate into the organic mass fraction calculation significantly improved their results
663 ($R^2=0.68$). *Zhang et al.* [2015] further improved the hygroscopicity parameterization by
664 incorporating additional species (NH_4^+ , Cl^- and equivalent black carbon, EBC); they
665 presented this improved parameterization in terms of $f(\text{RH}=85\%)$ instead of γ . Like *Zhang*
666 *et al.* [2015], *Zieger et al.* [2014; 2015] included, in addition to SO_4^{2-} , the contribution of
667 NO_3^- , NH_4^+ and EBC into the calculation of the organic mass fraction. Using data from two
668 different sites (Hyytiälä and Melpitz), *Zieger et al.* [2015] showed that the two data sets did
669 not show the same joint linear trend when using SO_4^{2-} to determine F_0 but the data sets
670 were consistent when the contribution of NO_3^- , NH_4^+ and EBC was included. Although all
671 studies point to a clear relationship between aerosol scattering enhancement and the
672 organic/inorganic mass fraction, the results from *Zhang et al.* [2015] and *Zieger et al.*
673 [2015] suggest that to obtain reliable estimations of γ or $f(\text{RH}=85\%)$ a complete chemical
674 characterization is needed. It is also important to note that these studies used submicron
675 chemical composition data and the coarse mode was not considered in the
676 parameterizations.

677 [TABLE 5]

678 High frequency chemical composition measurements occur primarily on a campaign
679 type basis and are fairly rare. Thus, it is useful to consider whether other aerosol
680 parameters, for example, aerosol optical properties, can be used to parameterize $f(\text{RH})$.
681 *Sheridan et al.* [2001] showed distinct populations of $f(\text{RH})$ as a function of aerosol SSA
682 and R_{sp} in the Southern Great Plains, OK (USA). $f(\text{RH}=85\%)$ values were lower for SSA <

683 0.8 (median value of 1.55) and $R_{sp} < 0.6$ (median 1.59) compared with a median value of
684 1.83 for all the data [Sheridan *et al.* 2001]. Doherty *et al.* [2005] also showed that during
685 ACE-ASIA $f(RH=85\%)$ decreases as R_{sp} decreases. Doherty *et al.* [2005] obtained a mean
686 $f(RH=85\%)$ of 2.33 for $R_{sp} > 0.80$, 2.17 for $0.45 < R_{sp} < 0.80$ and 1.76 for $R_{sp} < 0.45$, which
687 suggested that the higher the contribution of submicrometer particles to the scattering
688 coefficient the higher the scattering enhancement. Nessler *et al.* [2005] proposed a
689 polynomial parameterization of $f(RH)$ as a function of the SAE at Jungfraujoch, assuming
690 that the coarse mode was mainly dust and it was non-hygroscopic. At a continentally-
691 influenced marine site, Titos *et al.* [2014a] observed a clear tendency of increasing γ for
692 decreasing SAE and increasing SSA (larger and more scattering particles had higher
693 scattering enhancement) and proposed a parameterization of γ as a function of the dry SSA
694 valid for marine sites with anthropogenic influence. The potential of these
695 parameterizations lies in their simplicity, as the aerosol scattering enhancement can be
696 estimated by a single parameter such as the dry single scattering albedo, which can be
697 obtained at a wide variety of global sites.

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

704 **8 Final remarks and recommendations**

705 The enhancement of aerosol light-scattering as a function of RH is an important factor in
706 aerosol climate forcing calculations. This article reviews nephelometry measurements of

707 aerosol hygroscopicity over the last 50 years, including system design, data treatment and
708 results. The following remarks and recommendations can be derived from this review:

709 System design aspects:

- 710 • Control of RH using dilution of the aerosol sample with moist air limits the signal
711 and leads to difficulty in resolving the DRH due to discrepancies between maximum
712 RH experienced by the aerosol and measured RH. Use of an annular water vapor
713 permeable membrane to humidify the air sample eliminates the signal degradation
714 caused by dilution; however this technique can still result in exposure of the aerosol
715 sample to higher RH values than measured inside the nephelometer.
- 716 • For nephelometers with a halogen lamp light source, the temperature difference
717 between the inlet and the sensing volume can be reduced by modifying the
718 nephelometer [*Fierz-Schmidhauser et al.*, 2010a; *Brem et al.*, 2012].
- 719 • Comparisons between humidified tandem nephelometer systems are scarce. The
720 reasons behind the discrepancies observed are not fully known. Intercomparisons
721 between humidograph systems are needed to improve measurement understanding
722 and better define the historic $f(\text{RH})$ measurement record.
- 723 • We strongly support the recommendations made by *Zieger et al.*, [2013] to calibrate
724 humidograph systems with salts of known hygroscopicity and to perform optical
725 closure studies to assure an optimal functioning of the tandem nephelometer
726 humidograph system. The procedure described by *Brem et al.* [2012] can be used as
727 reference.

728 Data treatment:

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

735 Error sources:

- 736 • Differences between nephelometers when measuring at low RH have been
737 commonly attributed to sampling losses in the humidifier. The agreement between
738 the nephelometers should be reported and considered when calculating $f(\text{RH})$.
- 739 • Precise, fast-response and calibrated T/RH sensors, especially in the sensing volume
740 of the nephelometer, are needed. Additional sensors located up- and down-stream of
741 the humidifier are also necessary to know the RH to which the aerosol has been
742 exposed.
- 743 • Sample residence times inside the humidification system may affect observations of
744 hygroscopic growth as some aerosol types require longer to equilibrate to the RH to
745 which they are exposed.
- 746 • A Monte Carlo uncertainty study has shown that the more hygroscopic the aerosol
747 the higher the uncertainty in $f(\text{RH})$. The uncertainty also increases as RH increases,
748 especially for $\text{RH} > 80\%$. The assumption that scattering enhancement does not occur
749 below some reference RH value may lead to underestimation of the scattering
750 enhancement (up to 25%).

751 • Measurement uncertainties are expected to be higher than those reported here if
752 other issues such as losses in the humidifier system, insufficient residence times or
753 uncalibrated RH sensors, for example, are also considered. We have established a
754 lower limit for the uncertainty in $f(\text{RH})$ of around 30-40%.

755 Ambient measurement review:

756 • The review of $f(\text{RH})$ values from the literature reveals a large variability of $f(\text{RH})$
757 across measurement sites and aerosol types. In general, the highest $f(\text{RH})$ values
758 were measured in clean marine environments, with pollution having a major
759 influence on $f(\text{RH})$ values at those sites (pollution typically decreased the $f(\text{RH})$ of
760 marine aerosol). Dust aerosol tended to have the lowest reported hygroscopicity of
761 any of the aerosol types studied.

762 • Taking into account the differences in the instrumentation, methodology, size cut
763 and the uncertainties, the comparison of $f(\text{RH})$ values among studies is not
764 straightforward. For this reason, it is important that authors include detailed
765 information about the instrumentation and the data treatment in order to enable a
766 direct comparison with other studies and to reduce uncertainties.

767 • There is a clear relationship between $f(\text{RH})$ and the organic/inorganic mass fraction.
768 However, to obtain reliable estimations of γ or $f(\text{RH}=85\%)$ a complete chemical
769 characterization may be needed – considering sulphate and organic matter alone
770 may not be sufficient.

771 • Optical variables such as the single scattering albedo and the scattering Ångström
772 exponent have been used as proxies for $f(\text{RH})$. These simple parameterization

773 schemes are valuable for specific sites and/or aerosol types but have not been shown
774 to be general applicable.

775

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1128 **Table captions**

1129 Table 1: Aerosol light scattering enhancement factors for marine locations. The table lists
1130 the measurement site (study name if appropriate), the study time period, the dominant
1131 situation (if reported), the size cut, the $f(\text{RH})$ value, the RH range used to compute $f(\text{RH})$
1132 and the reference. Measurements were performed onboard: *aircraft or **cruise. $f(\text{RH}_{\text{meas}})$
1133 refers to mean \pm SD, unless noted (\dagger median, range of values are given between brackets).

1134 Table 2: Same as Table 1 but for continental (rural and urban) locations.

1135 Table 3: Same as Table 1 but for situations dominated by dust particles.

1136 Table 4: Same as Table 1 but for situations dominated by smoke.

1137 Table 5: Parameterizations of aerosol hygroscopicity, γ or $f(\text{RH}=85\%)$, as a function of the
1138 organic mass fraction, F_0 . OM = Organic Matter, SO_4^{2-} = sulphate, NO_3^- = nitrate, NH_4^+ =
1139 ammonia, EBC = Equivalent Black Carbon, R^2 = coefficient of determination.

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1141 **Figure captions**

1142 Figure 1: Humidogram examples fitted using Eq. 1-11 and corresponding coefficient of
1143 determination, R^2 , and root mean squared error, RMSE, for each fit and case. Measured
1144 data represent increasing RH scans and $f(\text{RH})$ refers to 550 nm wavelength. (a) Ambient
1145 aerosol in Granada, Spain (b) Laboratory generated ammonium sulphate.

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1147 Figure 2: Simulated $f(\text{RH})$ error (color scale) as a function of relative humidity, RH, and the
1148 hygroscopic parameter γ , for a reference RH of 0% (a) and a random reference RH in the
1149 range 0-40% (b).

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1151 Figure 3: Mean values of $f(\text{RH}=80-85\%)$ from Tables 1-4 for PM_{10} aerosol. The error-bars
1152 represent standard deviation if reported. For the marine and rural/urban sites, the dark blue
1153 and yellowish bars respectively refer to polluted conditions.