Enhancement of the light scattering coefficient of atmospheric aerosol particles by water uptake

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ENHANCEMENT OF THE LIGHT SCATTERING COEFFICIENT OF ATMOSPHERIC AEROSOL PARTICLES BY WATER UPTAKE

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for the degree of

Doctor of Sciences

presented by

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Summary

Besides gases the Earth’s atmosphere contains aerosols. Aerosols are defined as a collection of solid or liquid particles in air. The concern about aerosols is primarily due to their adverse health effects and their influence on the Earth’s climate system. Atmospheric aerosols influence the Earth’s radiation budget both directly and indirectly. The direct effect is the mechanism by which aerosols scatter and absorb sunlight, thereby changing the radiative balance of the Earth-atmosphere system. Aerosols indirectly influence the Earth’s radiation budget by modifying the microphysical and thus the radiative properties, and the water content and lifetime of clouds. Both effects have a net cooling effect on climate. They play an important role for understanding the observed climate change as counterpart of the warming greenhouse gases like CO$_2$ and others. Nevertheless, they remain moderately to poorly understood and quantified.

For a better quantification of the direct effect it is important to understand how aerosol light scattering and absorption properties are influenced in the atmosphere. The aerosol chemical composition and size distribution and the ambient relative humidity (RH) determine the amount of visible light scattered by aerosols. At high relative humidity (RH) the atmospheric aerosol contains a high fraction of liquid water. Wet aerosol particles are larger than their dry equivalents, therefore they scatter more light. At a fixed RH, the scattering depends mainly on the dry particle size distribution and on the particles’ hygroscopicity, which is determined by their chemical composition.

The goal of this thesis was to study how the light scattering of atmospheric aerosol particles increases by water absorption. The light scattering coefficient $\sigma_{sp}$ can be measured by sampling ambient air into a nephelometer. To ensure comparability between different research stations, it is recommended to measure $\sigma_{sp}$ at RH below 40%, which is considered a dry measurement. However, it is known from global circulation model studies that the negative radiative forcing of the aerosols is significantly higher when the ambient RH is accounted for. To measure $\sigma_{sp}$ at different RH, we built, in the context of this thesis, a humidification system for a commercial nephelometer (TSI Inc., model 3563) which allows to measure $\sigma_{sp}$ at a defined humidity between 40 and 95% RH. The system, consisting of a humidifier followed by a dryer and the nephelometer, is able to measure how hygroscopic properties and hysteresis effects of deliquescent atmospheric aerosol particles influence the $\sigma_{sp}$. The system can be continuously and remotely operated with very little maintenance. The light scattering enhancement factor $f(RH)=\sigma_{sp}(RH)/\sigma_{sp}(dry)$ was used to quantify the dependence of $\sigma_{sp}$ on RH. However, the RH does not always determine alone if an aerosol particle is liquid or solid. For deliquescent aerosols, which can exist in two phases at the same RH, known as hysteresis, the RH history determines the aggregate state. In the following we will use the following notations: When an aerosol particle experiences an increase of RH it is hydrated, whereas by a decrease of RH the particle gets dehydrated.

First we characterized the new humidified nephelometer with monodisperse ammonium sulfate and sodium chloride particles at four different dry particle sizes. Measurements of $\sigma_{sp}$
and \( f(RH) \) and their prediction based on Mie theory agreed within the range of uncertainty. Then we compared in a joint field campaign our instrument to the humidified nephelometer of DOE/ARM (US Department of Energy Atmospheric Radiation Measurements). This intercomparison indicated that the DOE/ARM instrument measured predominately the \( f(RH) \) that is representative of the lower hydration curve. Our humidified nephelometer measured both the \( f(RH) \) of the hydration and dehydration branch of the hysteresis curve. When both instruments measured aerosol that exhibited no distinct deliquescence they agreed well, which was not the case otherwise. Thus, we show that the measurement of the dehydration branch provides additional information about the aggregate state of the aerosol which improves the result of model calculations of the direct aerosol effect.

The light scattering enhancement factor is an aerosol property that is independent of concentration, i.e. an intensive aerosol property, and is expected to vary at different sites. Therefore we investigated the \( f(RH) \) and other intensive properties of free tropospheric and marine air. The humidified nephelometer measured at the clean continental background station Jungfraujoch, Switzerland, at 3580 m a.s.l., and at the marine site Mace Head, Ireland, which is only about 100 m from the shoreline and faces the open Atlantic Ocean. At each station the measurement extended over one month. At the Jungfraujoch we mostly measured light scattering enhancement factors \( f(RH) \) between 80 and 90\% RH. The \( f(RH=85\%) \) reached values up to 3.3, whereas the lowest \( f(RH=85\%) \) values of 1.2 were detected during a Saharan dust event (SDE). On average, excluding the SDE, the \( f(RH=85\%) \) was 2.23. The RH dependence of \( f(RH) \) over the whole RH range showed no hysteresis behavior (i.e. the particles were always wet), and was similar on three different days, during which we cycled the RH, indicating that on these days the aerosol had similar physical and chemical properties in the relevant size range. For Mace Head we split the data for two distinct air mass types, i.e., polluted and clean marine. The \( f(RH=85\%) \) of polluted air was on average 1.77 and of clean marine air 2.22, both for winter conditions with low biological activity in the sea. No distinct hysteresis behavior was observed for the polluted aerosol but a distinct hysteresis was encountered during clean marine conditions: Here the \( f(RH=55\%) \) values for the hydrated particles were on average 35\% higher than for the dehydrated particles.

The RH influences also intensive properties other than \( f(RH) \), such as the backscatter fraction \( b \) and the single scattering albedo \( \omega_0 \). For both sites we analyzed the change of those intensive properties due to water uptake of the aerosol particles. Generally \( b \) gets smaller with increasing RH, due to particle growth, and \( \omega_0 \) gets closer to 1, because the influence of the scattering upon the absorption becomes more important. At Mace Head the average \( \omega_0(\text{RH}=85\%) \) was 0.97 and at the Jungfraujoch 0.95, while at dry conditions the \( \omega_0 \) values were 0.95 and 0.91, respectively. The backscatter fraction changed at Mace Head from 0.11 at dry conditions to 0.09 at 85\% RH and at the Jungfraujoch from 0.13 to 0.09.

At both sites we compared measured to predicted \( f(RH) \), calculated with a model based on Mie theory. We used measured time resolved aerosol size distributions and hygroscopic growth factors as input. For the Jungfraujoch we additionally used time resolved refractive indices gained from aerosol chemical composition measurements, whereas for Mace Head we used a fixed refractive index. At Mace Head measured and modeled \( \sigma_{sp}(\text{dry}) \) agreed very well (slope=0.99, \( R^2=0.90 \)) and \( f(RH) \) agreed well (0.91, 0.77). Also at the Jungfraujoch the \( f(RH) \) was reproduced well (1.08, 0.89).

The results reveal that our humidified nephelometer is well suited to measure \( f(RH) \) and other intensive aerosol properties at different sites. Water uptake of aerosol particles changes their radiative properties. The applied model transforms \( \sigma_{sp}(\text{dry}) \) well into ambient \( \sigma_{sp} \) values. The results will help in better parameterizing optical parameters in global models.
Zusammenfassung


Das Ziel dieser Doktorarbeit war, herauszufinden wie die Lichtstreuung von atmosphärischen Aerosolpartikeln durch Wasseraufnahme zunimmt. Der Lichtstreuungskoeffizient \( \sigma_{sp} \) wird gemessen, indem die Außenluft in einem Nephelometer beprobt wird. Um zwischen Messungen verschiedener Forschungsstationen vergleichen zu können, wird empfohlen, den \( \sigma_{sp} \) bei einer RH kleiner als 40% zu messen, was dann als trockene Messung bezeichnet wird. Jedoch weiss man aus globalen Zirkulationsmodellen, dass der negative Strahlungsantrieb der Aerosole deutlich grösser ist, wenn man die Außenfeuchtigkeit einbezieht. Um nun \( \sigma_{sp} \) bei verschiedener RH zu messen, bauten wir im Rahmen dieser Doktorarbeit ein Befeuchtungssystem für ein kommerzielles Nephelometer (TSI Inc., Modell 3563), welches die Messung von \( \sigma_{sp} \) bei einer definierten Feuchtigkeit zwischen 40 und 95% RH erlaubt. Dieses System besteht aus einem Befeuchter, gefolgt von einem Trockner und dem Nephelometer und misst, wie hygroskopische Effekte von atmosphärischen Aerosolpartikeln den \( \sigma_{sp} \) beeinflussen. Das System kann fortlaufend, über Internet und mit wenig Unterhalt betrieben werden. Der Lichtstreuungs-Erhöhungsfaktor \( f(RH) = \sigma_{sp}(RH)/\sigma_{sp}(trocken) \) wurde benutzt, um die Abhängigkeit des \( \sigma_{sp} \) von der RH zu quantifizieren. Jedoch bestimmt die RH nicht immer allein, ob ein bestimmtes Aerosolpartikel flüssig oder fest ist. Für deliqueszierende Aerosolpartikel, welche bei der gleichen RH in zwei verschiedenen Phasen existieren können,
Zusammenfassung


Die RH beeinflusst auch andere intensive Aerosoleigenschaften als $f(RH)$, wie zum Beispiel die Rückstreufraktion $b$ und die Einzelstreu-Albedo $\omega_0$. Wir untersuchten für beide Messstationen die Änderung dieser intensiven Eigenschaften durch Wasseraufnahme der Aerosolpartikel. Generell wird $b$ kleiner mit zunehmender RH, weil die Partikel wachsen, und die $\omega_0$ nähert sich 1, weil die Lichtstreuung mehr und mehr über die Lichtabsorption dominiert. In Mace Head lag $\omega_0(RH=85\%)$ im Mittel bei 0.97 und auf dem Jungfraujoch bei 0.95, während bei tiefer Feuchte die Werte bei 0.95 beziehungsweise 0.91 lagen. Die Rückstreufraktion veränderte sich in Mace Head von 0.11 bei tiefer Feuchte zu 0.09 bei 85% RH und auf dem Jungfraujoch von 0.13 zu 0.09.

Für beide Messstationen verglichen wir die $f(RH)$-Messungen mit Werten, die anhand eines auf Mie-Theorie basierenden Modells berechnet wurden. Dazu benutzten wir zeitlich aufgelöste gemessene Aerosol Grössenverteilungen und hygroskopische Wachstumsfaktoren. Für die Berechnung der $f(RH)$-Werte auf dem Jungfraujoch verwendeten wir zusätzlich zeitlich aufgelöste Brechungsindizes, welche aus Messungen der chemischen Zusammensetzung der
Aerosole gewonnen wurden. Für Mace Head benutzten wir einen festen Brechungsindex. Die gemessenen und modellierten Werte von $\sigma_{sp}$(trocken) von Mace Head stimmten sehr gut (Steigung=0.99, $R^2=0.90$) und von $f$(RH) gut (0.91, 0.77) überein, und für das Jungfraujoch wurde $f$(RH) gut durch das Modell reproduziert (1.08, 0.89).

Die Resultate zeigen, dass unser befeuchtetes Nephelometer gut geeignet ist, um $f$(RH) und andere intensive Aerosoleigenschaften an verschiedenen Orten zu messen. Die Wasseraufnahme von Aerosolpartikeln ändert ihre Strahlungseigenschaften. Das angewendete Modell überführt trockene $\sigma_{sp}$ gut in $\sigma_{sp}$ bei Aussenfeuchtigkeit. Diese Resultate sind hilfreich für eine bessere Parametrisierung der optischen Aerosoleigenschaften in globalen Modellen.
Introduction

Everybody already had contact with the topic of this thesis and experienced light scattering and light scattering enhancement due to water uptake by aerosol particles. An example for an (almost) everyday experience with light scattering is the view on mountains, for example from Thun, Switzerland towards the Alps. Visibility of objects at some distance can change with the amount of aerosol particles between the observer and the target (here the mountains) and with the relative humidity of the air. The reasons for this will be explained in this introduction, and an example for this phenomenon is shown in Fig. 1.1.

Figure 1.1 displays three pictures of the view of the Alps. On the picture on top the mountains are nicely visible, and on the one in the middle and on the bottom the view on the mountains is blurred. The top and middle pictures are on the same day but at different relative humidity (RH) (top \(\sim 50\%\), middle \(\sim 90\%\)). We can assume that the aerosol concentration is about the same throughout the day. In comparison, on the top and bottom pictures the RH is about the same, so probably the higher aerosol concentration in the bottom picture reduces the visibility.

This thesis deals with the water uptake of aerosol particles and how this influences aerosol optical properties and climate. In the following, the introduction is organized by questions, from general questions about the Earth’s climate (Sect. 1.1) to climate change (Sect. 1.2), to one component — the atmospheric aerosol — which influences the climate of the Earth (Sect. 1.3 and 1.4), to the final question: Why are the results presented in this thesis of importance (Sect. 1.8)?

1.1 What factors determine the Earth’s climate?

(Section adapted from IPCC (2007))

The climate system is very complex and consists of the atmosphere, land surface, snow and ice, oceans and other water containing objects and living creatures. Climate is often
defined as average weather. It includes the mean and the variability of temperature, precipitation and wind over a period of time, ranging from months to millions of years (the classical period is 30 years). The climate system is influenced by its own internal dynamics and by changes of external factors that affect climate (called forcings) and therefore develops over time. External forcings originate from natural phenomena such as volcanic eruptions and solar variations as well as anthropogenic (man-made) changes in atmospheric composition. The radiation from the Sun powers the climate system.

There are three fundamental ways to alter the radiation balance of the Earth [IPCC, 2007]: 1) by changing the incoming solar radiation (e.g., by changes in the Earth’s orbit or by changes in the Sun); 2) by changing the fraction of solar radiation that is reflected (called albedo; e.g., by changes in cloud cover, atmospheric particles or vegetation); and 3) by altering the long-wave radiation from the Earth back towards space (e.g., by changing greenhouse gas (GHG) concentrations). Climate responds directly to such changes, as well as indirectly, through a variety of feedback mechanisms.

Solar energy of 1370 Watt per square meter and second reaches the top of the Earth’s atmosphere that is facing the Sun during daytime. Averaged over a whole day and the entire planet this results in a quarter of the 1370 Wm$^{-2}$, i.e., 343 Wm$^{-2}$. About 30% of the sunlight that reaches the top of the atmosphere is reflected back to space. Clouds and small particles in the atmosphere known as aerosol particles are responsible for roughly two thirds of this
reflectivity. Light-colored areas of Earth’s surface - mainly snow, ice and deserts - reflect the remaining one-third of the sunlight. The energy that is not reflected back to space (about 240 Wm$^{-2}$) is absorbed by the Earth’s surface and atmosphere. The Earth must radiate on average the same amount of energy back to space to keep the equilibrium between incoming and outgoing radiation. Most of it is emitted by long-wave radiation. However a surface temperature of only $-19^\circ$C would be necessary to emit 240 Wm$^{-2}$, which is much colder than the average surface temperature we have today on Earth (about $14^\circ$C) and which is found in 5 km above the surface. Greenhouse gases (e.g. H$_2$O, CO$_2$ CH$_4$, N$_2$O, ...) are the reason for the increase in average surface temperature of the Earth. They act as a partial filter for long-wave radiation from the surface, as part of the outgoing radiation is reflected by those gases and so contributes to a higher surface temperature. This process is known as greenhouse effect. The most important greenhouse gases are water vapor and carbon dioxide. The two most abundant constituents of the atmosphere — nitrogen and oxygen — have no such filtering effect on long-wave radiation.

Clouds can also reflect long-wave radiation back to the surface, but this effect is offset by their reflectivity of incoming radiation, such that on average, clouds tend to have a cooling effect on climate. Human activities intensify the greenhouse effect through the release of greenhouse gases. For instance, the amount of carbon dioxide in the atmosphere has increased by about 35% in the industrial era, and this increase is known to be due to human activities, primarily the combustion of fossil fuels and removal of forests. Consequently human activities have dramatically changed the chemical composition of the global atmosphere with serious implications for the climate (see Sect. 1.2).

More solar energy arrives in the tropics than at higher latitudes. Some of this energy is transported from the equatorial areas towards the poles via atmospheric and oceanic circulations. Energy is also needed to evaporate water from the sea or land, and this energy (latent heat) is released when water vapor condenses in clouds. The release of latent heat drives the atmospheric circulation, which drives much of the ocean circulation. The wind moves the surface waters of the ocean, and precipitation and evaporation alters the ocean’s surface temperature and salinity. Melting of ice sheets, changes in the type and distribution of vegetation or variation of the temperature of the atmosphere or ocean will influence the large-scale circulation features of the atmosphere and oceans.

### 1.2 Is the Earth’s climate changing?

In the 1980ies scientific and public awareness of CO$_2$ and temperature increase awoke. Therefore broad and balanced information about climate change became necessary, so the WMO (World Meteorological Organization) and the United Nations Environment Program (UNEP) founded the Intergovernmental Panel on Climate Change (IPCC) in December 1988. The IPCC should provide the governments of the world with a clear scientific view what is happening to the world’s climate [http://www.ipcc.ch](http://www.ipcc.ch). The initial task of the IPCC was to prepare a comprehensive review and recommendations with respect to the state of knowledge of the science of climate change; social and economic impact of climate change, possible response strategies and elements for inclusion in a possible future international convention on climate [http://www.ipcc.ch](http://www.ipcc.ch). Since then the IPCC published 4 reports, the last one in 2007 [IPCC, 2007](http://www.ipcc.ch). Its major findings are the following:

- Atmospheric CO$_2$ concentrations (379 ppm) in 2005 exceed by far the natural range over the last 650,000 years.

- For the next two decades a warming of about 0.2°C per decade is predicted for a range of different emission scenarios. Even if the concentrations of all greenhouse gases and
aerosols had been kept constant at year 2000 levels, a further warming of about 0.1°C per decade would be expected. Afterwards, temperature projections depend more and more on specific emissions scenarios.

- Temperature increased over the last 100 years (1906-2005) by 0.74°C. In the third IPCC report (IPCC, 2001) this increase was given as 0.6°C (1901-2000). The linear warming trend over the last 50 years (0.13°C per decade) is nearly twice that for the last 100 years (see Fig. 1.2a).

- Global average sea level has risen since 1961 at an average rate of 1.8 mm/yr and since 1993 at 3.1 mm/yr, with contributions from thermal expansion, melting glaciers and ice caps, and polar ice sheets (see Fig. 1.2b).

- The estimate for sea level rise in the end of the 21st century is 1.8 to 5.9 mm/yr depending on emission scenario. There is very high confidence that the net effect of human activities since 1750 has been one of warming.

- Between 1970 and 1994 global GHG emissions due to human activities have grown by 70%.

Figure 1.2: (adapted from IPCC (2007)): Observed changes in (a) global average surface temperature, and (b) global average sea level from tide gauge (blue) and satellite (red) data. The differences are relative to corresponding averages for the period 1961-1990. Smoothed curves represent decadal averaged values while circles show yearly values. The shaded areas are the uncertainty intervals estimated from a comprehensive analysis of known uncertainties.

Radiative forcing is a measure of how much a substance influences the climate system at a certain time. It is defined by the IPCC (2007) as a measure of the influence a factor has in altering the balance of incoming and outgoing energy in the Earth-atmosphere system and is an index of the importance of the factor as a potential climate change mechanism. Climate model calculations predict an approximately linear relationship between global mean-radiative forcing $\Delta F$[Wm$^{-2}$] and the equilibrium global mean surface temperature $\Delta T_S$[K] (Seinfeld and Pandis, 1998):

$$\Delta T_S = \frac{l}{r} \Delta F,$$

(1.1)
where \( l \) is the climate sensitivity parameter ranging from 0.3 to 1.4 Km\(^2\)W\(^{-1}\) (IPCC, 1995). The variability of \( l \) originates primarily from different treatments of cloud feedback by Atmospheric General Circulation Models.

Figure [1.3] shows a summary of the main components of the radiative forcing of climate change. Values are given in Wm\(^{-2}\) and are for changes in 2005 relative to preindustrial conditions (1750). Human activities cause significant changes in long-lived greenhouse gases, ozone, water vapor, surface albedo, aerosols and contrails. The only significant natural forcing between 1750 and 2005 occurred in solar irradiance. Positive radiative forcings lead to a warming of the climate and negative radiative forcings to a cooling. The total net radiative forcing between 1750 and 2005 is 1.6 Wm\(^{-2}\), with CO\(_2\), methane and other greenhouse gases as strongest contributors to a positive forcing, and with the effects of aerosols reducing the positive forcing.

**Figure 1.3:** Global mean radiative forcings (RF or \( \Delta F \)) and their 90% confidence intervals in 2005 for various agents and mechanisms. Columns on the right-hand side specify best estimates and confidence intervals (RF or \( \Delta F \) values); typical geographical extent of the forcing (spatial scale); and level of scientific understanding (LOSU) indicating the scientific confidence level (IPCC, 2007).

### 1.3 What are aerosols?

An aerosol is defined as an assembly of liquid or solid particles suspended in a gaseous medium long enough to be able to observe or measure them (Baron, 1993).

The size of aerosol particles ranges from a few nanometers up to about 100 \( \mu \)m in diameter. They can be classified into four main size categories (Whitby, 1978). The nucleation and Aiken mode consist of particles with diameters smaller than 100 nm. Particles in this size range are formed from condensation of gases or are directly emitted. Accumulation mode particles have diameters in the range of 100 nm to 1-2 \( \mu \)m and many of them are formed by coagulation of smaller particles and condensation. The largest particles are in the coarse
mode. Particle number concentrations in the atmosphere range from less than 1000 cm$^{-3}$ at a remote location such as the Jungfraujoch (Nyeki et al., 1998) up to $\sim$500000 cm$^{-3}$ along the main transit highway through the Swiss Alps (A2) (Weimer et al., 2009).

Atmospheric aerosol particles are either directly emitted as particles (primary aerosol) or formed in the atmosphere from gaseous precursors by a gas-to-particle conversion process (secondary aerosol). The size and composition of particles changes by condensation of gaseous species or by evaporation, by coagulation with other particles, by chemical reactions or by water uptake to become cloud droplets. Particles are eventually removed from the atmosphere by two major processes: deposition at the Earth surface (dry deposition) or incorporation into cloud droplets and snow during the formation of precipitation (wet deposition) (Seinfeld and Pandis, 1998). They have a lifetime in the troposphere from a few days to a few weeks, depending on precipitation pattern and size of the particles (coarse particles settle faster).

The main components of atmospheric aerosol particles are sulfate, ammonium, nitrate, elemental and organic carbon, sodium, chloride, trace metals, mineral dust, and water (Hueglin et al., 2005; Zhang et al., 2007; Cozic et al., 2008). Aerosols originate either from natural or from anthropogenic emissions. Significant natural primary sources are deserts, soil dust, sea salt, volcanic eruptions. These sources produce mainly coarse particles. Secondary natural aerosols are sulfate and organics from biogenic origin. Anthropogenic contributions arise primarily from combustion processes for heating and transport, industrial processes, agriculture, and dust from roads (Seinfeld and Pandis, 1998). Anthropogenic aerosols are mainly found in the fine mode.

Aerosols are important for at least two reasons. First, they influence the Earth’s climate system, and second, particulate air pollution has adverse health effects, as outlined in the following (Sect. 1.5).

### 1.4 How do aerosols influence the Earth’s climate?

Figure 1.3 splits the radiative forcing by aerosol particles into a direct and a cloud albedo (indirect) effect. The two aerosol effects on the Earth’s radiative balance are important since they amount to about 75% of the current forcing of CO$_2$ (yet with opposite sign), however, the level of scientific understanding (LOSU) is only medium to low.

The main reasons of uncertainty are on the one hand due to uncertainties in the aerosol loading in the atmosphere (due to the aerosols variability in space and time, their short residence time in the atmosphere (about a week) and their episodical removal by precipitation), and on the other hand due to an insufficient knowledge of the involved mechanisms and processes (see Sect. 1.4.1 and 1.4.2). In contrast, the long-lived greenhouse gases have lifetimes of hundreds of years and are well mixed over the Earth.

Concerning aerosols, the dependence of light scattering on particle size and on relative humidity (RH) further contributes to the uncertainties (Schwartz, 1996), which is the major topic of this thesis.

#### 1.4.1 Direct effect

Aerosols influence the climate directly by scattering and absorbing solar radiation (Schwartz, 1996). The magnitude of the direct radiative forcing of aerosols depends on the amount of radiation scattered back to space, which itself depends on the size and optical properties of the particles, their concentration and the solar zenith angle (Seinfeld and Pandis, 1998).
1.4 How do aerosols influence the Earth’s climate?

Table 1.1: Typical values for the albedo (reflectance) of the Earth’s surface (from http://www.eoearth.org/article/Albedo [original sources: Oke (1992); Ahrens (2006)].

<table>
<thead>
<tr>
<th>Soil</th>
<th>dark and wet&lt;br&gt;light and dry</th>
<th>≥0.05&lt;br&gt;≤ 0.4&lt;br&gt;0.15-0.45</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grass</td>
<td>long&lt;br&gt;short</td>
<td>≥ 0.16&lt;br&gt;≤ 0.26</td>
</tr>
<tr>
<td>Tundra</td>
<td></td>
<td>0.18-0.25</td>
</tr>
<tr>
<td>Forests</td>
<td>deciduous&lt;br&gt;coniferous</td>
<td>0.15-0.2&lt;br&gt;0.05-0.15</td>
</tr>
<tr>
<td>Water</td>
<td>small zenith angle&lt;br&gt;large zenith angle</td>
<td>0.03-0.1&lt;br&gt;0.1-1.0</td>
</tr>
<tr>
<td>Snow</td>
<td>old&lt;br&gt;fresh</td>
<td>≥ 0.4&lt;br&gt;≤ 0.95</td>
</tr>
<tr>
<td>Ice</td>
<td>sea&lt;br&gt;glacier</td>
<td>0.3-0.45&lt;br&gt;0.2-0.4</td>
</tr>
<tr>
<td>Clouds</td>
<td>thin&lt;br&gt;thick</td>
<td>0.3-0.5&lt;br&gt;0.6-0.9</td>
</tr>
</tbody>
</table>

Some aerosol species cause a positive forcing, such as fossil fuel black carbon (+0.2 (±0.15) Wm\(^{-2}\)) and biomass burning (+0.03 (±0.12) Wm\(^{-2}\)), while others cause negative forcing such as sulfate (-0.4 (±0.2) Wm\(^{-2}\)), organic carbon (-0.05 (±0.05) Wm\(^{-2}\)), nitrate (-0.1 (±0.1) Wm\(^{-2}\)) and mineral dust (-0.1 (±0.2) Wm\(^{-2}\)) (IPCC, 2007). The direct radiative forcing summed over all aerosol types is negative. The radiative forcing \(\Delta F\) is calculated with the following equation from Haywood and Shine (1995):

\[
\Delta F \approx -DS_0T_\text{atm}^2(1 - A_C)\omega_0\beta\delta \left\{ \left( 1 - R_S \right)^2 - \left( \frac{2R_S}{\beta} \right) \left[ \left( \frac{1}{\omega_0} \right) - 1 \right] \right\},
\]

where \(D\) is the fractional day length, \(S_0\) is the solar constant (1370 Wm\(^{-2}\)), \(T_\text{atm}\) is the fractional transmittance of the atmosphere, \(A_C\) is the fraction of the surface covered by clouds, \(\omega_0\) is the single scattering albedo of the aerosol (for the definition see Eq. 4.7), \(\beta\) is the upscatter fraction of the aerosol, \(\delta\) is the aerosol optical depth, and \(R_S\) is the albedo (reflectance) of the underlying Earth’s surface (typical values see Tab. 1.1).

The upscatter fraction is the fraction of light that is scattered by a particle in the upward hemisphere relative to the local horizon. It depends on the particle size, shape and the solar zenith angle. The upward hemisphere is not the same as the back hemisphere (scattering angles of 90° to 270° with respect to the incoming light beam). The optical depth of a layer is the product of the light extinction coefficient and the depth of the layer.

A derivation of Eq. 1.2 can be found in Seinfeld and Pandis (1998). \(\Delta F\) is zero (and changes from negative (cooling effect) to positive (heating effect) or vice versa), if \(\omega_0\) is equal to the critical \(\omega_\text{crit}\). \(\omega_\text{crit}\) depends on the surface albedo and the upscatter fraction (Haywood and Shine, 1995):

\[
\omega_\text{crit} = \frac{2R_S}{2R_S + \beta(1 - R_S)^2},
\]

Values of \(\omega_0 > \omega_\text{crit}\) result in a cooling of the Earth surface. Figure 1.4 shows the critical single scattering albedo which defines the boundary between negative (cooling) and positive (heating) radiative forcing. A typical global mean surface albedo (\(R_S\)) is about 0.15 and a representative value of the spectrally and solar zenith angle averaged \(\beta\) is about 0.29 (Seinfeld and Pandis, 1998). For these values \(\omega_\text{crit}\) is about 0.6.
Chapter 1 Introduction

1.4.2 Indirect effect

Aerosols serve as cloud condensation and ice nuclei. If there were no aerosol particles no cloud droplets would be formed because super-saturations of several hundred percent would be required for cloud formation (Wilson (1900), cited in Andreae and Rosenfeld (2008)). There are several ways how aerosols indirectly influence the climate:

- **First indirect effect:** An increase in aerosol number concentration as a result of anthropogenic emissions may lead to an increase of cloud droplets. When the same amount of water is distributed over more cloud droplets, less water per droplet is available, and the reflectance (albedo) of the cloud increases, which means that the cloud becomes brighter (Twomey, 1977). This effect is also called cloud albedo effect or Twomey effect.

- **Second indirect effect:** To precipitate a cloud droplet needs a certain size. The formation of precipitation in clouds depends on the cloud droplet size distribution; precipitation is accelerated for a given liquid water content, with fewer, larger droplets than with greater number of small droplets (Seinfeld and Pandis, 1998). One possible effect of reduced cloud droplet size is an increase in cloud life time resulting from a decreased tendency for precipitation (Albrecht, 1989). The resulting increase in the global albedo would be in addition to the increase due the Twomey effect and would further contribute to a cooling of the Earth’s surface. This effect is also known as Albrecht effect.

- **When solar radiation is absorbed by soot particles in clouds, the particles emit thermal radiation. As a consequence the air mass is heated and the increase of temperature could cause evaporation of cloud droplets. This process is called semi-direct effect.**

Two more effects occur in cold clouds, where ice crystals exist:

- **The glaciation effect** refers to an increase in ice nuclei (aerosol particles that serve to form ice particles). More ice nuclei result in a transfer of water vapor from liquid droplets to ice crystals, because of the lower water vapor pressure over ice, which results
in a rapid glaciation of a super-cooled liquid water cloud. Unlike cloud droplets, these ice crystals grow in an environment of high super-saturation with respect to ice, quickly reaching precipitation size, with the potential to turn a non-precipitating cloud into a precipitating cloud (IPCC, 2007).

- The thermodynamic effect refers to a delay in freezing by the smaller droplets resulting in clouds with colder temperatures that reach higher altitudes.

Since the processes in cold clouds are not yet well understood the uncertainty of the last two above mentioned effects are very large. For some of the effects not even the sign of the radiative effect is known (IPCC, 2007).

1.5 How do aerosols influence human health?

Based on some severe air pollution events a temporal correlation between extremely high concentrations of particulate and sulfur oxide air pollution and acute increases in mortality was established in the 1970ies (Pope et al., 2002). In the mean time long-term studies have shown that total, cardiovascular and lung cancer mortality are positively correlated with ambient PM2.5 (particles with an aerodynamic diameter $<2.5\mu m$) concentrations and reduced PM2.5 concentrations were associated with reduced mortality risk (Laden et al., 2006). Moreover Pope et al. (2002) showed that long-term exposure to combustion related particulate air pollution is an important risk factor for cardiopulmonary and lung cancer mortality.

Water uptake also influences the deposition of aerosol particles in the respiratory system, since the deposition mechanisms are influenced by the size of the particles. Since this thesis deals exclusively with the climate relevant effects of water uptake, the health effects are not further elaborated.

1.6 What is light scattering? By what is it influenced?

(Section adapted from Seinfeld and Pandis (1998))

When a beam of light impacts a particle, electric charges in the particle are exited. The excited electric charges reradiate energy in all directions (scattering) and may convert a part of the incident radiation into thermal energy (absorption). Electromagnetic radiation transports energy. This amount of energy per square meter and time is called intensity ($F_0$) and is measured in units of Wm$^{-2}$. The power scattered by a particle is proportional to the incident intensity,

$$F_{\text{scat}} = C_{\text{scat}} * F_0,$$

where $C_{\text{scat}}$, in units of m$^2$, is the single particle cross-section. For absorption the energy absorbed is described analogously, where $C_{\text{abs}}$ is the single particle absorption cross-section.

Conservation of energy requires that the light removed from the incident beam by the particle is accounted for by scattering in all directions and absorption in the particle. For the interaction of solar radiation with atmospheric aerosols, elastic light scattering is the process of interest. The combined effect of scattering and absorption is referred to as extinction and the extinction cross-section $C_{\text{ext}}$, can be defined by

$$C_{\text{ext}} = C_{\text{scat}} + C_{\text{abs}}.$$

$C_{\text{ext}}$ has the units of an area; in the language of geometrical optics, one would say the particle casts a ‘shadow’ of area $C_{\text{ext}}$ on the radiative energy passing the particle. This shadow can be considerably greater or much less than the particle’s geometric shadow. The dimensionless scattering efficiency of a particle, $Q_{\text{scat}}$, is $C_{\text{scat}}/A$, where $A$ is the cross-sectional (geometric) area of the particle.

The absorption and scattering of light by a spherical particle is a classical problem in physics, the mathematical formalism of which is called Mie theory (Mie, 1908), treated in a series of text books, e.g. Bohren and Huffman (2004). The key parameters that govern the scattering and absorption of light by a particle are (1) the wavelength ($\lambda$) of the incident radiation, (2) the size of the particle, and (3) chemistry of the particle. The size of the particle is usually expressed as the dimensionless parameter:

$$\alpha = \frac{\pi D_p}{\lambda}, \quad (1.6)$$

or in other words the ratio of the circumference of the particle (with diameter $D_p$) to the wavelength of light. The chemistry of the particle is important because it influences the complex refractive index, which describes the particle optical property relative to the surrounding medium:

$$N = n + ik. \quad (1.7)$$

The real part $n$ and the imaginary part $k$ of the refractive index represent the non-absorbing and absorbing component, respectively, of the refractive index and are both functions of $\lambda$. The refractive index $N$ is normally normalized by the refractive index of the medium, $N_0$, and denoted by $m$

$$m = \frac{N}{N_0}, \quad (1.8)$$

where the medium of interest to us is air.

The discussion above relates to the scattering of light by a single particle. A rigorous treatment of the scattering by an ensemble of particles is very complicated. If the average distance between particles is large compared to the particle size, it can be assumed that the total scattering intensity is the sum of the intensities scattered by individual particles, and single particle scattering theory can be used. Such an assumption is even valid for the most concentrated atmospheric conditions. Consider for example a total particle concentration of $10^6$ cm$^{-3}$, consisting of monodisperse 1 $\mu$m diameter spheres, which is a number concentration above that of most atmospheric conditions. Even at this extreme aerosol loading, the volume fraction occupied by the particles in the air is only $(\pi/6)\cdot10^{-6}$.

Consider the solar beam traversing an atmospheric layer containing aerosol particles. Light extinction occurs at the attenuation of the incident light by scattering and absorption as it traverses the layer. The fractional reduction in intensity over an incremental depth in the layer $dz$ can be expressed as $dF = \sigma_{\text{ext}} F dz$, where $\sigma_{\text{ext}}$ is the extinction coefficient, having units of inverse length [m$^{-1}$],

$$\sigma_{\text{ext}} = C_{\text{ext}} N, \quad (1.9)$$

where $N$ is the total particle number concentration (particles m$^{-3}$). Equation (1.9) is written for a collection of monodisperse particles.

Thus $\sigma_{\text{ext}}$ is the fractional loss of intensity per unit path length, and

$$\frac{dF}{dz} = -\sigma_{\text{ext}} F. \quad (1.10)$$
1.7 What is the influence of water uptake on light scattering?

If \( F_0 \) is the intensity at \( z=0 \) (the top of the layer), then the intensity at any distance \( z \) into the layer is

\[
\frac{F}{F_0} = \exp \left( -\sigma_{\text{ext}} z \right).
\]

(1.11)

As noted above, the dimensionless product \( \delta = \sigma_{\text{ext}} z \) is called optical depth of a layer and Eq. 1.11 is called Beer-Lambert law.

For a population of monodisperse, spherical particles at a number concentration of \( N \), the extinction coefficient is related to the dimensionless extinction efficiency \( Q_{\text{ext}} \) by

\[
\sigma_{\text{ext}} = \frac{\pi D_p^2}{4} N Q_{\text{ext}}.
\]

(1.12)

For a population of different sized particles of identical refractive index \( m \) with a number size distribution of \( n(D_p) \) Eq. 1.12 changes to

\[
\sigma_{\text{ext}} = \int_0^{D_p\text{max}} \frac{\pi D_p^2}{4} Q_{\text{ext}} n(D_p) dD_p.
\]

(1.13)

The extinction coefficient can be expressed as the sum of a scattering coefficient \( \sigma_{\text{scat}} \) and an absorption coefficient \( \sigma_{\text{abs}} \),

\[
\sigma_{\text{ext}} = \sigma_{\text{scat}} + \sigma_{\text{abs}}
\]

(1.14)

with similar relations to \( Q_{\text{scat}} \) and \( Q_{\text{abs}} \).

We can decompose \( \sigma_{\text{scat}} \) and \( \sigma_{\text{abs}} \) into contributions from the gas and particulate components of the atmosphere:

\[
\sigma_{\text{scat}} = \sigma_{\text{sg}} + \sigma_{\text{sp}}
\]

(1.15)

\[
\sigma_{\text{abs}} = \sigma_{\text{ag}} + \sigma_{\text{ap}}
\]

(1.16)

where

\[
\sigma_{\text{sg}} = \text{scattering coefficient due to gases (the so called Rayleigh scattering coefficient)}
\]

\[
\sigma_{\text{sp}} = \text{scattering coefficient due to particles}
\]

\[
\sigma_{\text{ag}} = \text{absorption coefficient due to gases}
\]

\[
\sigma_{\text{ap}} = \text{absorption coefficient due to particles}
\]

A ratio \( \sigma_{\text{scat}}/\sigma_{\text{sg}} \) of unity indicates particle free air (\( \sigma_{\text{sp}} = 0 \)). Thus the higher this ratio, the greater is the contribution of particulate scattering to total scattering.

### 1.7 How is the influence of water uptake on light scattering?

The concentration of water vapor can reach up to 3% (by volume) in the Earth’s atmosphere. It is mainly found in the lower atmosphere and is highly variable. Often the water content for a given ambient temperature is expressed as relative humidity (RH), which is defined as the ratio of the partial pressure of water \( (p_{\text{H}_2\text{O}}) \) to its saturation water vapor pressure at the same temperature \( (p_{\text{H}_2\text{O}}^0) \):

\[
\text{RH} = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}}^0}.
\]

(1.17)

The relative humidity or water activity \( (a_w) \) over a droplet in equilibrium is defined with the Köhler theory. It depends on the particle diameter, the temperature, on properties of water, and on the solubility of the involved chemical substances (e.g. inorganic salts, organics, soot,
...). In general if the RH increases, the aerosol takes up water and the diameter of soluble species increases.

The behavior of particles due to enhanced RH can be split into three categories: some aerosol species such as soot or mineral dust do not significantly grow in diameter with increasing RH [Weingartner et al., 1997; Sjogren et al., 2008], since they are insoluble. Some aerosol species are soluble; they take up water, whereas their size changes smoothly as the RH increases or decreases, they are hygroscopic but do not show hysteresis behavior (e.g. \( \text{H}_2\text{SO}_4 \), some organics, ...). The third group of aerosol species is also hygroscopic and shows hysteresis behavior. But what does that mean? Starting with a solid particle (mostly inorganic salts) at low RH; when the RH increases, the solid particle remains solid until the RH reaches a characteristic deliquescence relative humidity (DRH). At the DRH, the solid particle spontaneously absorbs water, producing a saturated aqueous solution. Further increase of the RH leads to additional water condensation onto the salt solution to maintain thermodynamic equilibrium. On the other hand, as the RH of the air surrounding the wet particle is decreased, evaporation of water occurs and the liquid particle shrinks in diameter. However the solution generally does not crystallize at the DRH, but remains supersaturated resulting in a metastable state until the RH decreases below a critical efflorescence relative humidity (ERH) at which crystallization occurs. This hysteresis phenomenon showing different DRH and ERH points is illustrated in Fig. 1.5. Additionally the hygroscopic behavior of \( \text{H}_2\text{SO}_4 \) is shown.

![Figure 1.5: Diameter change of (NH\(_4\))\(_2\)SO\(_4\), NH\(_4\)HSO\(_4\), and H\(_2\)SO\(_4\) particles as a function of relative humidity. \( D_{p0} \) is the diameter at 0% RH (from Seinfeld and Pandis (1998).](image)

Aerosol light scattering strongly depends on the particle size, therefore a change in size due to water uptake or loss has a strong impact on the amount of light scattering. In addition the particle refractive index also depends on water content of the particle. Figure 1.6 shows the influence of a change in dry particle size and chemical composition, on the light scattering enhancement factor \( f(\text{RH}) \) defined as

\[
f(\text{RH}) = \frac{\sigma_{sp}(\text{RH})}{\sigma_{sp}(\text{RH} = \text{dry})}.
\] (1.18)

The \( f(\text{RH}) \) decreases with increasing particle diameter and shows large differences for different inorganic salts.
1.8 Why did we study the enhancement of the light scattering coefficient of atmospheric aerosol particles by water uptake?

One of the major aims of this thesis was to determine the $f(RH)$ by measuring in parallel the dry scattering coefficient ($\sigma_{sp}(RH=\text{dry})$) and the scattering coefficient at a certain enhanced RH ($\sigma_{sp}(RH)$). As different locations are expected to exhibit different $f(RH)$, these measurements were performed at a number of sites with differing aerosol characteristics.

At most sites the scattering coefficients are measured at dry conditions (<40% RH) to be comparable with measurements at other locations. However, these values differ from the ambient, climate relevant ones. Not only the scattering coefficients but also the intensive aerosol properties $\omega_0$ and $\beta$ change with RH. Many global circulation model studies found that the negative radiative forcing of the aerosols is significantly enhanced when the absorbed water at ambient RH was accounted for (Haywood and Ramaswamy, 1998; Penner et al., 1998; Grant et al., 1999; Kiehl et al., 2000). Therefore, we built a humidification system for a nephelometer, an instrument which detects scattering and backscattering coefficients (see Sect. 2.1), to measure $\sigma_{sp}$ at different RH. The humidification system was designed to be able to measure both branches of the hysteresis curve (see Fig. 1.5), because they represent the two extremes of particle size as a function of RH for radiative forcing calculations (Pilinis et al., 1995). Humidification of aerosol particles with subsequent detection of the scattering coefficient is not a new topic. A history of the development of humidified nephelometers will be given in Sect. 2.2.

At many sites measurements of scattering coefficients have been preformed for many years e.g. at Mauna Loa, USA (since 1974), at the Jungfraujoch (since 1995), at Hohenpeißenberg, Germany (since 1997), at Neumayer, Antarctica (since 2000) and at other sites for a few years e.g. Mt. Waliguan, China (since 2005), Cape Point, South Africa (since...
As explained above, at all these stations $\sigma_{sp}$ is not measured at its climate relevant RH, but under dry conditions. Therefore it is desirable that either $\sigma_{sp}$ is additionally measured at ambient RH or $\sigma_{sp}(\text{dry})$ can be transformed into $\sigma_{sp}(\text{RH})$ values. Such transformation can be done by models, based on Mie theory, for which certain parameters such as size distribution, chemical composition, or hygroscopicity are needed. The model output then needs to be compared to measurements of $\sigma_{sp}(\text{RH})$, which is another task of this thesis.

References


1.8 Why did we study the enhancement of the light scattering coefficient?


2

Methodology

This chapter describes in a first section how the nephelometer (nephelometer comes from the greek word for clouds, nephos and is the instrument we used to measure scattering coefficients ($\sigma_{sp}$)) works, how the measured $\sigma_{sp}$ have to be corrected and how the nephelometer is calibrated. To be able to measure $\sigma_{sp}$ at different relative humidity (RH) (20-95% RH), the aerosol needs to be humidified, which can be done in many different ways and which has been done since more than 40 years. The development of humidification systems for nephelometers and their applications is presented in the Sect. 2.2 in relation to how we constructed our humidified nephelometer (presented in Sect. 2.3).

2.1 Nephelometer

2.1.1 How the nephelometer operates

(Section adapted from TSI (2005))

A small, turbine blower draws an aerosol sample through the large diameter inlet into the measurement volume (sensing volume on Fig. 2.1). There, the sample is illuminated over an angle of 7 to 170° by a halogen lamp directed through an optical light pipe and opal glass diffuser.

The sample volume is viewed by three photomultiplier tubes (PMT) through a series of apertures set along the axis of the main instrument body. Aerosol scattering is viewed against the backdrop of a very efficient light trap. The light trap, apertures, and a highly light-absorbing coating on all internal surfaces of the instrument combine to give a very low scatter signal from the walls of the instrument. In front of the PMT tubes there are filters that split and direct the light, which has been scattered by the aerosol in the sensing volume. The light is directed into three band pass filters, blue, green and red. A constantly rotating reference chopper has separate areas to provide three types of signal detection. The first area gives a measure of the aerosol light scattering signal allowed by an opening in the
rotating chopper. The second area blocks all light from detection and gives a measurement of the PMT dark current which is subtracted from the measurement signal. The third area is a translucent portion of the chopper, illuminated by the halogen lamp, which provides a measure of the light-source signal. In this way, over time, any change in the light source or in detector efficiency is compensated.

In backscatter mode, the backscatter shutter rotates under the lamp to block light in the 7 to 90° range. When light is blocked, only light scattered in the backward direction is transmitted to the PMT detectors. The backscatter signal can be subtracted from the total signal to calculate forward-scattering signal data. When this measurement is not of interest, the backscatter shutter can be ‘parked’ in the total scatter position.

Periodically, an automated valve built into the inlet can be activated to divert the entire aerosol sample through a high-efficiency (HEPA) filter. This gives a measure of the clean-air signal for the local environment (so called zero measurement). This signal is subtracted, along with the PMT dark current signal, from the aerosol-scatter signal to give only that portion of the scatter signal provided by the sample aerosol.

Particle-scattering parameters for all three wavelengths of total and backscatter signal are continuously averaged and passed to a computer or data logger for permanent storage.

### 2.1.2 Correction

It is required to correct nephelometer measurements of $\sigma_{sp}$ for angular nonidealities, when the whole scattering range (0-180°) is accounted for, since the nephelometer measures $\sigma_{sp}$ only between 7 and 170°. A correction factor $C$ may be defined as

$$C = \frac{\sigma_{true}}{\sigma_{neph}},$$

where $\sigma_{true}$ is the Mie-calculated 0-180° or 90-180° scattering coefficient and $\sigma_{neph}$ derives from a modified Mie-integral (Heintzenberg, 1978) using the measured angular sensitivity of the nephelometer (Anderson and Ogren, 1998). The angular sensitivity is taken from Anderson et al. (1996) and correction factors are listed in Tab. 2.1. To calculate the correction factor $C$, the Ångström exponent is needed:

$$\hat{a}_{s}(\lambda_1, \lambda_2) = -\frac{\log(\sigma_{sp}^{\lambda_1} / \sigma_{sp}^{\lambda_2})}{\log(\lambda_1 / \lambda_2)}$$

The correction factor $C$ uses the $a$ and $b$ values from Tab. 2.1 and the $\hat{a}_{s}$-values form uncorrected nephelometer measurements of $\sigma_{sp}$ at two wavelength: $\hat{a}_{s}(450/550)$ at 450 nm, $\hat{a}_{s}(450/700)$ at 550 nm, $\hat{a}_{s}(550/700)$ at 700 nm.
2.2 Development of humidified nephelometers

Table 2.1: Correction factors for total scatter as a linear function of the Ångström exponent (see Eq. 2.2) \( C = a + b \cdot \tilde{a}_s \) (values from Anderson and Ogren (1998)).

<table>
<thead>
<tr>
<th></th>
<th>450 nm</th>
<th></th>
<th>550 nm</th>
<th></th>
<th>700 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td></td>
<td>(b)</td>
<td></td>
<td>(a)</td>
</tr>
<tr>
<td>No cut</td>
<td>1.365</td>
<td>-0.156</td>
<td>1.337</td>
<td>-0.138</td>
<td>1.297</td>
</tr>
<tr>
<td>Sub-(\mu)m</td>
<td>1.165</td>
<td>-0.046</td>
<td>1.152</td>
<td>-0.044</td>
<td>1.120</td>
</tr>
</tbody>
</table>

2.1.3 Calibration

(Section adapted from TSI (2005))

The nephelometer is a photon counting instrument. Particles and gas molecules scatter photons (\(\sigma_{sp}\) and \(\sigma_{sg}\) in Sect. 1.6) which are detected and counted using highly sensitive photomultiplier tubes. These photon counts are converted into counting frequencies and correlated to light scattering coefficients using calibration constants. These constants are determined by filling the nephelometer’s interior measurement volume with two span gases (particle free air and CO\(_2\)), one at a time, that have largely different scattering coefficients and measuring a few key parameters. By measuring the photon frequency, temperature, and pressure for each span gas measurement, knowing the scattering coefficient for each of the span gases at a known temperature and pressure, and using two simple equations, the calibration constants are easily calculated by the nephelometer software.

2.2 Development of humidified nephelometers

All publications of measurements with humidified nephelometers that were published before 2009 were preformed with one of the systems described in this section.

The first humidified nephelometer was built by Pilat and Charlson (1966). They nebulized aerosols, exposed them to a controlled humidity, let them pass through a scattering instrument and then through a humidity measuring instrument. They humidified the aerosol in a heated chamber (temperature \(T=50^\circ\text{C}\)) and mixed the aerosol with a stream of moist air and a stream of dry air. The humidity of the aerosol was varied by changing the individual flow rates of the moist and the dry air streams (see Fig. 2.2). The light scattering was either measured by an integrating nephelometer or an aerosol photometer.

With this humidified nephelometer Pilat and Charlson (1966) measured the dependence of polydisperse NaCl aerosol particles on relative humidity (RH) and compared it to calculated ratios of scattering coefficients at certain RHs and scattering coefficients at RH=0\% (Fig. 2.3). They used the Rayleigh scattering equation to perform the calculation. For aerosol particles small in size compared to the wavelength \((D_p < 0.1\lambda)\) the Rayleigh scattering equation can be used to calculate the light scattering coefficient as a function of particle size, refractive index and wavelength of the light. In this range the scattering coefficient is proportional to the 6\(^{th}\) power of the aerosol radius.

Pilat and Charlson (1966) found that the calculated ratio of the scattering coefficients is approximately proportional (except for the change in refractive index) to the 6\(^{th}\) power of the ratio of wet to dry aerosol radii. However, at high RH the observed ratio of the scattering coefficients was somewhat less than the calculated value. The authors assume that this is because the NaCl particles were too large to assume Rayleigh scattering.
Figure 2.2: Aerosol generating flow system of Pilat and Charlson (1966).

Figure 2.3: Ratio of scattering coefficients of wet aerosol $S(R_T)$ to dry aerosol $S(R_T=0)$ as a function of RH from Pilat and Charlson (1966). Calculation is done for two dry particle radii ($r_0$).

Figure 2.4: Block Diagram of experiment by Covert et al. (1972).
Another humidification system for a nephelometer was developed by Covert et al. (1972). Figure 2.4 shows the set-up of this apparatus. The aerosol is drawn through their system by a blower at the outlet with a flow of 300-600 liters per minute (lpm). The desired variation of the RH of the aerosol particles is achieved by addition of a controlled, warm, moist air stream of about 10% of the original flow to the aerosol sample. This air stream is introduced in a mixing chamber under highly turbulent flow conditions (see Fig. 2.5). Turbulent mixing is necessary since otherwise the RH would not increase uniformly throughout a given air parcel and some portions of the stream would experience increasing, then decreasing humidity, while others only experience continuously increasing humidity. This process occurs in atmospheric processes, but in the experiment it would violate the condition that aerosols experience only increasing RH. After the mixing chamber a series of chambers of different volumes (10 and 33 l) allows aging of the humidified aerosol from 1 to 6 seconds, before the scattering coefficient is measured in the nephelometer. Near the middle of the scattering chamber a temperature sensor and a sampling tube to a dew point sensor are located, to calculate the RH in the nephelometer.

The humidity control of the Covert et al. (1972) system can scan the humidity from 20-90% in a short time, typically in 4 minutes. They chose such a small scanning time to have homogeneous atmospheric aerosol, which cannot be assumed for longer time periods. With their system they measured polydisperse substances in the laboratory, and atmospheric aerosols from three cities of the western United States. At Seattle (Fig. 2.6a) they measured at a time with low wind velocity and enhanced humidity. The humidity spectrum showed no sign of deliquescent behavior by the aerosol, but simply that it was very hygroscopic. The light scattering coefficient increased by a factor of 2 between 20 and 85% RH and by a factor of 3 by 90% RH. At Altadena and Denver Covert et al. (1972) also did not detect deliquescent behavior. This indicates that the aerosol is of mixed composition.

For the reasons mentioned above it is an excellent idea to scan the humidity from 20-90% RH in 4 minutes, specially when using only one nephelometer, but to get precise results the RH sensors must have a very fast response time. In the set-up we used for our measurements (see Sect. 2.3) we were not able to deal with such fast RH changes, even if we used as Covert et al. (1972) a dew point sensor and a temperature sensor to calculate the RH in the
Figure 2.6: Results from Covert et al. (1972).

nephelometer. Therefore it is questionable how precise the curves shown in Fig. 2.6 especially at high RH really are.

The same system was operated by Charlson et al. (1974) to describe a method for sensing aerosols of $H_2SO_4$, $NH_4HSO_4$ and $(NH_4)_2SO_4$. Generally at that time it was difficult to measure which cation is attached the $SO_4^{2-}$-anion.

Therefore the humidified nephelometer was operated with the injection of a few parts per million of $NH_3$ into the sample flow, causing the reaction of $H_2SO_4$ and $NH_4HSO_4$ to form $(NH_4)_2SO_4$. Both $H_2SO_4$ and $NH_4HSO_4$ aerosols experience a monotonic increase of the ratio of scattering at a certain RH and dry scattering with RH. In contrast $(NH_4)_2SO_4$ deliquesce at 80% RH (Tang and Munkelwitz, 1993). Conclusions could be drawn in which form $SO_4^{2-}$ had been present, when there was a difference between measurements with and without $NH_3$ injection, by the analysis of $\sigma_{sp}$ vs. RH.

Larson et al. (1982) developed a new type of humidified nephelometer for in situ chemical analysis of $H_2SO_4$ - $(NH_4)_2SO_4$ particles. They measured the response of sulfate compounds to thermal decomposition at specific relative humidities which provides semi-quantitative chemical analysis for sulfate compounds and ammonium to sulfate molar ratios. Figure 2.7 shows their system, in which first the sample air is humidified, then rapidly heated to a controlled temperature and then rapidly cooled such that the RH is between 65 and 70%. The scattering coefficients of this cooled sample are measured with an integrating nephelometer. The maximum air temperature at the exit of the heater ranges from ambient (no heating) to 380°C.

The set-up of Larson et al. (1982) is well suited to measure salt aerosols, but would not be applicable for atmospheric measurements of semi-volatile species, since they would evaporate at the temperatures applied (Bergin et al., 1997; ten Brink et al., 2000).

As Larson et al. (1982), Rood et al. (1985) expanded the humidograph or humidified nephelometer to a themidograph. The humidified nephelometer is used to determine the hygroscopic nature of atmospheric aerosol by measuring the aerosols’s light scattering coefficients as a function of RH. The themidograph exploits an aerosol’s hygroscopic and thermal
2.2 Development of humidified nephelometers

Figure 2.7: Schematic diagram of the themidograph apparatus developed by Larson et al. (1982).

decomposition characteristics to estimate the aerosol’s $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratio and sulfate mass concentration.

Even if Covert et al. (1972) took special care that the RH is evenly distributed to the whole air volume and so to the aerosols, Rood et al. (1985) found that the mixing of the dry air and steam was such that some of the particles were briefly exposed to a RH greater than the final averaged RH value measured at the nephelometer. This resulted in marginal resolution of an aerosol’s deliquescent step as shown in Fig. 2.8.

Figure 2.8: Comparative humidograms from the humidified nephelometer of Covert et al. (1972) (old system) and Rood et al. (1985) (new system). Humidograms were generated with $(\text{NH}_4)_2\text{SO}_4$ test aerosol and under increasing RH.

In the system developed by Rood et al. (1985), the aerosol displays a sharp change in the scattering coefficient at 79.9% RH (Tang, 1980), because this system avoids an unequal distribution of the RH in the air. Both systems are depicted schematically in Fig. 2.9. As in the Covert et al. (1972) system the aerosol is diluted with dry air prior to humidification.

Dilution with dry air is possible for laboratory measurements, but it reduces the aerosol concentration which decreases the detection signal for probes with low aerosol concentrations e.g. for ambient air. Therefore a different technique would be needed to measure the RH dependence of atmospheric aerosols at remote locations.

In the humidifier of Rood et al. (1985), air passes through a hollow cylinder in which the inside wall is covered with nylon mesh and wetted with a $\text{H}_2\text{SO}_4$ solution. The wetted wall is gradually heated such that the amount of heat flux through the wall controls the increasing dew point temperature of the aerosol. The air stream exiting the humidifier is rapidly heated to a peak $T=60^\circ\text{C}$ and then cooled to ambient temperature prior to entering the nephelometer. In the heating section, the RH decreases to $<20\%$ due to the increased
temperature. Such a decrease in RH is sufficient to effloresce the previously deliquesced particles. Subsequent cooling, with an induced draft heat exchanger, increases the aerosol’s RH to its final value. Near the exit of the cooler all air has returned to room temperature but none of the air has dropped below that temperature. Therefore nowhere in the cooler section have the particles been exposed to a RH greater than that entering the nephelometer (Rood et al., 1985).

If the humidograph’s humidifier is replaced with a humidifier consisting of two concentric wetted walls, the instrument has the ability to examine the response of particles to decreasing RH conditions and efflorescence. In this humidifier, air passes through an annular space in which the inner and outer walls are covered with felt and nylon mesh, respectively, and are kept wet with a H$_2$SO$_4$ solution. The outer wall of the annular space is heated to a controlled temperature $<10^\circ$C above room temperature. Heat flux through the wet outer wall determines the resultant dew point temperature of the aerosol. The inner wall is not heated. As the aerosol particles pass through the humidifier, they are not only exposed to a RH greater than 80%, but also only experience RHs below 80% downstream of the humidifier. Enhanced RH within the humidifier, compared to the nephelometer, results from a reduction in the temperature due to evaporative cooling. Therefore Rood et al. (1985) can expose deliquescent aerosol particles to an RH above their DRH and then expose these same particles to a gradually decreasing RH. In this way, it is possible to study the hysteresis loop of these aerosols.

![Block diagrams of the humidified nephelometer](image)

Figure 2.9: Block diagrams of the humidified nephelometer of Covert et al. (1972) (a) and the further developed system of Rood et al. (1985) (b).

The thermidograph-humidograph system was used to sample aerosol in Riverside, CA during the summer of 1983. Fig. 2.10a-c present thermidograph results for ambient, ambient with NH$_3$ addition and ambient preheated to 200°C with NH$_3$ addition, respectively. The ambient thermidograph curves with and without NH$_3$ addition are quite similar. Rood et al. (1985) interpreted this result as indication that the ambient aerosol was already chemically neutralized by NH$_3$. Upon preheating this neutralized aerosol, the resultant thermidogram curve had the same structure as (NH$_4$)$_2$SO$_4$ test aerosol. Humidograms taken at approximately the same time as the above thermidograms are also presented in Fig. 2.10. Humidograms of ambient (Fig. 2.10d) and ambient preheated to 100°C (Fig. 2.10e) indicate the presence of a hygroscopic aerosol that does not change its hygroscopic properties upon preheating to 100°C. When the aerosol is preheated to 200°C, along with NH$_3$ addition (Fig. 2.10f), a sharp deliquescence step appears at 78% RH. Rood et al. (1985) concluded that combined results from the thermidograph and the humidograph indicate the presence of a neutralized sulfate aerosol mixed with other more volatile compounds.
2.2 Development of humidified nephelometers

Figure 2.10: Thermograms (ambient (a), ambient with NH$_3$ addition (b) and ambient preheated to 200°C with NH$_3$ addition (c)) and humidograms (ambient (d), ambient preheated to 100°C (e) and ambient preheated to 200°C with NH$_3$ addition (f)) of Riverside CA aerosol measured by Rood et al. (1985).

Rood et al. (1987) further improved their set-up by using three nephelometers (Fig. 2.11). Their set-up made it possible to measure ambient metastably of hygroscopic aerosol particles. One part of the aerosol sample was lead to a nephelometer that operated outdoors at ambient temperature and RH conditions. Its flow was periodically heated to a maximum temperature of 25°C.
of 30°C above ambient conditions for 0.1 s and then rapidly cooled to ambient temperature immediately upstream of the nephelometer. Heat was applied to the continuous flow sample for 5-min periods twice an hour. Water associated with particles in stable equilibrium will recondense onto the particles upon cooling to ambient conditions, but water associated with the particles in metastable equilibrium do not return to the particles as a result of hysteresis. Evaporation of metastable liquid H$_2$O results in a decrease in particle size causing a decrease in the scattering coefficient. The aerosol particles are considered to exist in metastable equilibria if the ratio of $\sigma_{sp}$ measured at ambient RH without upstream heating to $\sigma_{sp}$ measured at ambient RH with upstream heating is significantly greater than one.

The remaining sample flow was split into a nephelometer operating at dry conditions and a thesmidograph [Rood et al. (1985)].

With their system [Rood et al. (1987)] found in a one week sampling time that the ambient aerosol in Riverside, California typically existed as droplets (86% of the time). The aerosol contained metastable liquid H$_2$O most of the time. Metastable H$_2$O contributed 5 to 20% of the total particle light scattering coefficient. The aerosol particles with diameters less than 2 μm exhibited deliquescence between 73 and 75% RH.

In my opinion the above described system is an excellent tool to study light scattering enhancement factors plus the occurrence of ambient metastability. The only disadvantage is that it consists of three nephelometers, which is extremely cost intensive, needs a lot of space and is not easy to transport.

![Figure 2.12: Schematic of the aerosol sampling instrumentation of Koloutsou-Vakakis et al. (2001). A part of the figure is covered, because it has nothing to do with the set-up of the humidified nephelometer.](image)

In the set-up of [Koloutsou-Vakakis et al. (2001)] two nephelometers run in parallel. Upstream of both nephelometers the aerosol flows through either of two impactors with 50% cut-off points at aerodynamic diameters of 1 or 10 μm. The aerosol flow alternates through the impactors every 7.5 minutes. This configuration allows the measurement of scattering coefficients by particles with diameters smaller than 1 μm and 10 μm. One nephelometer
2.2 Development of humidified nephelometers

measures the scattering coefficients of the ambient aerosol at RH<40%. The second nephelometer is a scanning RH nephelometer, also referred to as a humidograph, in the second aerosol sampling path. The aerosol passes through a humidifier and then through a three-wavelength integrating nephelometer (TSI, model 3563). The humidifier consists of a Teflon membrane that allows transport of water vapor to the aerosol, which is inside a stainless steel tube. The amount of water vapor that passes into the aerosol stream is determined by controlling the temperature of the water. The humidifier eliminates direct contact of liquid water with the aerosol flow, eliminates the need of dilution to control the RH of the aerosol, and thus eliminates exposure of the aerosol particles to air that is not the same composition as the ambient air. The temperature difference from the inlet to the outlet of the humidifier is <5°C (Carrico et al., 1998). The total length of the humidifier is 35 cm. RH is measured at the inlet of the nephelometer with a capacitive type RH sensor. As an additional control, RH is also determined downstream of the humidifier with a dew point hygrometer and a thermocouple at the nephelometer’s inlet.

Figure 2.13: Controlled RH nephelometry system (humidified nephelometer) flow diagram as employed by Carrico et al. (1998).

In the system of Carrico et al. (1998) the aerosol sample passes through an impactor with a 50% cutpoint at $D_p=10 \mu m$, and every second hour additionally through an impactor with a 50% cutpoint at $D_p=1 \mu m$ (see Fig. 2.13). The aerosol is thermally treated up to 35°C to lower the RH to a low reference value of 22% before passing through the low-RH reference nephelometer (TSI, Inc. Model 3563) for measurements of $\sigma_{sp}$ and $\sigma_{bsp}$. The aerosol then passes through a humidifier, an annular concentric tube in which passage of water vapor through a Teflon membrane is controlled by heating liquid water in its outer annulus. Measurements of $\sigma_{sp}$ and $\sigma_{bsp}$ occur with the scanning RH nephelometer for 40<RH<84%. Afterwards the aerosol passes through a water trap and particle filter, a mass flow controller and a vacuum pump. During each measurement cycle of the humidograph of Carrico et al. (1998), the RH of the low-RH reference nephelometer is held constant at RH equal to about 22%. For the first 15 minutes of each cycle, the RH-scanning nephelometer measures at RH equal to 40%. During the second 15 minutes the RH-scanning nephelometer is scanned from 40% RH to 84% RH. For the third 15 minutes period the RH-scanning nephelometer
is controlled at RH equal to 82%. The final 15 minutes of each cycle consist of zeroing the nephelometer with particle free air, writing data to the file, switching the impactor upper particle size cut and equilibrating the RH-scanning nephelometer to RH equal to 40%. To calculate \( f(\text{RH}) \) the low RH reference nephelometer allows compensation for changes in low RH \( \sigma_{sp} \) and \( \sigma_{bsp} \) that can occur over the duration of one measurement cycle.

The authors of the above described system observed that sea-salt particles dominated the aerosol scattering properties for both sub and supermicrometer particles during clean marine and non-clean marine periods during their one-month measurements at Cape Grim, Tasmania. Humidograms describing \( f(\text{RH}) \) demonstrated aerosol hygroscopic growth between 68 and 75% RH. The dry scattering coefficients for \( D_p < 10 \mu m \) are about 5 times higher than for \( D_p < 1 \mu m \), underscoring the dominance of supermicrometer particles in contributing to aerosol light scattering. The \( f(\text{RH}=82\%) \) of particles smaller than 10 \( \mu m \) was 1.98.

We compared our humidified nephelometer to a system based on the humidified nephelometer of Carrico et al. (1998) (see Sect. 3.2.3). Today NOAA (National Oceanic and Atmospheric Administration) runs such humidified nephelometers at 7 baseline stations in the USA, in Antarctica and in American Samoa plus several other instruments at mobile or cooperative platforms all over the world.

Carrico et al. (2000) further improved the instrument by using Peltier thermoelectric coolers. These coolers allow RH > 80% to be achieved locally upstream of the RH-scanning nephelometer while performing decreasing RH scans within the nephelometer to investigate the decreasing RH branch of the hysteresis loop. The aerosol sample maximum temperature, immediately downstream of the humidifier, was 39°C in an effort to keep \( T < 40°C \) to avoid appreciable losses of volatile species (Bergin et al., 1997; Dougle et al., 1998) including \( \text{NO}_3^- \) and volatile organic carbon.

It is an important improvement to be able to measure both branches of the hysteresis curve, which we wanted to continue, but with another method (see below).

### 2.3 The new humidified nephelometer

(Adapted from Fierz-Schmidhauser et al., 2010 and Sect. 3.2.1)

We built a new humidification system for an integrating nephelometer (TSI Inc., Model 3563). We learnt from publications about previous humidified nephelometers (see above) that our instrument should be able to measure aerosol metastability, that it should be easy to use and therefore could be operated continuously and that it should be cost-effective. Our instrument is designed to measure ambient aerosol, thus heating to high temperatures is avoided and dilution with dry air is not necessary.
2.3 The new humidified nephelometer

Figure 2.15: PSI humidified nephelometer, with humidifying box (left), nephelometer (right), DPS and computer (front).

Figure 2.15: PSI humidified nephelometer, with humidifying box (left), nephelometer (right), DPS and computer (front).
The instrumental set-up is as follows (see also Fig 3.1): First, the aerosol enters a humidifier, which consists of a Gore-Tex® tube (diameter = 1 cm, length ≈ 40 cm), which is surrounded by a thin water layer in a heatable metal tube. The dryer consists of a single Nafion tube (Perma Pure LLC) with an inner diameter of 1.7 cm and a length of 1 m. The aerosol flows through the inner part of the tube and can be dried by adjusting the flow and accordingly the pressure (200 mbar to ambient pressure) of an air stream around the Nafion tube (not shown in Fig. 3.1). Then, $\sigma_{sp}$ of the aerosol particles is measured by the nephelometer at a monitored temperature and RH.

A mass flow controller (MFC) regulates the air flow through the nephelometer and provides the flow in combination with a pump instead of the small, turbine blower the standard nephelometer uses. Combined temperature and capacitive RH sensors (Rotronic HygroClipS, accuracy $\pm$0.3°C and $\pm$1.5% RH, according to the manufacturer) are used throughout the system to measure air temperature and RH, respectively (see Fig. 3.1). In addition, a dew point sensor (DPS) (Edge Tech, Model 2000 Dewprime DF, accuracy $\pm$0.1°C) measures the dew point temperature in order to calculate (together with $T_5$) the RH inside the nephelometer accurately. Due to the relatively long response time of the DPS (up to several minutes) these RH readings were only applicable during stationary RH conditions. Figure 2.15 shows a picture of the humidified nephelometer measuring at the high alpine station Jungfraujoch (results see Chapter 4).

In the unmodified nephelometer, the heat of the halogen lamp (75 W) causes a temperature difference of about 4.5°C between the inlet and the sensing volume of the nephelometer ($T_5$–$T_4$) at 16.6 lpm. Consequentially, the RH in the sensing volume decreases from e.g. 90% RH to about 70% RH. In our set-up we reduced this temperature difference to less than 1°C.

Aerosol passing through the system encounters the highest RH just before the dryer ($RH_3$). RH is then lowered by the dryer, and lowered further in the nephelometer because of the $\sim$1°C temperature increase. As a consequence, substances that may exist in two phases deliquesce if their DRH is exceeded before the dryer. These particles will remain liquid even if the RH is subsequently lowered on the way to the nephelometer. Since we refer to this lower RH in the nephelometer, the deliquescence step change appears at a lower RH than the literature value. As an example for this phenomenon, Fig. 3.2 shows a measured humidogram of $f(RH)$ for sodium chloride, where the x-axis represents the RH in the nephelometer and the color scale represents the RH at the most humid location ($RH_3$). The literature value for DRH of sodium chloride is 75.3% RH (at 298 K) (Tang and Munkelwitz, 1993). The measured phase transition occurs at $RH_3$=75%, but appears at the lower sample RH of about 70% in the nephelometer. Due to the limited drying capability of the dryer, the ERH could not be determined during this experiment.

We define two different operating conditions for the humidified nephelometer: hydration and dehydration. Hydration is when the dryer is turned off and the RH within the instrument is monotonously rising to the entrance of the nephelometer. We define dehydration in a similar manner: at the exit of the humidifier (at $RH_3$) the aerosol particles are exposed to RH$>80%$. In the following, they encounter a lower RH in the dryer, which is now turned on.

References


Measurement of relative humidity dependent light scattering of aerosols

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**Abstract**

Relative humidity (RH) influences the water content of aerosol particles and therefore has an important impact on the particles’ ability to scatter visible light. The RH dependence of the particle light scattering coefficient ($\sigma_{sp}$) is therefore an important measure for climate forcing calculations. We built a humidification system for a nephelometer which allows the measurement of $\sigma_{sp}$ at a defined RH in the range of 40–90%. This RH conditioner consists of a humidifier followed by a dryer, which enables us to measure the hysteresis behavior of deliquescent aerosol particles.

In this paper we present the set-up of a new humidified nephelometer, a detailed characterization with well defined laboratory generated aerosols, and a first application in the field by comparing our instrument to another humidified nephelometer.

Monodisperse ammonium sulfate and sodium chloride particles were measured at four different dry particle sizes. Agreement between measurement and prediction based on Mie theory was found for both $\sigma_{sp}$ and $f(RH)=\sigma_{sp}(RH)/\sigma_{sp}(\text{dry})$ within the range of uncertainty. The two humidified nephelometers measuring at a rural site in the Black Forest (Germany) often detected different $f(RH)$, probably caused by the aerosol hysteresis behavior: when the aerosol was metastable, therefore was scattering more light, only one instrument detected the higher $f(RH)$. 


3.1 Introduction

Atmospheric aerosols influence the Earth’s radiation budget both directly and indirectly. The change in the Earth’s radiative balance due to aerosol light scattering and absorption is called the direct aerosol effect. The radiative forcing can be negative or positive, depending on the chemical and microphysical properties of the involved aerosols and the Earth’s surface albedo. The current global anthropogenic impact of the direct aerosol effect is estimated to be $-0.5 \pm 0.4 \text{ Wm}^{-2}$, compared to the total anthropogenic radiative forcing of $+1.6 \pm 0.6$ to $+2.4 \text{ Wm}^{-2}$ (IPCC, 2007). The total aerosol forcing uncertainty is substantially larger than that of greenhouse gases ($+0.8/-1.5 \text{ vs. } +0.27 \text{ Wm}^{-2}$) (Ramanathan et al., 2001; IPCC, 2007).

In this paper we will focus on the aerosol light scattering coefficient $\sigma_{sp}$ and how it is influenced by the relative humidity (RH) in the atmosphere. Wet aerosol particles are larger than their dry equivalents, therefore they scatter more light, which has a direct influence on the radiative forcing (White and Roberts, 1977; Tang et al., 1981; Sloane, 1984). However, the water content of the air, expressed in RH, does not always determine alone if a chemically defined aerosol particle is liquid or solid. For deliquescent aerosols, which can exist in two phases at the same RH, known as hysteresis (Orr Jr. et al., 1958), the RH history determines the aggregate state. Pure deliquescent aerosols undergo a sudden phase transition from solid to liquid in response to increasing RH. This phase transition occurs at a defined RH, called deliquescence relative humidity (DRH). Once the RH is above the DRH and the particle is liquid, decreasing RH does not make the particle recrystallize at the DRH. The particle solute concentration becomes supersaturated resulting in a metastable state until the RH decreases below a critical value at which recrystallization occurs. This RH is called efflorescence relative humidity (ERH). Mixed deliquescent aerosols can exhibit one or more phase changes as shown by Tang and Munkelwitz (1993). If the particles are not deliquescent but hygroscopic they grow or shrink monotonically with increasing or decreasing RH.

The exact knowledge of the DRH and ERH points is of great importance because they define – based on the RH history of an air parcel – which fraction of the atmospheric aerosol is present as purely liquid droplets. This fraction is scattering much more light than the fraction that is solid. Rood et al. (1989) found that metastable droplets existed more than 50% of the time in the atmosphere at three different locations in the USA. 5–15% of the total particle scattering was attributed to metastable liquid water for RH values between 45 and 75%.

The scattering coefficient, $\sigma_{sp}$, can be measured by sampling ambient air into an integrating nephelometer. To ensure comparability between different GAW (Global Atmosphere Watch) stations, the World Meteorological Organization (WMO) recommends to measure $\sigma_{sp}$ at RH below 40% (WMO/GAW, 2003). Furthermore, WMO recommends to measure $\sigma_{sp}$ as a function of RH. This measurement is needed to model the direct climate forcing by aerosol particles (Charlson et al., 1992; Schwartz, 1996) and is an important input parameter for models (Boucher and Anderson, 1995; Pilinis et al., 1995; Nessler et al., 2005). The information about the aggregate state improves the result of such model calculations.

Many ambient measurements of the light scattering enhancement factor $f(RH)=\sigma_{sp}(RH)/\sigma_{sp}(\text{dry})$ were performed during the last 40 years (Covert et al., 1972; Sheridan et al., 2001; Eldering et al., 2002; Kim et al., 2006; Haywood et al., 2008; Yan et al., 2009), but just a few included measurements on the metastability of aerosol particles (Rood et al., 1987; Carrico et al., 2003; Wang et al., 2007; Fierz-Schmidhauser et al., 2010).

Since data about the aggregate state (liquid or solid) of the aerosol are still scarce, we built a humidification system for a nephelometer that allows for the measurement of $\sigma_{sp}$ at a
defined humidity in the range of 40 to 90% RH. The system is able to measure the hygroscopic aerosol behavior and hysteresis effects and it can be continuously and remotely operated with very little maintenance. This paper discusses the experimental set-up of this instrument and a characterization with laboratory aerosols. In the second part we present a comparison of our instrument with another humidified nephelometer, which is, to our knowledge, the first direct comparison of two humidified nephelometers in the field.

3.2 Experimental Methods

3.2.1 Set-up of the humidified nephelometer

We built a new humidification system for a three-wavelength (450, 550, 700 nm) total/backscatter integrating nephelometer (TSI Inc., Model 3563). Figure 3.1 shows the instrumental set-up. First, the aerosol enters a humidifier, which consists of a Gore-Tex® tube (diameter = 1 cm, length \( \approx 40 \text{ cm} \)), which is surrounded by a thin water layer in a heatable metal tube. Water temperature is controlled by a PID-(proportional-integral-derivative) controller that uses the reading of an RH sensor (RH\(_3\)) as input. The humidifier is able to increase the RH to values of up to 95% at the applied flow rate of 16.6 liters per minute (lpm) (the maximum temperature of the aerosol at the exit of the humidifier is \(<32^\circ\text{C}\) to avoid volatilization losses). After passing through a 1 m metal tube the aerosol passes through a dryer, whose efficiency is monitored by another RH sensor (RH\(_4\)). The dryer consists of a single Nafion tube (Perma Pure LLC) with an inner diameter of 1.7 cm and a length of 1 m. The aerosol flows through the inner part of the tube and can be dried by adjusting the flow and accordingly the pressure (200 mbar to ambient pressure) of an air stream around the Nafion tube (not shown in Fig. 3.1). At 16.6 lpm the dryer is capable of reducing the RH from 85% to 55% at room temperature. Then, \(\sigma_{sp}\) of the aerosol particles is measured by the nephelometer at a monitored temperature and RH (temperature sensor T\(_5\), RH\(_5\) and dew point sensor (DPS)).

Figure 3.1: Set-up of the humidified nephelometer, with five temperature (T) and capacitive RH sensors, a dew point sensor (DPS) and a mass flow controller (MFC).

A mass flow controller (MFC) regulates the air flow through the nephelometer. When the aerosol is humidified, the inlet volumetric flow will change slightly (e.g. by about \(-1.5\%\) at 85% RH). To avoid RH dependent variations of the inlet flow rate, we programmed the set point of the mass flow controller such that the volumetric flow at the inlet of the humidified nephelometer system is constant (16.6 lpm), independently of how much water vapor is added and removed by the RH conditioning unit. We did not correct for changes in the aerosol
Concentration due to dilution (enrichment) effects by adding (removing) water vapor because this bias is small (<3% at $T=20^\circ C$ and 1000 mbar).

Combined temperature and capacitive RH sensors (Rotronic HygroClipS, accuracy $\pm 0.3^\circ C$ and $\pm 1.5\%$ RH, according to the manufacturer) are used throughout the system to measure air temperature and RH, respectively (see Fig. 3.1). We moved the original RH and $T$ sensor in the nephelometer (described by TSI as the sample RH) to the nephelometer inlet (not shown in Fig. 3.1) and replaced it with a Rotronic HygroClipS ($RH_5, T_5$) which has a higher accuracy than the original sensor (the original sensor overestimates RH by up to 15% RH at high RH). However, the temperature measurement by the TSI sensor is necessary for the nephelometer calibration and was therefore kept in the system. In addition, a DPS (Edge Tech, Model 2000 Dewprime DF, accuracy $\pm 0.1^\circ C$) measures the dew point temperature in order to calculate (together with $T_5$) the RH inside the nephelometer accurately. Due to the relatively long response time of DPS (up to several minutes) these RH readings were only applicable during stationary RH conditions. As an accurate RH measurement is crucial for such instruments, all RH sensors are calibrated every two months in the RH range of 11 to 98% by measuring RH over various saturated salt solutions (LiCl, NaCl, (NH$_4$)$_2$SO$_4$, K$_2$SO$_4$). Within four subsequent calibrations the slopes between expected and measured RH range between 0.956 and 1.019, with a $R^2 > 0.99$.

In the unmodified nephelometer, the heat of the halogen lamp (75 W) causes a temperature difference of about 4.5$^\circ C$ between the inlet and the sensing volume of the nephelometer ($T_5-T_4$) at 16.6 lpm. Consequentially, the RH in the sensing volume decreases from e.g. 90% RH to about 70% RH. In our set-up we reduced this temperature difference to less than 1$^\circ C$ with the following modifications: An air-cooled infrared filter (KPF65, Filtrop AG with $>90\%$ transmission for wavelengths between 420 and 760 nm) was placed between the lamp and the sensing volume. On the outside of the sensing volume cooling fins enlarge the surface, where four additional blowers surround the nephelometer and adjust its temperature close to room temperature.

Aerosol passing through the system encounters the highest RH just before the dryer ($RH_3$). RH is then lowered by the dryer, and lowered further in the nephelometer because of the $\sim 1^\circ C$ temperature increase. As a consequence, substances that may exist in two phases deliquesce if their DRH is exceeded before the dryer. These particles will remain liquid even if the RH is subsequently lowered on the way to the nephelometer. Since we refer to this lower RH in the nephelometer in all our figures, the apparent deliquescence step change appears at a lower RH than the literature value. As an example for this phenomenon, Fig. 3.2 shows a measured humidogram of $f(RH)$ for sodium chloride, where the x-axis represents the RH in the nephelometer and the color scale represents the RH at the most humid location ($RH_3$). The literature value for DRH of sodium chloride is 75.3% RH (at 298 K) (Tang and Munkelwitz, 1993). The measured phase transition occurs at $RH_3=75\%$, but appears at the lower sample RH of about 70% in the nephelometer. Due to the limited drying capability of the dryer, the ERH could not be determined during this experiment.

We define two different operating conditions for the humidified nephelometer: hydration and dehydration. Hydration is when the dryer is turned off and the RH between the entrance of the dryer and the entrance of the nephelometer is not changing within more than 3% (see Fig. 3.6a in Sect. 3.5). We define dehydration in a similar manner: after the humidifier (at $RH_3$) the aerosol particles are exposed to RH $> 80\%$. In the following, they encounter a lower RH in the dryer, which is now turned on (see Fig. 3.6b).

The residence time of the aerosol at high RH depends on the operating conditions. During hydration the aerosol experiences $\sim 3\, s$ at high RH before entering the nephelometer while during dehydration this time is shortened to $\sim 1\, s$. 

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3.2 Experimental Methods

3.2.2 Laboratory measurements of monodisperse inorganic aerosol particles

Well defined aerosols, ammonium sulfate (\((NH_4)_2SO_4\)) and sodium chloride (NaCl), were generated by nebulizing the corresponding aqueous salt solutions (concentration = 10 g/l) with a nebulizer (model TSI 3076). The dried aerosol particles (RH<10%) were fed to a DMA (differential mobility analyzer) for selection of a specified particle electrical mobility (singly charged particles with diameter \(D_p=100\, \text{nm}, 150\, \text{nm}, 240\, \text{nm}\) and \(300\, \text{nm}\)). The quasi monodisperse aerosol (0.3 lpm) exiting the DMA was mixed with filtered room air (17.2 lpm), and the resulting air flow was split for a CPC (condensation particle counter, TSI 3010, 0.9 lpm) and the humidified nephelometer (16.6 lpm). Between every RH cycle of the humidified nephelometer an SMPS (scanning mobility particle sizer) measured the polydisperse dry number size distribution entering the DMA in the diameter size range of \(D_p=14\) to \(791\, \text{nm}\). With these data we calculated the size distribution of the quasi monodisperse aerosol at the entrance of the nephelometer, including the number of singly, doubly and triply charged particles. Even though multiply charged particles are considerably less numerous than the singly charged ones they can significantly contribute to light scattering due to their larger size. The percentage of doubly and triply charged particles in terms of numbers ranged from 9.5 to 24%, and from 1.5 to 6%, respectively. For the 100-nm particles with 24% doubly charged particles and 6% triply charged particles the singly charged particles are only contributing about 10% to the total scattering and the triply charged particles contribute about 19% to the total scattering. For the 300-nm particles with 9.5% doubly charged particles and 1.5% triply charged particles the respective numbers are 32% and 38%.

During the time that a RH cycle took place, the number concentration of the quasi monodisperse salts changed slightly (maximum 15%). Therefore \(\sigma_{sp}\) was normalized by the measured total particle number concentration.

For comparison with theoretical \(\sigma_{sp}\) values a model based on Mie theory was used. The particles were assumed to be spherical with a homogeneous composition. Assuming spherical particles is justified for this application, since the influence of non-sphericity on \(\sigma_{sp}\) is less than \(\pm 5\%\) for cubic salt particles smaller than \(1\, \mu\text{m}\) (Chamaillard et al., 2006). The core Mie
routine is based on the code of Bohren and Huffman (2004). As inputs for the prediction the dry DMA size distribution, the complex refractive index and the RH in the nephelometer were used. The influence of the water uptake on the particle diameter was calculated by using the hygroscopic growth factors from Topping et al. (2005). For the wet refractive index a volume weighting between the refractive indices of water and the according salt was chosen.

The scattering coefficients were corrected for the truncation error according to Anderson and Ogren (1998), with the correction for particles with diameters smaller than 1 \( \mu m \). Particle losses in the humidifier and dryer were determined with monodisperse aerosol and accounted for in the prediction of \( \sigma_{sp} \). At the standard flow of 16.6 lpm the particle losses are 5, 3.5, 2.5 and 2.5% for \( D_p=100, 150, 240 \) and 300 nm, respectively.

For both the measured and the theoretical scattering coefficients \( \sigma_{sp} \) we calculated the light scattering enhancement factor \( f(\text{RH}) \):

\[
 f(\text{RH}) = \frac{\sigma_{sp}(\text{RH})}{\sigma_{sp}(\text{RH = dry})} . \tag{3.1}
\]

The model output uncertainty of \( \sigma_{sp} \) and \( f(\text{RH}) \) was determined by recalculating \( \sigma_{sp} \) with errors added to each input parameter (RH (±2%), \( D_p \) (±2 nm), number concentration \( N \) (±10%); the error of the complex refractive index was neglected). Resulting typical errors of \( f(\text{RH}) \) are up to ±50% for the 100-nm size particles and ±20% for the 300-nm particles. These added errors will appear in the figures as the grey regions. The most dominant source of uncertainty for \( \sigma_{sp} \) is the number size distribution of the quasi monodisperse aerosol, whereas for \( f(\text{RH}) \) the correct RH in the nephelometer is crucial.

### 3.2.3 Field measurements

To compare our humidified nephelometer (PSI humidified nephelometer, Paul Scherrer Institute) with the humidograph of DOE/ARM (US Department of Energy Atmospheric Radiation Measurements), we operated the two instruments in parallel for about one month (9 to 31 August 2007). The DOE/ARM humidograph consists of two integrating nephelometers (TSI Inc., model 3563) with a humidifier in between them (Carrico et al., 1998). \( \sigma_{sp} \) is measured by the first nephelometer at low-RH conditions and by the second at varying RH. No dryer is employed in this instrument (hydration mode only) and the residence time of the aerosol at high RH before entering the nephelometer is \( \sim 0.2 \) s. No infrared blocking and cooling system is used in the DOE/ARM system. However, the thermal gradient across this nephelometer is small. This gradient is about 1.0°C at low RH and about -0.5°C at high RH, meaning that the nephelometer interior is slightly cooler than the nephelometer inlet at high RH values. The humidifier ends at the inlet of the humidified nephelometer, so the nephelometer inlet is warm from the humidifier.

This instrument was running at the DOE/ARM Mobile Facility (AMF) in the context of the Convective and Orographically Induced Precipitation Study (COPS) field campaign in Heselbach (Black Forest, Germany) from March to December 2007 (Wulfmeyer et al., 2008).

During the comparison both systems got their samples from the 12-m high community inlet of the AMF. The DOE/ARM system sampled with 30 lpm volumetric flow rate whereas the PSI humidified nephelometer ran at a flow rate of 16.6 lpm. Upstream of the PSI humidified nephelometer the air stream passed through a PM10 impactor (selecting particles with an upper size cut (50% removal efficiency) of an aerodynamic diameter of less than 10 \( \mu \)m) and for 10 days additionally through a PM1 cyclone. The tubes in front of the impactors were
heated such that the RH of the air was below 35% during the size cut, whereas the temperature never exceeded 34°C to limit losses of semi-volatile species (Bergin et al., 1997; ten Brink et al., 2000). The DOE/ARM instrument changed between PM10 and PM1 every half an hour. The inlet before the DOE/ARM impactors was heated to achieve 40% RH. Additional heating in the reference nephelometer and in a heated tube before the DOE/ARM humidifier brought the sample RH of the reference nephelometer on average to 25.7% (standard deviation: ±4.5% RH) prior to humidification in the DOE/ARM system.

Every hour the RH measurement cycle started with a zero measurement (particle free air to correct for the scattering contribution from air molecules). Then the RH was raised in both humidified instruments stepwise to 80–85% within 30 min, and was then decreased back to RH values of about 40% during the second half an hour. The RH in the PSI humidifier always stayed above 80% while the RH in the PSI nephelometer was decreased to 55% under these dehydration conditions. If the aerosol shows a hysteresis behavior both branches of the hysteresis curve can be measured with this set-up provided that the aerosol had gone below the ERH point in the DOE/ARM reference nephelometer.

To calculate the $f(RH)$ the $\sigma_{sp}$ from the reference nephelometer of DOE/ARM were taken. Because the DOE/ARM instrument changed between PM10 and PM1 every half hour and the PSI instrument did not, a comparison between the two instruments was only possible for half of the measured time. For comparing the two humidified nephelometers at 80% RH values of $f(RH)$ between 78 and 82% RH were taken.

3.3 Results and Discussion

In this section we first present the validation of the PSI humidified nephelometer with a defined laboratory aerosol. Measurements are compared to model predictions. In the second part we present field results where the new instrument (PSI humidified nephelometer) is compared with the DOE/ARM humidified nephelometer. Even though the nephelometer measures at three different wavelengths ($\lambda=450, 550$ and 700 nm) all results are shown at 550 nm wavelength. For the other wavelengths we obtained similar results.

3.3.1 Laboratory measurements

Measurements with ammonium sulfate

By using $\sigma_{sp}$ at different RH values we calculated $f(RH)$ with Eq. (3.1) for all humidities and sizes. Figure 3.3 shows the obtained $f(RH)$ versus the RH in the nephelometer for the four measured quasi monodisperse sizes (with singly charged particles with diameters between 100 and 300 nm). Open diamonds represent $f(RH)$ while the aerosol was hydrated, whereas the closed diamonds show $f(RH)$ during the dehydration stage of the measurement cycle. The black error bars indicate the measurement uncertainty of ±10% of $\sigma_{sp}$ (Anderson et al., 1996). The grey line shows predicted values with corresponding uncertainties. The uncertainties are calculated as described in Sect. 3.2.2.

As explained in Sect. 3.2.2, the highest RH in the system is encountered upstream of the dryer (at RH3 in Fig. 3.1). As a consequence, ammonium sulfate deliquesces if RH exceeds 79.9% RH (at 298 K (Tang and Munkelwitz, 1993)) at this point, even if the RH further downstream in the nephelometer is lower. Therefore, in all the humidograms in Fig. 3.3 the phase transition appears at the lower sample RH of ~72% of the nephelometer. Below 72% RH points on the upper branch of the hysteresis curve only occur for dehydration conditions.
Chapter 3 Measurement of relative humidity dependent light scattering of aerosols

Figure 3.3: $f(RH)$ vs. RH in the nephelometer of ammonium sulfate particles with a dry diameter of 100, 150, 240, and 300 nm. The grey line represents the predicted $f(RH)$ with corresponding uncertainties. Black open diamonds show the measured $f(RH)$ of hydrating aerosols, while black closed diamonds represent dehydrating aerosols. The phase transition at deliquescence occurred at RH=$79.9\%$ at the most humid location in the system (RH$_3$).

The lowest RH reached while drying was $\sim62\%$ RH, therefore we could not detect the ERH. The measurements agree with the model prediction within their rather large uncertainties.

For $f(RH)$, a very good agreement with model predictions is found at all measured sizes (difference between model prediction and measurement between 4.4 and 6.9%). The $f(RH)$ agrees much better with the model predictions than the $\sigma_{sp}/N$ (difference between -16.3 and 29.0%) (Fig. 3.7 in Sect. 3.5) because systematic errors mainly in the number size distribution are compensated. $f(RH)$ is largest for the 100-nm particles (4.5 at 80% RH) and smallest for the largest selected particles (2.5 at 80% RH).

Measurements with sodium chloride

Similar measurements with quasi monodisperse NaCl particles were performed. $\sigma_{sp}/N$ of NaCl at dry conditions is comparable to that of ammonium sulfate (see Figs. 3.7 and 3.8 in Sect. 3.5), but differs for aqueous particles of the two salts. The $f(RH)$ of NaCl is larger than of ammonium sulfate (Fig. 3.9 and 3.3). Due to a higher hygroscopicity the scattering of the 100-nm particles at 80% RH was enhanced by a factor of 15 compared to 4.5 for ammonium sulfate. Predicted and measured $f(RH)$ of NaCl agree within the uncertainty for all selected sizes.
3.3 Results and Discussion

3.3.2 Field measurements

A field comparison between the PSI and the DOE/ARM humidified nephelometers was performed in the Black Forest (Germany) from 9 to 31 August 2007. DOE/ARM measured $\sigma_{sp}$ in a reference (low RH) and humidified nephelometer as described above. Both humidified nephelometers detected lower $\sigma_{sp}$ than the reference nephelometer when they were measuring below 40% RH. This difference was attributed to sampling losses and was empirically corrected by multiplying $\sigma_{sp}$ of the humidified nephelometers by 1.058 (DOE/ARM, PM10), 1.066 (DOE/ARM, PM1) and 1.031 (PSI, both size cuts).

Figure 3.4 shows the $f$(RH) at 80% RH of both instruments, which includes all $f$(RH) values at RH between 78 and 82%. In the beginning of the comparison (9–20 August), the PSI humidified nephelometer measured $\sigma_{sp}$ for the PM10 size range, and from 21 to 29 August for PM1. The $f$(RH=80%) obtained by the PSI humidified nephelometer was on average 21% (PM10) and 16% (PM1) higher than the one of DOE/ARM, which will be discussed below. $f$(RH) values at 80% RH ranged from 1.2 to 1.8 (PSI) and 1.1 to 1.5 (DOE/ARM) respectively.

The most likely explanation for the difference in the $f$(RH) of the two instruments is that they occasionally probe the two different branches of the hysteresis curve, since the RH history in the two instruments is not the same. To illustrate this hypothesis, we plotted four example humidograms (with 3–4 RH cycles each) in Fig. 3.5 showing $\sigma_{sp}$ vs. the RH in the nephelometers. Humidograms A and B are from the time period where the PSI humidified nephelometer measured PM10, whereas humidograms C and D illustrate periods, when the size cut was PM1. The black curves display $\sigma_{sp}$ of the DOE/ARM humidified nephelometer and the colored curves show $\sigma_{sp}$ of the PSI humidified nephelometer. The color of these curves represents the highest RH in the PSI system (at RH₃). The instruments agree within 15% for all RH in humidograms B and C (see boxes in Fig. 3.4). No distinct deliquescence is observed. For these selected time periods the $f$(RH=80%) of the two instruments also agree within 11% (PM1) or 10% (PM10) (see Fig. 3.4). Humidograms A and D were measured when the $f$(RH=80%) of the two humidified nephelometers differed a lot (DOE/ARM: 1.25, PSI: 1.6). During this time $\sigma_{sp}$ showed a distinct hysteresis behavior, which is seen by the PSI humidified nephelometer (see Fig. 3.5). The $\sigma_{sp}$ values of the hydration branches of the PSI humidified nephelometer in humidogram A agree within 10% with the DOE/ARM $\sigma_{sp}$. 
values up to about 65 to 70% RH in the nephelometers; those in humidogram D agree within 10% up to 50–55% RH. When the RH in the PSI humidified nephelometer is 70%, the highest RH reached in its system is about 78–80% RH. With increasing RH $\sigma_{sp}$ in the PSI humidified nephelometer increases rapidly, most probably because the DRH level was exceeded. At the same RH the DOE/ARM humidified nephelometer measures much lower $\sigma_{sp}$ since the aerosol particles did not experience the RH at which they would deliquesce. When we compare $\sigma_{sp}$ of DOE/ARM at 80% RH to $\sigma_{sp}$ of PSI at 80% RH of the most humid location they agree within 7%. As long as the highest RH in the PSI humidified nephelometer stays above 80%, the particles are liquid and therefore scatter more light than they do at the same RH in the DOE/ARM instrument.

Other hypotheses for the observed differences are evaporation of semi-volatile substances in the tubes or in the humidifier, due to different residence times and temperatures; alternatively, aerosol particles in the DOE/ARM system might not experience sufficient residence time to equilibrate in the elevated humidity. The latter artifact would not always be apparent because it is expected to be dependent on the particle chemical composition. It has been shown that some organic/inorganic aerosol mixtures show mass transfer limitations of water and may require residence times of a few seconds for equilibration at 85% RH (contrary to pure inorganic salts which equilibrate within timescales of $<1$ s) [Sjogren et al., 2007; Duplissy et al., 2009]. Measurements of the aerosol composition, including organic aerosol speciation, would be needed to evaluate these hypotheses; unfortunately, such measurements were not available during the comparison period.

Figure 3.5: Humidograms of the scattering coefficient vs. RH in the nephelometer at four selected time periods for PM10 (A) and (B) and PM1 (C) and (D). The black curves are measured by the DOE/ARM humidified nephelometer. The colored curves show $\sigma_{sp}$ from the PSI humidified nephelometer, where the color represents the RH at the most humid location in its system (RH$_3$). Hysteresis behavior is seen in humidograms (A) and (D).
3.4 Conclusions

We built a humidification system for a nephelometer that allows for the measurement of $\sigma_{sp}$ at a defined humidity in the range of 40 to 90% RH. The system is able to measure the hygroscopic aerosol behavior and hysteresis effects. Monodisperse ammonium sulfate and sodium chloride particles were measured at four different dry particle sizes. Agreement between measurement and prediction based on Mie theory was found for both $\sigma_{sp}$ and $f$(RH) within the range of uncertainty.

The intercomparison between the two humidified nephelometers (PSI and DOE/ARM) indicated that the DOE/ARM instrument measured predominately the $f$(RH) that is representative of the lower hydration curve. The PSI humidified nephelometer measured the $f$(RH) of the hydration and dehydration branch of the hysteresis curve. When both instruments measured aerosol that exhibits no distinct deliquescence they agreed well. Moreover the measurement of the dehydration branch provides additional information which is important since aged atmospheric aerosols are usually in this deliquesced phase [Weingartner et al., 2002]. Carrico et al. (2003) found that ambient aerosol was typically on the upper branch of the hysteresis curve for marine and polluted air masses and on the lower branch for dust-dominated aerosols. Measurements of that type are needed at many different locations over the world in order to reduce the large uncertainties in the radiative forcing due to the direct aerosol effect. In order to decide if the ambient aerosol is actually metastable, another nephelometer measuring at ambient conditions would be needed. Alternatively, this could also be done in a single instrument, by heating and cooling the aerosol and then detecting if there is a difference in the scattering before and after heating, as shown by Larson et al. (1982) and Rood et al. (1987).

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3.5 Additional information

Figure 3.6a sketches the measured T and RH development for humidification only (hydration mode) and Fig. 3.6b shows the progression of RH and T if the dryer is on (dehydration mode).

Figure 3.7 shows the RH dependence of the measured scattering coefficient normalized by the number concentration ($\sigma_{sp}/N$) for quasi monodisperse ammonium sulfate particles (singly charged particles with diameters between 100 and 300 nm). For perfectly monodisperse aerosols this value equals the scattering cross-section per particle. Note that this value is strongly size dependent and therefore biased by the influence of the larger, multiply charged particles. This is taken into account in the Mie calculation of the $\sigma_{sp}/N$ values (grey lines). Open diamonds represent $\sigma_{sp}/N$ while the aerosol was hydrated, whereas the closed diamonds show $\sigma_{sp}/N$ during the dehydration stage of the measurement cycle. The black error bars indicate the measurement uncertainty of ±10% of $\sigma_{sp}$. The grey line shows predicted values with corresponding uncertainties. The dry $\sigma_{sp}$ varied within typical ambient values, i.e. from 2·10$^{-6}$ m$^{-1}$ of the 100-nm particles to 4·10$^{-5}$ m$^{-1}$ of the 300-nm particles. The corresponding number concentrations were 1400 cm$^{-3}$ and 350 cm$^{-3}$, respectively. This resulted e.g. in
~130 times higher $\sigma_{sp}/N$ for the 300-nm particles compared to the 100-nm particles. The highest RH in the system is encountered upstream of the dryer (at $T_3$, $RH_3$ in Fig. 3.1). As a consequence, ammonium sulfate deliquesces if RH exceeds 79.9% RH (at 298 K) at this point, even if the RH further downstream in the nephelometer is lower. Therefore, in all the humidograms in Fig. 3.7 the phase transition appears at the lower sample RH of about 72% of the nephelometer. Below 72% RH, points on the upper branch of the hysteresis curve only occur for dehydration conditions. The lowest RH reached while drying was 62% RH, therefore we could not detect the ERH. The measurements agree with the model prediction within their rather large uncertainties (the difference of $\sigma_{sp}/N$ between model prediction and measurement is between -16.3 and 29.0%).

Figure 3.8 shows the measured and predicted scattering coefficient normalized by the number concentration ($\sigma_{sp}/N$) for monodisperse sodium chloride particles with the same dry diameter as for the ammonium sulfate measurement (Fig. 3.7 and Fig. 3.3). As explained above, the highest RH in the system is encountered upstream of the dryer (at $T_3$, $RH_3$ in Fig. 3.1). As a consequence, sodium chloride deliquesces if 75.3% RH (at 298 K), is exceeded at this point and not in the nephelometer. Therefore, in all the humidograms in Figs. 3.8 and 3.9 the phase transition appears at the lower sample RH of about 70% of the nephelometer. The difference of $\sigma_{sp}/N$ between model prediction and measurement ranges between -16.6 and 25.7%. Figure 3.9 shows the corresponding $f(RH)$ measurement for sodium chloride particles (the difference of $f(RH)$ between model prediction and measurement is between -3.7 and 8.2%).

DOE/ARM measured absorption coefficients ($\sigma_{ap}$) with a PSAP (particle soot absorption photometer) and light scattering coefficients ($\sigma_{sp}$) with a nephelometer. Figure 3.10 shows these values from 9 to 20 August for PM10 and from 21 to 29 August for PM1. The PM1 scattering and absorption data exhibited a clear diurnal pattern, with highest values in the late morning and in the night. The increase in the morning is probably due to higher particle concentrations from local emissions as well as low vertical mixing, as the number concentration (not shown) exhibits the same pattern. The following midday decrease is likely due to dilution through enhanced vertical mixing. This vertical mixing (with aged air from the residual layer) is also reflected in an enhanced $f(RH)$ (see Fig. 3.4), as particles with more secondary material are more hygroscopic, grow more and consequently have a higher $f(RH)$. 
Figure 3.7: Scattering coefficient normalized by the number concentration vs. RH in the nephelometer of quasi monodisperse ammonium sulfate particles with dry diameters between 100 and 300 nm. The grey line represents the predicted values, with their corresponding uncertainties. The black open diamonds show the measured $\sigma_{sp}/N$ while hydrating, whereas the black closed diamonds illustrate the corresponding dehydration values. The black error bars illustrate the measurement uncertainty of the nephelometer.
Figure 3.8: Scattering coefficient normalized by the number concentration vs. RH in the nephelometer of quasi monodisperse sodium chloride particles with diameters between 100 and 300 nm. The grey line represents the predicted values, with their corresponding uncertainties. The black open diamonds show the measured $\sigma_{sp}/N$ while hydrating, whereas the black closed diamonds illustrate the corresponding dehydration values. The black error bars illustrate the measurement uncertainty of the nephelometer.
3.5 Additional information

Figure 3.9: $f$(RH) vs. RH in the nephelometer of sodium chloride particles with a diameter of 100, 150, 240, and 300 nm. The grey line represents the predicted $f$(RH) with corresponding uncertainties. Black open diamonds show the measured $f$(RH) of hydrating aerosols, while black closed diamonds represent dehydrating aerosols.

Figure 3.10: PM10 and PM1 scattering ($\sigma_{sp}$) and absorption coefficients ($\sigma_{ap}$) measured by DOE/ARM with a nephelometer and a PSAP (particle soot absorption photometer) at 550 nm wavelength. Time resolution is 1 min.
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Abstract

Ambient relative humidity (RH) determines the water content of atmospheric aerosol particles and thus has an important influence on the amount of visible light scattered by particles. The RH dependence of the particle light scattering coefficient ($\sigma_{sp}$) is therefore an important variable for climate forcing calculations. We used a humidification system for a nephelometer which allows for the measurement of $\sigma_{sp}$ at a defined RH in the range of 20–95%. In this paper we present measurements of light scattering enhancement factors $f(RH)=\sigma_{sp}(RH)/\sigma_{sp}(dry)$ from a 1-month campaign (May 2008) at the high alpine site Jungfraujoch (3580 m.a.s.l.), Switzerland. At this site, $f(RH=85\%)$ varied between 1.2 and 3.3. Measured $f(RH)$ agreed well with $f(RH)$ calculated with Mie theory using measurements of the size distribution, chemical composition and hygroscopic diameter growth factors as input. Good $f(RH)$ predictions at RH < 85% were also obtained with a simplified model, which uses the Ångström exponent of $\sigma_{sp}(dry)$ as input. RH influences further intensive optical aerosol properties. The backscatter fraction decreased by about 30% from 0.128 to 0.089, and the single scattering albedo increased on average by 0.05 at 85% RH compared to dry conditions. These changes in $\sigma_{sp}$, backscatter fraction and single scattering albedo have a distinct impact on the radiative forcing of the Jungfraujoch aerosol.
Chapter 4 Light scattering enhancement factors at the Jungfraujoch

4.1 Introduction

Atmospheric aerosols influence the Earth radiation budget by scattering and absorbing light. Further they act as cloud condensation nuclei and therefore influence the radiative properties and the lifetime of clouds. These two effects are called direct and indirect aerosol effect and are estimated to have an anthropogenic radiative forcing of \(-0.5\) and \(-0.7\) Wm\(^{-2}\), compared to \(+2.66\) Wm\(^{-2}\) by greenhouse gases [IPCC, 2007]. The anthropogenic aerosol forcing uncertainty is substantially larger than that of the greenhouse gases \((+0.8/-1.5\) vs. \(0.27\) Wm\(^{-2}\)) [IPCC, 2007]. Therefore there is an urgent need to constrain this uncertainty.

To better quantify the direct effect it is important to understand how aerosol light scattering properties are influenced in the atmosphere. At high relative humidity (RH) liquid water comprises a major fraction of the atmospheric aerosol, and therefore the light scattering of aerosols expressed by the scattering coefficient \(\sigma_{sp}\) depends on RH. The factor that quantifies this dependence is the light scattering enhancement factor \(f(RH)=\sigma_{sp}(RH)/\sigma_{sp}(dry)\).

At a fixed RH, \(f(RH)\) depends mainly on the dry particle size distribution and on the particles’ hygroscopicity, which is determined by their chemical composition. For a constant chemical composition \(f(RH)\) increases with decreasing particle size (see, e.g. Fierz-Schmidhauser et al. (2010)).

Many studies have presented measurements of atmospheric aerosol light scattering enhancement factors \(f(RH)\), e.g. for biomass burning aerosol [Kotchenruther and Hobbs, 1998; Kim et al., 2006], dust and pollution aerosol [Carrico et al., 2003; Kim et al., 2006], as well as for aerosols at rural (Day and Malm, 2001), continental (Koloutsou-Vakakis et al., 2001; Sheridan et al., 2001) or urban (Yan et al., 2009) sites or close to the sea [Carrico et al., 1998; 2003; Wang et al., 2007]. The highest \(f(RH)\) were detected in Gosan, Korea, during measurements of pollution aerosols from China of 2.75 (at 85% RH) and of volcanic aerosols during ACE-Asia of 2.55 (at 82% RH). During ACE-Asia, Carrico et al. (2003) measured a very low \(f(RH)\) of 1.18 (at 82% RH) for dust dominated aerosol. In Brazil, biomass burning aerosol measurements revealed \(f(RH)\) as low as 1.16 at 80% RH [Kotchenruther and Hobbs, 1998].

The aerosol scattering coefficient \(\sigma_{sp}\) can be measured by an integrating nephelometer. To measure \(\sigma_{sp}\) at different RH, we built a humidification system for a commercial nephelometer (TSI Inc., model 3563) which allows for the measurement of \(\sigma_{sp}\) at a defined humidity below 95% RH [Fierz-Schmidhauser et al., 2010]. The system is able to measure how hygroscopic properties and hysteresis effects of the atmospheric aerosol influence \(\sigma_{sp}\), and it can be continuously and remotely operated with very little maintenance. In May 2008 this humidified nephelometer measured in parallel with a dry nephelometer (RH<20%) at the high alpine site Jungfraujoch (JFJ). The Jungfraujoch is located at 3580 m a.s.l in the Swiss Alps and is designated a clean continental background station in Central Europe. JFJ is well suited for the study of background aerosols in climate research [Nykic et al., 1998].

The scattering enhancement at higher RH influences the direct climate forcing by aerosol particles [Charlson et al., 1992; Schwartz, 1996]. It is therefore desirable to be able to transform dry \(\sigma_{sp}\), into ambient \(\sigma_{sp}\) values. For this purpose we measured the size distribution and the chemical composition of the JFJ aerosol and performed a closure study using a model based on Mie theory, which can calculate the light scattering enhancement factor \(f(RH)\) at different RH. We compared our model to another model developed by Nessler et al. (2005a).

In this paper we present model calculations of \(f(RH)\) with different model assumptions (constant or variable chemical composition and size distribution) for the month of May 2008.
The predicted $f$(RH) results are compared to the measured $f$(RH). Finally we present the impact of RH on other intensive aerosol properties and the radiative forcing.

4.2 Experimental

4.2.1 Measurement site

All data presented here were measured at the high alpine research station Jungfraujoch (JFJ, 46°33′N, 7°59′E). The measurement campaign took place from 1 to 29 May, 2008. The JFJ measurement site lies on an exposed mountain saddle on the north crest of the Bernese Alps, Switzerland, at 3580 m altitude. The JFJ is a Global Atmosphere Watch (GAW) site and aerosol measurements have been performed in this framework since 1995. It is also part of the Swiss National Monitoring Network for Air Pollution (NABEL) and the Federal Office of Meteorology and Climatology (MeteoSwiss). Baltensperger et al. (1997) and Collaud Coen et al. (2007) give more information on the JFJ site and the long-term aerosol measurements performed there. Due to its high elevation the JFJ resides predominantly in the free troposphere (FT) but can be affected by continental and regional pollution sources through vertical transport: During the warmer months injections of more polluted planetary boundary layer (PBL) air occur due to thermal convection. Consequently most extensive aerosol parameters undergo an annual cycle with maxima in the summer months and minima in the winter months (Baltensperger et al., 1991, 1997; Nyeki et al., 1998; Weingartner et al., 1999; Collaud Coen et al., 2007). A diurnal cycle due to mixing of convectively transported PBL aerosol with the air from the free troposphere is superimposed on this seasonal cycle, which often occurs during the spring and summer seasons. This diurnal cycle was clearly present during the first period of this campaign. Throughout the year the station is within clouds about one third of the time (Baltensperger et al., 1998).

4.2.2 Instruments

Scattering coefficients at dry conditions and at high RH

Since 1995 an integrating nephelometer (TSI Inc., model 3563) has measured the dry scattering coefficients $\sigma_{sp}$ and dry backscattering coefficients $\sigma_{bsp}$ of total suspended particulate matter (TSP) at three wavelengths ($\lambda=450$, 550 and 700 nm) at the JFJ. During the campaign in May 2008 the RH in this nephelometer was always below 20% RH. No drying of the air is needed to achieve this low RH, since the temperature difference between the ambient atmosphere and the laboratory is typically more than 25°C. This temperature increase can lead to evaporation of volatile aerosol particles, but mainly in the diameter size range below 100 nm (Nessler et al., 2003).

We built a novel humidification system for a second integrating nephelometer to measure the RH dependence of $\sigma_{sp}$ and $\sigma_{bsp}$ at a defined RH in the range of 20–95% RH. The humidification system consists of a humidifier that rises the RH of the aerosol up to RH=95%, followed by a dryer, which dries the aerosol to the desired RH (Fierz-Schmidhauser et al., 2010). The RH in the nephelometer is measured with a combined temperature and capacitive RH sensor (Rotronic HygroClipS, accuracy ±0.3°C and ±1.5% RH, according to the manufacturer), which replaces the original RH sensor of the nephelometer. We further modified the nephelometer to achieve a temperature difference between inlet and sensing volume of the nephelometer of less than 1°C by placing an air-cooled infrared filter between the lamp and the sensing volume and by enlarging the outside of the nephelometer sensing volume with
cooling fins, where four additional blowers surround the nephelometer and adjust its temperature close to room temperature (Fierz-Schmidhauser et al., 2010). This system enables us to measure the hysteresis behavior of deliquescent aerosol particles. The light scattering enhancement factor \( f(RH) \) is defined as the ratio of \( \sigma_{sp} \) at high and low RH:

\[
f(RH) = \frac{\sigma_{sp}(RH)}{\sigma_{sp}(RH = \text{dry})}.
\]

The light backscattering enhancement factor, \( f_b(RH) \), is defined similarly with \( \sigma_{bsp} \). During the majority of the measurement period the humidified nephelometer measured at 85% RH (±10% RH). During four time periods, humidity cycles of the scattering enhancement, commonly referred to as humidograms, were determined. When both nephelometers measured at dry conditions (RH < 40%) (3 May 20:00 LT–5 May 10:00 LT) the two instruments agreed well with a slope of 1.03, an intercept of \( 5 \times 10^{-7} \, \text{m}^{-1} \) and a correlation coefficient of \( R^2 = 0.982 \) (at \( \lambda = 550 \, \text{nm} \)). \( \sigma_{sp} \) and \( \sigma_{bsp} \) were corrected for the truncation error according to Anderson and Ogren (1998) (no size cut). They used the Ångström exponent \( d_a \) of the scattering coefficient, which is defined as:

\[
\sigma_{sp} = c \lambda^{-d_a}.
\]

The factor \( c \) (turbidity coefficient) is related to the aerosol concentration and \( \lambda \) is the wavelength of the light. Dividing \( \sigma_{bsp} \) by \( \sigma_{sp} \) results in the backscatter fraction \( b \), which is the percentage of radiation that is scattered back at angles between 90° and 180°. \( b \) increases with decreasing particle size. If the sun is in the zenith, \( b \) is equal to the upscatter fraction \( \beta \). \( \beta \) is the fraction of light that is scattered by a particle into the upward hemisphere relative to the local horizon, and consequently depends on the zenith angle and the particle size. In this study, \( \beta \) is parameterized from the measured \( b \) using the following equation for the global mean (Wiscombe and Grams (1976) in Sheridan and Ogren (1999)):

\[
\beta = 0.0817 + 1.8495b - 2.9682b^2.
\]

Often, the actual RH in the nephelometer differed slightly from the target RH of \( \text{RH}_{\text{target}} = 85\% \). Several humidograms measured at different times could be well described with the following empirical relationship:

\[
f(RH) = \left(1 + a \frac{\text{RH}}{1 - \text{RH}} \right)^{\frac{7}{3}}, \tag{4.4}
\]

where \( a \) is the only free parameter. This empirical relationship allows recalculation of \( f(RH) \) to different RH values, assuming that it generally holds. Recalculated \( f(RH) \) at \( \text{RH}_{\text{target}} = 85\% \) were determined in this way from \( f(RH) \) measured at \( 75\% \leq \text{RH}_{\text{meas}} \leq 95\% \):

\[
f_{\text{recalc}}(\text{RH}_{\text{target}}) = \left(1 + a_{\text{meas}} \frac{\text{RH}_{\text{target}}}{1 - \text{RH}_{\text{target}}} \right)^{\frac{7}{3}}.
\]

\[
f_{\text{recalc}}(\text{RH}_{\text{target}}) = \left(1 + \left[f_{\text{meas}}^{\frac{7}{3}} - 1 \right] \frac{1 - \text{RH}_{\text{meas}}}{\text{RH}_{\text{meas}} \frac{\text{RH}_{\text{target}}}{1 - \text{RH}_{\text{target}}} \right)^{\frac{7}{3}}. \tag{4.5}
\]

**Particle number size distributions**

A scanning mobility particle sizer (SMPS) measured the dry particle size distribution in the particle mobility diameter range 12 nm < \( D_p < 562 \, \text{nm} \). This instrument consists of a Kr-85 source to neutralize the aerosol before the aerosol enters a differential mobility analyzer (DMA) followed by a condensation particle counter (CPC, TSI Inc., model 3772). The SMPS had a closed loop configuration for the sheath and excess air. The volumetric sheath air flow rate was held constant at 5 lpm (liters per minute) by means of a mass flow controller combined
with temperature and pressure sensors. The sample flow rate was 1 lpm. In addition, an optical particle counter (OPC, Grimm Dustmonitor 1.108) measured the dry size distribution of the larger particles in the optical diameter range 0.3 \( \mu m < D_p < 25 \mu m \). In the OPC the individual particles are classified according to their light scattering behavior, which depends on the particle size, morphology and refractive index. The comparison of the size distribution spectra of the OPC and the SMPS showed that the OPC diameters need to be slightly shifted (multiplication of the diameter by 1.12 on average) to larger sizes to get good agreement. This shift increases the scattering coefficients on average by 20% and the \( f(\text{RH}=85\%) \) by 3%.

A similar disagreement between SMPS and OPC was found in a different study at the JFJ site by Cozic et al. (2008).

The combined SMPS and OPC data were used as input for the Mie calculation. All diameter corrected data from the OPC were taken, whereas the SMPS data were just used up to \( D_p = 340 \text{ nm} \), to avoid the influence of doubly and triply charged particles for larger diameters. A comparison of the integrated size distribution of the SMPS and OPC to a second CPC, measuring the total number concentration, showed that the SMPS measured \( \sim 20\% \) less than the CPC, if large nucleation events \( (D_p < 30 \text{ nm}) \) were excluded for the comparison. The combined SMPS and OPC data were used as an input for the model calculations (see Sect. 4.2.3).

**Hygroscopic properties**

A hygroscopicity tandem differential mobility particle sizer (H-TDMA), based on the instrument presented by Weingartner et al. (2002), was operated to measure the hygroscopic diameter growth factors \( (g(\text{RH})) \), defined as the diameter ratio of high RH and dry conditions. The H-TDMA functions as follows: Particles are dried to RH\(<10\%\) and brought to charge equilibrium before a first DMA is used to select a dry monodisperse size of the polydisperse aerosol. These particles with a well defined dry diameter then pass through a humidifier before the resulting equilibrium diameters are measured using a second DMA operated at a well defined high RH (typically 90%). The mean growth factor \( g(\text{RH}) \), measured at RH\(=90\%\pm3\%\), was obtained from the raw measurement distributions using the TDMAinv inversion algorithm (Gysel et al., 2009). Dry diameters measured in this study were 35, 50, 75, 110, 165 and 265 nm.

**Chemical composition**

An Aerodyne high resolution time-of-flight aerosol mass spectrometer (AMS) measured the size resolved aerosol chemical composition of non-refractory submicron aerosol particles. The instrument has been characterized in detail elsewhere (DeCarlo et al., 2006; Canagaratna et al., 2007). Briefly, aerosol is introduced into the instrument via an aerodynamic lens which focuses the aerosol into a tight beam. The particle beam impacts on an inverted conical tungsten vaporizer at 600\(^\circ\)C, where the non-refractory components are flash vaporized. The resulting gas phase plume is ionized by electron ionization at 70 eV. A high mass resolution mass spectrometer (H-TOF, Tofwerk AG, Thun, Switzerland) produces mass spectra which are processed using custom software to give mass concentrations of non-refractory species. At the JFJ the AMS measured with a collection efficiency of 1. This collection efficiency was determined based on intercomparisons of the AMS with both SMPS and dry nephelometer measurements at JFJ. This particular instrument has been deployed at several other locations where intercomparisons with other instruments including other AMS instruments consistently report a collection efficiency of 1 for ambient aerosol. Table 4.1 lists the mean concentrations measured at the JFJ.
Light absorption coefficient

The aethalometer (AE-31, Magee Scientific) has measured light absorption coefficients ($\sigma_{ap}$) of TSP at seven wavelengths ($\lambda$=370, 470, 520, 590, 660, 880, 950 nm) at the JFJ since 2001. According to Weingartner et al. (2003) $\sigma_{ap}$ was calculated with:

$$\sigma_{ap} = \frac{A}{Q} \frac{\Delta \text{ATN}}{\Delta t} \frac{1}{CR(\text{ATN})},$$

(4.6)

where $A$ is the filter spot area, $Q$ the volumetric flow rate and $\Delta \text{ATN}$ the change in attenuation during the time interval $\Delta t$. $C$ has a value of 2.81 for the JFJ and is a wavelength independent empirical correction factor (Collaud Coen et al., 2010). It corrects for multiple reflections of the light beam at the filter fibers, which enhances the optical path in the filter of the aethalometer. $R$ corrects for the loading dependent shadowing effect. $R=1$ is used for the aged aerosol at JFJ (Weingartner et al., 2003).

The black carbon (BC) concentration was calculated from $\sigma_{ap}$ at 880 nm using an optical absorption cross-section of the manufacturer ($16.6/C\text{ m}^2/\text{g}=5.91\text{ m}^2/\text{g}$). It is a common practice to use this wavelength for the determination of equivalent BC concentrations since smaller wavelengths may have stronger contributions by other aerosol components (such as organic matter or mineral dust).

The aerosol single scattering albedo $\omega_0$ describes the relative contributions of scattering and absorption to the total light extinction:

$$\omega_0 = \frac{\sigma_{sp}}{\sigma_{sp} + \sigma_{ap}},$$

(4.7)

Since $\omega_0$ is wavelength dependent $\sigma_{sp}$ and $\sigma_{ap}$ need to be at the same wavelength. Therefore we transformed $\sigma_{ap}$ measured by the aethalometer to the nephelometer wavelengths 450, 550 and 700 nm by using the measured Ångström exponent for the absorption $\tilde{a}_a$ (in analogy to Eq. 4.2).

4.2.3 Mie calculations to predict $f$(RH)

Using measured physical and chemical properties

We predicted $f$(RH) with a model based on Mie theory (Mie, 1908) where the core Mie routine is based on the code of Bohren and Huffmann (2004). The particles are assumed to be spherical and homogenously internally mixed. As input the number size distribution and the complex refractive index $m$ of the measured aerosol are needed. The SMPS and OPC measured number size distribution; both were combined at 340 nm (see Sect. 4.2.2 (particle number size distribution)). The complex refractive index was calculated using the chemical composition measurements of the AMS and the aethalometer. A time resolved mean refractive index was then determined by a volume fraction averaging:

$$m(\lambda) = \sum \frac{m_f i}{\rho_i} m_i(\lambda),$$

(4.8)

where $m_f i$ is the mass fraction, $\rho_i$ is the density and $m_i(\lambda)$ is the wavelength dependent complex refractive index of the compound $i$. We took the values for $m_i$ and $\rho_i$ as listed in Table 4.1.

Hygroscopic growth was accounted for in two alternative ways: either by directly using the size resolved H-TDMA measurements of diameter growth factors or by calculating the
Table 4.1: Microphysical properties of selected aerosol compounds used for the model predictions. The imaginary part of the complex refractive index \( m \) was omitted for all components except for black carbon (BC). All values are interpolated to the nephelometer wavelengths. Mean concentrations (and standard deviations) are for the entire measurement period.

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>Organics</th>
<th>( \text{NH}_4 \text{NO}_3 )</th>
<th>( \text{(NH}_4 \text{)}_2\text{SO}_4 )</th>
<th>( \text{NH}_4\text{HSO}_4 )</th>
<th>( \text{H}_2\text{SO}_4 )</th>
<th>BC</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>1.559 ( ^b )</td>
<td>1.536 ( ^b )</td>
<td>1.438 ( ^d )</td>
<td>1.75+0.46i ( ^e )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>1.556 ( ^a,^* )</td>
<td>1.530 ( ^b )</td>
<td>1.473 ( ^c,^* )</td>
<td>1.75+0.44i ( ^e )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>1.553 ( ^b )</td>
<td>1.524 ( ^b )</td>
<td>1.432 ( ^d )</td>
<td>1.75+0.43i ( ^e )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \rho_i ) [g/cm(^3)]</td>
<td>1.4 ( ^f )</td>
<td>1.72 ( ^g )</td>
<td>1.77 ( ^g )</td>
<td>1.78 ( ^g )</td>
<td>1.83 ( ^g )</td>
<td>1.7 ( ^a )</td>
</tr>
<tr>
<td>mean conc. ( [\mu g/m^3] ) (std)</td>
<td>0.703</td>
<td>0.370</td>
<td>0.450</td>
<td>0.097</td>
<td>0.013</td>
<td>0.057</td>
</tr>
</tbody>
</table>


The AMS measurements can also be used to calculate the hygroscopic growth factor from AMS and aethalometer measurements. The H-TDMA growth factors \( g(\text{RH}=90\%) \) were extrapolated to different RH using Eq. (3) from Gysel et al. (2009), which uses the \( \kappa \)-model introduced by Petters and Kreidenweis (2007). For the wet refractive index a volume weighting between the refractive indices of water and the according dry aerosol was chosen (Hale and Querry, 1973).

Using the Ångström exponent as only directly measured input

Nessler et al. (2005a) proposed a specific algorithm for the JFJ site to adapt dry nephelometer measurements to ambient conditions. They used a coated sphere model also based on Mie theory to calculate \( f(\text{RH}) \). The fine-mode has been modeled assuming an insoluble core and a homogeneous soluble coating, which absorbs an increasing amount of water with increasing RH. The relative amounts of insoluble and soluble material in the fine mode were derived from experimental chemical composition and hygroscopic growth data. To get a representative range of the JFJ size distributions, Nessler et al. (2005a) combined 15 months of averaged SMPS and OPC data and fitted them with the sum of three log-normal distributions. By varying the geometric standard deviations, median diameters, and coarse mode concentrations within the \( \pm 15\% \) interval of the fitted parameters, they obtained size distributions considered representative for the JFJ aerosol. The coarse mode is considered to be insoluble (no hygroscopic growth), as it is mainly mineral dust which is detected in this size range. The Ångström exponent \( \alpha_s \) (see Eq. (4.2)), is used as a proxy for the relative contributions of fine and coarse mode particles, and is beside the RH in the nephelometer the only input parameter required to calculate \( f(\text{RH}) \). The parameterization is given for a separate
summer and a winter case and is valid in the range of $-0.25\deg<s<2.75$ and $0\%<RH<90\%$. Our measurement period lies within the proposed summer case scenario.

### 4.3 Results and discussion

First we give an overview of the measured light scattering enhancement factors $f(RH)$ in combination with other measurements, then we demonstrate how $f(RH)$ can be predicted and finally we investigate the impact of RH on further climate relevant intensive properties.

#### 4.3.1 Measured $f(RH)$

**Overview**

Figure 4.1 shows an overview of the measured scattering coefficient $\sigma_{sp}$ and the light scattering enhancement factor $f(RH)$ at 85% RH of the CLACE 2008 campaign in May 2008 at the JFJ. Every data point represents hourly averaged data. All time scales are Central European Summer Time (CEST=UTC+2h). Figure 4.1a displays the scattering coefficient $\sigma_{sp}$ at 550 nm wavelength. The nephelometer measured hourly averaged $\sigma_{sp}$ values between 0 and $1.1\cdot10^{-4} m^{-1}$. The highest scattering signal occurred on 28 May, during a strong Saharan dust event (SDE). The mean $\sigma_{sp}$ of the measurement campaign is shown in Table 4.2 (without SDE and for SDE only). $\sigma_{sp}$ shows higher values during the first half of the measurement campaign (1 to 16 May) than during the second half, until the SDE started (16 to 26 May). We will treat the time period of the SDE separately (Sect. 4.3.1 (Saharan dust events)). We explain the low scattering coefficients of the second half of the measurement campaign by high cloud coverage and precipitation. $\sigma_{sp}$ values below $10^{-6} m^{-1}$ for hourly means were included in the calculation of means of $\sigma_{sp}$ but not for further data analysis. We highlighted these data points in light green in the curve of $\sigma_{sp}$ in Fig. 4.1. For the prediction of $f(RH)$ (see Sect. 4.3.2) $\sigma_{sp}$ values below $5\cdot10^{-6} m^{-1}$ were not used, and are shown in grey in Fig. 4.1a.

Figure 4.1b presents light scattering enhancement factors $f(RH=85\%)$ at 450, 550 and 700 nm wavelength. These data points originate from scattering coefficients that were measured by the humidified nephelometer at a RH between 75 and 95% and were recalculated to RH=85% with Eq. 4.5. During most of the time the instrument measured at 85% RH ($\pm10\%$ RH), and $f(RH=85\%)$ varied between 1.2 and 3.3 (mean shown in Table 4.2). Daily averaged values of $f(RH=85\%)$ were between 1.65 and 2.82, with low values (<2) on 6, 18 and 26 May and values above 2.7 on 10, 12 and 13 May. A back trajectory analysis (FLEXTRA) for the days with $f(RH=85\%)>2.7$ showed that the air masses reaching JFJ often did not pass below 1000 m.a.s.l. within the last 7 days. The few times they did it nonetheless was over the Atlantic Ocean. On these days we measured inorganic mass fractions higher than 0.57 (see Fig. 4.4), largest particle mean diameters and high hygroscopic growth factors ($g(RH=90\%)>1.55$ for particles with a dry diameter of 265 nm). The air masses that reached JFJ on days with low $f(RH)$ either passed at less than 1000 m.a.s.l. in eastern Europe (6 May), in southwestern and mideastern Europe (19 May), or in northern Africa (26 May). By passing over populated areas the air probably picked up more organic matter which results in a decrease of $f(RH)$. This hypothesis can be only confirmed for one day, because of the other days. On 6 May the mean mass fraction of the inorganic compounds was 0.43 (see Fig. 4.1).

In the beginning of the measurement campaign (1–3 May) the $f(RH=85\%, \lambda=700\text{nm})$ was lower compared to $f(RH=85\%, \lambda=450\text{nm})$ while it was larger in the middle of the measurement campaign (11–14 May). This spectral behavior is explainable by a smaller
4.3 Results and discussion

Figure 4.1: Time series of the scattering coefficient ($\sigma_{sp}$) at 550 nm wavelength (a), measured $f$(RH) recalculated to RH=85% of three distinct wavelengths (b) and mass fraction of the chemical composition measured by the AMS and the aethalometer (c). SDE indicates the time period, when a Saharan dust event was present. The scattering coefficients shown in light green are below $10^{-6}$ m$^{-1}$, those shown in grey are below $5 \cdot 10^{-6}$ m$^{-1}$.

Table 4.2: Scattering coefficient $\sigma_{sp}$, light scattering enhancement factor $f$(RH=85%), light backscattering enhancement factor $f_b$(RH=85%), backscatter fraction $b$, single scattering albedo $\omega_0$, Ångström exponent $a_s$ and hygroscopic growth factor of 265 nm dry particles $g(D_p=265 \text{ nm}, \text{ RH}=90\%)$ averaged over the whole campaign excluding Saharan dust event (SDE) and averaged exclusively during the SDE.

<table>
<thead>
<tr>
<th></th>
<th>campaign average</th>
<th>excluding SDE</th>
<th>exclusively SDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{sp}$ (550 nm) [m$^{-1}$]</td>
<td>1.19$\cdot 10^{-5}$</td>
<td>2.05$\cdot 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>$f$ (RH=85%)</td>
<td>2.23</td>
<td>1.72</td>
<td></td>
</tr>
<tr>
<td>$f_b$ (RH=85%)</td>
<td>1.60</td>
<td>1.54</td>
<td></td>
</tr>
<tr>
<td>$b$</td>
<td>0.128</td>
<td>0.089</td>
<td>0.122</td>
</tr>
<tr>
<td>$\omega_0$</td>
<td>0.907</td>
<td>0.954</td>
<td>0.930</td>
</tr>
<tr>
<td>$a_s$</td>
<td>1.787</td>
<td>0.839</td>
<td>1.671</td>
</tr>
<tr>
<td>$g(D_p=265 \text{ nm}, \text{ RH}=90%)$</td>
<td>1.522</td>
<td>n.a.</td>
<td></td>
</tr>
</tbody>
</table>
coarse mode fraction and generally smaller particles in the latter case, which is confirmed by higher Ångström exponents between 1.9 and 2.5.

### Saharan dust event (SDE)

In the end of the measurement campaign a strong Saharan dust event took place (26 May 12:00 LT to 29 May 12:00 LT). During a SDE the aerosol exhibits properties significantly different from the background conditions [Schwikowski et al., 1995; Collaud Coen et al., 2004]. Such a SDE event significantly increases the coarse mode mass concentration but it also has an important influence on the accumulation mode. The H-TDMA was not running at this time, but typically shows an external mixture at 250 nm when there is significant influence of dust particles, which was also reported by Sjogren et al. (2008). The \( f(RH=85\%) \) during the most intensive time of the SDE was the lowest during the whole measurement campaign, with an hourly averaged value of 1.2. Similarly, Carrico et al. (2003) measured in the ACE-Asia campaign during the most dust-dominated period a \( f(RH) \) at 82% RH of 1.18. Our findings also agree with the ones of Li-Jones et al. (1998), who investigated the \( f(RH) \) of long-range transported Saharan dust.

### Diurnal variations

At the JFJ extensive aerosol properties undergo diurnal variations, most strongly observed in spring and summer (Baltensperger et al., 1997; Lugauer et al., 1998; Weingartner et al., 1999). In May 2008 (without SDE) \( \sigma_{sp} \) also varied throughout the day with a maximum in the late afternoon to early evening and a minimum before noon. The maximum was on average 1.5 times higher than the minimum \( (9.5 \cdot 10^{-6} \text{ m}^{-1}) \). The intensive parameter \( f(RH=85\%) \) did not experience a clear diurnal pattern in the same time period. A further analysis shows that here \( \sigma_{sp} \) increased due to an increase in the aerosol load rather than a change in the chemical composition or the size distribution. The time period of 6 to 11 May had long sunshine duration, favoring thermal convection. During this period the diurnal pattern of \( \sigma_{sp} \) was much more distinct, with the maximum being more than three times higher than the minimum \( (8.5 \cdot 10^{-6} \text{ m}^{-1}) \). In this period, averaged \( f(RH) \) values did indeed exhibit a diurnal variation, with the maximum roughly at the same time as \( \sigma_{sp} \), suggesting that the chemistry (or the size distribution) of the aerosol from the PBL was different from the one in the free troposphere. It can, however, be expected that also the reverse diurnal variation is possible, with \( f(RH) \) being minimal when \( \sigma_{sp} \) shows its maximum.

### Humidograms

During four time periods the RH in the humidified nephelometer was cycled between 20 and 95% RH thus providing \( f(RH) \) over a wide range of RH, also commonly referred to as humidograms. No distinct efflorescence or deliquescence effects were seen, which is in line with previous H-TDMA humidograms recorded at this site (Weingartner et al., 2002; Sjogren et al., 2008). Figure 4.2 presents \( f(RH) \) (top) and \( f_b(RH) \) (bottom) at 550 nm wavelength of four measured humidograms. Each humidogram consists in maximum of two RH cycles, with 10-min means at each RH. The humidograms plotted with the diamond markers (6/7, 13 and 14 May) all have a similar shape and similar magnitude of \( f(RH) \). On 6 May there is much more variability in the \( f(RH) \) data compared to 13 and 14 May, also seen in Fig. 4.1 for \( \sigma_{sp} \) data, which is attributed to a lower signal to noise ratio due to a lower aerosol loading. The humidogram in yellow was measured when the Saharan dust event was strongest. The aerosol grows very little with increasing RH, resulting in an \( f(RH) \) at 85% of ~1.2.
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Figure 4.2: Light scattering enhancement factor $f(RH)$ (top) and light backscattering enhancement factor $f_b(RH)$ (bottom) at 550 nm wavelength vs. RH at four different time periods when the RH in the humidified nephelometer was cycled (max. 2 cycles per period).

There is no significant difference of $f_b(RH)$ between the SDE and the other days. Smaller particles scatter relatively more light in the backward direction, so when water is added the $f_b(RH)$ is much smaller than the $f(RH)$. During an SDE the particles are larger and grow less and therefore the $f_b(RH)$ increases by about the same factor as without a SDE.

4.3.2 Prediction of $f(RH)$

RH dependence

The scattering coefficients were calculated for each measurement point of the humidified nephelometer. The calculated dry and humid scattering coefficients were $\sim 20\%$ below the measured ones (with a correlation coefficient $R^2 = 0.97$ at 550 nm wavelength), which we attribute to a systematic bias in the measured model input parameters. The scattering coefficient at dry conditions depends on the aerosol chemical composition (via the refractive index), on the shape of the aerosol size distribution (or mean size) and on the aerosol concentration. The influence of the refractive index is not large enough to account for the encountered discrepancy of 20%. It is speculated that this discrepancy is mainly caused by a small systematic error in
the measurement of the size distribution (i.e., either in the determination of the diameter or number concentration, or a combination of both). Since $f$(RH) is not sensitive to the total number concentration and only slightly sensitive to the aerosol size distribution shape, we can neglect the constant difference in the absolute values.

The predicted $f$(RH) depends on the aerosol size distribution, on the chemical composition of the aerosol and on the RH in the nephelometer. The chemical composition is used to determine the refractive index and the hygroscopic growth factor $g$(RH). $g$(RH) can be calculated from measurements of the chemical composition by the AMS and the aethalometer or direct measurements from the H-TDMA.

Figure 4.3 presents the same humidograms as in Fig. 4.2 (top) (6/7, 13, 14 and 28 May), along with predicted humidograms. The black points in all four panels represent the measured $f$(RH). The colored points show the $f$(RH) predicted by different model approaches (see Sect. 4.2.3). The red points denote $f$(RH) predictions based on $g$(RH) values calculated from the AMS and aethalometer data, whereas the blue lines show $f$(RH) predictions from the $g$(RH) values obtained by the H-TDMA. The grey points were calculated using the approach of Nessler et al. (2005a).

On 6/7 May (Fig. 4.3a) all instruments needed for these predictions were running. All model approaches agree well with the measurements and are similar up to 80% RH. Above 80% RH, the algorithm by Nessler et al. (2005a) overestimates $f$(RH), whereas the Mie calculations based on $g$(RH) values derived either from H-TDMA or AMS/aethalometer measurements underestimate $f$(RH). Neither AMS/aethalometer nor H-TDMA data are available on 13 May and only partly on 14 May (Fig. 4.3b, c). Predictions available for these days agree quite well with measurements, with the limitation that the algorithm by Nessler et al. (2005a) overestimates $f$(RH) above 85% RH. On 28 May (Fig. 4.3d), when the SDE was present, the Mie calculation with $g$(RH) from the AMS results in a $f$(RH) that is quite different from the measured one (no H-TDMA data were available on this day). This is reasonable since Saharan dust contains a large fraction of refractory material (Schwikowski et al., 1995; Collaud Coen et al., 2004; Cozic et al., 2008) which is not detected by the AMS. In addition, the AMS does not measure super-micrometer particles, which are much more abundant during a SDE. The Nessler algorithm predicts $f$(RH) quite well during the SDE. As explained above, the only input variable is the Ångström exponent (values in Table 4.2), which is a proxy for the detected size distribution. At low values ($\bar{a}_s<1$) the aerosol size distribution is dominated by the coarse mode which exhibits much less hygroscopic growth than the accumulation mode.

Figure 4.4a and b present the sensitivity of the model predictions to the source of the hygroscopic growth data. The x-axes always show the measured $f$(RH), whereas the y-axes display the predicted $f$(RH), with $g$(RH) obtained from the H-TDMA (Fig. 4.4a) and from the AMS data (Fig. 4.4b). The colors indicate the RH in the nephelometer. All points in grey are $f$(RH) values from scattering coefficients smaller than the threshold of 5·$10^{-6}$ m$^{-1}$. They have a high uncertainty and were therefore not used for the linear regression (blue line) and the correlation coefficient. We excluded all data from the time period of the SDE because of missing H-TDMA data.

By using all measured input parameters we get a good agreement between measured and predicted $f$(RH). However, when $g$(RH) from the AMS is used instead of $g$(RH) from the H-TDMA measurements, the predicted $f$(RH) is lower than the measured $f$(RH) at high RH and higher at low RH. We conclude that we are able to perform a closure of the $f$(RH) measurements with our model calculations using a combination of SMPS, OPC, AMS, aethalometer and H-TDMA data.

The same correlation plot but with predictions using the approach by Nessler et al. (2005a) is shown in Fig. 4.4c. The correlation between measurement and prediction is good.
4.3 Results and discussion

Figure 4.3: Humidograms showing measured (black symbols) and predicted $f$(RH) vs. RH in the nephelometer for four example days in May 2008. The grey lines are calculated according to the approach by Nessler et al. (2005a). The red and blue lines are calculated with Mie theory using a combination of size distribution, chemical composition and hygroscopicity data. The latter are inferred either by the H-TDMA (blue lines) or the AMS/aethalometer data (red points). (d) shows a humidogram from the time period of the Saharan dust event (SDE). For 13 and 28 May, no H-TDMA data was available, whereas no AMS/aethalometer data was available on 13 and 14 May.
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Figure 4.4: Comparison of predicted and measured $f(RH)$ (6-min means, entire measured RH range, SDE excluded). (a) prediction includes size distribution and uses $g(RH)$ from the H-TDMA measurements. (b) same as (a) but using $g(RH)$ calculated from the AMS/aethalometer data as a proxy for the chemical composition. (c) predicted $f(RH)$ according to Nessler et al. (2005a) vs. measured $f(RH)$. (d) $f(RH)$ predicted according to Nessler et al. (2005a) vs. $f(RH)$ predicted with the method using $g(RH)$ of the H-TDMA. The color code represents the RH in the nephelometer, whereas the grey symbols are data points with $\sigma_{sp} < 5 \times 10^{-6} \text{m}^{-1}$. The blue solid line represents a non-linear least square regression.

At higher RH the Nessler algorithm overestimates $f(RH)$ slightly. As described above, Nessler et al. (2005a) give 90% RH as an upper limit. In Fig. 4.4d we compare the prediction using $g(RH)$ from the H-TDMA with the model of Nessler. The two models predict similar $f(RH)$ up to about 85% RH, but at higher RH either the Nessler approach overestimates $f(RH)$, or the H-TDMA measurements underestimate $f(RH)$ with the assumptions made.

Sensitivity of $f(RH)$ to size distribution shape and chemical composition

To investigate the influence of the size distribution and chemical composition on $f(RH)$, we repeated the model predictions by keeping one or both parameters constant. For a constant shape of the size distribution, the monthly mean normalized size distribution was multiplied with the concentration for each data point instead of using the measured size distributions. For a constant chemical composition one mean refractive index and the mean $g(RH)$ from the H-TDMA at the diameter of 265 nm were taken.

For the sensitivity analysis we only considered $f(RH)$ at RH between 80 and 86% and used hourly means. The x-axes of all four panels of Fig. 4.5 show the best possible prediction
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Figure 4.5: Sensitivity analysis of $f$(RH) on the chemical composition and size distribution. Hourly means of different predictions vs. the best possible prediction (using size distribution, chemical composition and hygroscopic growth measurements, excluding the SDE) of $f$(RH) at RH=80–86%: $f$(RH) predicted with constant size distribution (a), predicted with constant chemical composition (b), and with combined constant size distribution and constant chemical composition (c). (d) shows measured $f$(RH) with standard deviation vs. the best possible prediction of $f$(RH). The color code represents the RH in the nephelometer, whereas the grey symbols are data points with \( \sigma_{sp} < 5 \times 10^{-6} \). The blue solid line represents a non-linear-least-square regression.

considering measurements of the size distribution, the chemical composition and $g$(RH), which is used as a reference case for the simplified predictions. The marker color represents the RH in the nephelometer and the grey symbols represent $f$(RH) values with $\sigma_{sp}$ below the threshold of $5 \times 10^{-6}$. Figure 4.5a shows the model prediction using a constant size distribution on the y-axis, which reproduces the reference prediction within ±8%. This shows that variations of the shape of the number size distributions have very little effect on the variability of $f$(RH) at the Jungfraujoch. A major reason for this is that the shape of the size distribution varies little at the JFJ (Weingartner et al., 1999), which was also true for this time period. If the time period of the SDE would have been included in this sensitivity analysis the conclusion could be different, because during the SDE the shape of the size distribution varied more than during the rest of the measured time period. Figure 4.5b shows the model prediction using constant mean chemical composition. Neglecting the temporal variability of the chemical composition reduces the correlation to the reference case significantly. This demonstrates that the temporal variability of the chemical composition has some influence on the variability of $f$(RH). Nevertheless deviations from the reference case remain smaller than a factor of 1.25, showing that knowing the mean chemical composition is still sufficient
for a fair prediction of \( f(RH) \) for this month of measurement, always excluding SDE. The model prediction keeping both chemical composition and size distribution constant has the lowest correlation with the reference case, even though absolute deviations remain similar to the previous simplification.

The effects of changing chemical composition become even more important than shown in the above sensitivity analysis, if SDEs are included. Figure 4.2 clearly shows that \( f(RH) \) drops dramatically if the scattering is dominated by non-hygroscopic dust particles. The fact that knowing the mean chemical composition and typical size distribution of the Jungfraujoch aerosol is sufficient for fair predictions of \( f(RH) \) explains the good performance of Nessler’s approach when comparing predictions with measurements across a wide range of RH (see Fig. 4.4), where changes in RH have the dominant influence on \( f(RH) \). Furthermore, Nessler’s approach is also able to capture SDEs (see Fig. 4.3) by inferring the relative contributions of hygroscopic fine mode particles and non-hygroscopic coarse mode dust particles from the Ångström exponent, which is a measure of the average size of the aerosol particles population. In contrast, the other two approaches which use AMS and aethalometer or H-TDMA derived growth factors for prediction of \( f(RH) \) are both biased during SDE events because they essentially miss the dust component. The AMS does not measure refractory material such as dust and is limited to the submicron size range. The H-TDMA, which also captures non-hygroscopic dust particles, is limited to particles with diameters below 265 nm. The dominant contribution of dust is found at sizes above 265 nm and therefore the overall contribution of dust is underestimated also with the H-TDMA approach.

4.3.3 RH dependence of derived climate relevant properties

RH dependence of the backscatter fraction and the single scattering albedo

Beside \( f(RH) \) other intensive properties depend on RH: the Ångström exponent \( \dot{a}_s \), the backscatter fraction \( b \) and the single scattering albedo \( \omega_0 \). In this section we will focus on \( b \) and \( \omega_0 \). Figure 4.6 presents frequency distributions of hourly means of \( b \) and \( \omega_0 \) at 550 nm wavelength from 1 to 26 May, excluding the last three days of the measurement campaign, when the Saharan dust event was present. Data points with \( \sigma_{sp} < 10^{-6} \text{ m}^{-1} \) were also omitted.

Figure 4.6a displays the relative frequency of 262 h of measured \( b \) at RH < 20% and RH = 85%. The \( b(RH=85\%) \) originates from \( \sigma_{sp} \) and \( \sigma_{bsp} \) values at RH between 75 and 95% recalculated to RH = 85% using Eq. 4.5. The \( b(RH<20\%) \) is between 0.08 and 0.18 for 90% of the time, with the mode being at 0.115. The \( b(RH=85\%) \) is lower (between 0.06 and 0.11 for 90% of the time), since the aerosol particles are larger and hence scatter more in the forward direction. The mean \( b(RH<20\%) \) and \( b(RH=85\%) \) are listed in Table 4.2.

Figure 4.6b presents the frequency distribution of \( \omega_0(RH<20\%) \) and \( \omega_0(RH=85\%) \). The latter was determined from \( \sigma_{sp} \) values recalculated to RH = 85% as described above and dry \( \sigma_{ap} \) values assuming that the absorption does not change with RH (Nessler et al., 2005b). Out of 259 h of measurement \( \omega_0(RH<20\%) \) was between 0.83 and 0.95 for more than 90% of the time and between 0.91 and 0.94 for more than 50% of the time. In contrast, \( \omega_0(RH=85\%) \) was below 0.9 for less than 7% of the time, and between 0.96 and 0.98 for about 50% of the time. On average \( \omega_0 \) increases by \( \sim 0.05 \) due to water uptake (see also Table 4.2).

Since the interest is not only on the two RH ranges shown in Fig. 4.6, we display box plots of \( b \) and \( \omega_0 \) for different RH bins in Fig. 4.7. Here we present a subset of the whole dataset where humidograms were measured (totally 51 h of measurements).

The backscatter fraction \( b \) decreases with increasing RH from about 0.13 at 20±5% RH to about 0.09 at 90±5% RH. The decrease is not perfectly monotonous, but we assume that
Figure 4.6: Frequency distribution (hourly means) of the backscatter fraction $b$ (a) and of the single scattering albedo $\omega_0$ (b) at 85% RH (white) and below 20% RH (grey). The Saharan dust event (SDE) at the end of the campaign as well as data points with $\sigma_{sp}<10^{-6}$ m$^{-1}$ were excluded.
Figure 4.7: Box- and whisker-plot of the backscatter fraction (a) and the single scattering albedo (b) sorted in bins with a width of 10% RH. Every box contains $N$ 10-min data, measured within $\pm 5\%$ of the indicated RH. The circles are the mean values, the horizontal lines in the boxes are the medians, the bottom and top limits of the boxes are the 25th and 75th percentiles and the whiskers extend to the 10th and 90th percentiles.

This is mainly due to the low number of points measured at 50% RH. $\omega_0$ shows the opposite behavior above 50% RH, it increases with increasing RH. The observed deviation at 50% RH is again caused by poor statistics which is based on 12 data points. For both $b$(RH=50%) and $\omega_0$(RH=50%) a single outlier influences the mean values.

**RH dependence of the radiative forcing**

As $\sigma_{sp}$, $\omega_0$ and $b$ are all RH dependent, the radiative forcing $\Delta F$, given by the radiative forcing equation by Haywood and Shine (1995), is also RH dependent:

$$\Delta F(\text{RH}) \approx -DS_0T^2_{\text{atm}}(1 - A_C) \omega_0(\text{RH})\beta(\text{RH})\delta(\text{RH}) \cdot \left\{ (1 - R_S)^2 - \frac{2R_S}{\beta(\text{RH})} \left[ \frac{1}{\omega_0(\text{RH})} - 1 \right] \right\}.$$

(4.9)

The following parameters in the equation are RH independent: fractional daylight $D$, solar flux $S_0$, atmospheric transmission $T_{\text{atm}}$, fractional cloud amount $A_C$, surface reflectance $R_S$. The RH dependent upscatter fraction $\beta$ was calculated from the backscatter fraction $b$ with Eq. (4.3). The spectrally weighted aerosol optical depth $\delta$ depends on RH via $\sigma_{sp}$ and $\sigma_{ap}$. With Eq. (4.7) $\sigma_{ap}$ can be displaced in the following way:

$$\sigma_{ap}(\text{RH}) = \frac{\sigma_{sp}(\text{RH})}{\omega_0(\text{RH})} - \sigma_{sp}(\text{RH}),$$

(4.10)
which results in an RH dependent aerosol optical depth of:

$$\delta = \int \frac{\sigma_{sp}(RH)}{\omega_0(RH)} dz.$$  \hspace{1cm} (4.11)

To investigate the RH dependence of the radiative forcing $\Delta F$, we calculate $\Delta F(RH)/\Delta F(RH = 20\%)$ which is now only dependent on $R_S$, $f(RH)$, $\omega_0$ and $b$:

$$\frac{\Delta F(RH)}{\Delta F(RH = 20\%)} = \frac{\beta(RH)}{\beta(RH = 20\%)} f(RH) \cdot \frac{(1 - R_S)^2 - \left(\frac{2R_S}{\beta(RH)}\right) \left[\left(\frac{1}{\omega_0(RH)}\right) - 1\right]}{(1 - R_S)^2 - \left(\frac{2R_S}{\beta(RH=20\%)}\right) \left[\left(\frac{1}{\omega_0(RH=20\%)}\right) - 1\right]}.$$  \hspace{1cm} (4.12)

$R_S$ is taken as 0.15 (global average, [Hummel and Reck (1979)]) and the RH dependence of $\omega_0$ and $b$ is taken from the parameterization presented above (Fig. 4.7).

Figure 4.8 clearly shows that the radiative forcing increases for RH $> 50\%$ and is more than twice as high at 90\% RH as at 40\% RH. Two effects influence this behavior: first and most important is the RH dependence of $\sigma_{sp}$, shown as green curve, where $\omega_0$ and $b$ are assumed to be RH independent. The total RH dependence of $\Delta F$ gets slightly smaller, when the RH dependence of $\omega_0$ and $b$ is taken into account. The reason for this is that $b$ decreases with increasing RH.

![Figure 4.8: Ratio of radiative forcing at a certain RH to radiative forcing at dry conditions (RH=20%) for $R_S=0.15$, depending on RH for three different cases where the RH dependence of the following parameters is considered: only $\sigma_{sp}$ (green curve), $\sigma_{sp}$, $\omega_0$ and $\beta$ (red curve), and only $\omega_0$ and $\beta$ (yellow curve). The red area shows the $R_S$ dependence of the red curve (0.05 $< R_S < 0.25$).](image)

To be able to transform the radiative forcing from one RH to another we studied the red curve of Fig. 4.8. It tells us that the radiative forcing increases by 24\%, 19\%, 14\%, 11\%, if the RH increases from 70\% to 75\%, 75\% to 80\%, 80\% to 85\% and 85\% to 90\%, respectively.

The radiative forcing due to aerosols does not only depend on the aerosol properties but also on the surface albedo of the ground underneath the aerosol. The last term of Eq. (4.9) in curly brackets determines whether an aerosol layer above a certain surface leads to cooling or warming ([Haywood and Shine, 1995]). The sensitivity of the red curve on $R_S$ is shown with
the red area, which displays the variability of the red curve with $R_S$ between 0.25 (upper limit) and 0.05 (lower limit). For the aerosol sampled at JFJ and so in the free troposphere the critical $R_S$, at which this aerosol layer would change from a net cooling to a net warming effect, is at $R_S=0.51$ for dry conditions and $R_S=0.61$ at 80% RH. Surface reflectance of this level would be found above snow and ice.

### 4.4 Summary and conclusions

During a month-long measurement campaign at the high alpine site Jungfraujoch we measured light scattering enhancement factors $f(RH)$ at different RH, but mostly between 80 and 90% RH. $f(RH=85\%)$ reached values up to 3.3, whereas the lowest $f(RH=85\%)$ values of 1.2 were detected during a Saharan dust event (SDE). The RH dependence of $f(RH)$ was similar on three different days, excluding the SDE event, indicating that on these days the aerosol had similar physical and chemical properties in the relevant size range.

Measured $f(RH)$ were compared to predictions obtained with two different model approaches: the first model uses Mie theory with measured size distributions, chemical composition and a hygroscopicity parameter to calculate $f(RH)$. The second simplified approach is based on the model of Nessler et al. (2005a), which uses Mie theory and the measured Angström exponent of the dry scattering coefficient to calculate $f(RH)$. Both models reproduce $f(RH)$ quite well. The Nessler model works fine up to RH values of 85%, whereas at higher RH it overestimates $f(RH)$. With the first model we additionally performed a sensitivity analysis on the input parameters (chemical composition and size distribution). We found that the variability of the chemical composition has a dominant influence of the variability of $f(RH)$, but also a mean size distribution is required to predict $f(RH)$ well.

The RH influences also other intensive properties than $f(RH)$: the backscatter fraction $b$ and the single scattering albedo $\omega_0$. $b$ gets smaller with increasing RH, due to particle growth and $\omega_0$ gets closer to 1 with increasing RH, because the influence of the scattering upon the absorption gets more important. By combining all three investigated RH dependent variables $\omega_0$, $b$ and $f(RH)$ we can estimate the RH dependence of the radiative forcing due to aerosols. At 90% RH the radiative forcing is 2.3 times higher than at 20% RH for the conditions found at the JFJ in May 2008.

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### References

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5

Light scattering enhancement factors in the marine boundary layer (Mace Head, Ireland)

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Abstract

Direct climate aerosol radiative forcing is influenced by the light scattering of atmospheric aerosols. The chemical composition, the size distribution and the ambient relative humidity (RH) determines the amount of visible light scattered by aerosols. We measured light scattering coefficients at RH varying from 30 to 90% of the marine atmosphere at the Mace Head Atmospheric Research Station on the west coast of Ireland. At this site two major air mass types can be distinguished: clean marine and polluted air. In this paper we present measurements of light scattering enhancement factors $f(RH) = \sigma_{sp}(RH)/\sigma_{sp}(dry)$ from a 1-month field campaign (January-February 2009). At this site in winter the mean $f(RH=85%)$ (standard deviation) for marine air masses at the wavelength of 550 nm was 2.22 ($±0.17$) and 1.77 ($±0.31$) for polluted air. Measured $\sigma_{sp}(RH)$ and $f(RH)$ agreed well with calculations from Mie theory using measurements of the size distribution and hygroscopic diameter growth factors as input. In addition, we investigated the RH influence on additional intensive optical properties: the backscatter fraction and the single scattering albedo. The backscatter fraction decreased by about 20%, and the single scattering albedo increased on average by 1-5% at 85% RH compared to dry conditions.
5.1 Introduction

Atmospheric aerosols influence the Earth’s radiation budget by two effects: the direct and indirect effect. Aerosols indirectly influence the Earth’s radiation budget by modifying the microphysical and thus the aerosol radiative properties, and the water content and lifetime of clouds. The direct effect is the mechanism by which aerosols scatter and absorb sunlight, thereby altering the radiative balance of the Earth-atmosphere system (IPCC, 2007). Three aerosol optical properties are important to determine the aerosol direct radiative forcing: the aerosol extinction coefficient which is the sum of aerosol scattering coefficient ($\sigma_{sp}$) and aerosol absorption coefficient ($\sigma_{ap}$) and which specifies how much aerosol particles attenuate electromagnetic radiation; the single scattering albedo ($\omega_0$), which is defined as the ratio of light scattering to total light extinction; and the angular distribution of light scattering which can be parameterized by the asymmetry parameter, the upscatter fraction or backscatter fraction (Kiehl and Briegleb, 1993).

These three aerosol optical properties can be measured, at least approximately, with a nephelometer, which measures the light scattering and backscattering coefficient ($\sigma_{bsp}$), and combined with an aethalometer, which measures the light absorption coefficient, like it is done at various World Meteorological Organisation (WMO) Global Atmosphere Watch (GAW) stations. To better compare between different measurements at these stations, the WMO recommends measurements to be below 40% relative humidity (RH), which is considered a dry measurement (WMO/GAW, 2003). However, many global circulation model studies found that the negative radiative forcing of the aerosols is significantly higher when the ambient RH was accounted for (Haywood and Ramaswamy, 1998; Penner et al., 1998; Grant et al., 1999; Kiehl et al., 2000).

To measure $\sigma_{sp}$ and $\sigma_{bsp}$ at different RH, we used a humidification system upstream of a commercial nephelometer (TSI Inc., model 3563) which allows for the measurement of $\sigma_{sp}$ and $\sigma_{bsp}$ at a defined humidity below 90% RH (Fierz-Schmidhauser et al., 2010b). The system is able to measure how hygroscopic properties and hysteresis effects of the atmospheric aerosol influence the scattering properties. The light scattering enhancement factor $f(RH)=\sigma_{sp}(RH)/\sigma_{sp}(dry)$ was used to quantify the dependence of $\sigma_{sp}$ on RH.

Several measurements of $f(RH)$ of various aerosol types and at different locations in the world have been made. Kotchenruther and Hobbs (1998); Gras et al. (1999); Kim et al. (2006) measured $f(RH)$ of biomass burning aerosol. Dust and pollution aerosol was measured by Carrico et al. (2003) and Kim et al. (2006). Fitzgerald et al. (1982); Yan et al. (2009) studied urban aerosol. Fierz-Schmidhauser et al. (2010a) and Zieger et al. (2010) measured $f(RH)$ in the free troposphere and the Arctic, respectively, with the same instrument as we used in this study.

In this paper we describe field measurements of aerosol extensive (concentration dependent) and intensive (independent of the amount of aerosol present) properties. The measured properties are $\sigma_{sp}$, $\sigma_{bsp}$, $\sigma_{ap}$, the single scattering albedo, the backscatter fraction, the wavelength dependence of scattering (scattering Ångström exponent), the hygroscopic growth factor, the light scattering enhancement factor and the number size distribution. Measurements were conducted at the GAW Atmospheric Research Station at Mace Head, Ireland. This site is considered representative of the mid-latitude marine troposphere (O’Dowd et al., 2001). We discuss the $f(RH)$ and compare it to other measurements of $f(RH)$ of marine aerosol from Tasmania (Carrico et al., 1998), from the southwest coast of Portugal (Carrico et al., 2000), from the Canary Islands (Gasso et al., 2000), from the Pacific between Hawaii and Japan (Carrico et al., 2003) and the northeast coast of North America (McInnes et al., 1998; Wang et al., 2007). Using measured size distributions and hygroscopic growth factors,
we perform a closure/comparative study using a model based on Mie theory, which calculates the $f(RH)$ at different RH.

5.2 Experimental

5.2.1 Measurement site

The GAW Atmospheric Research Station at Mace Head is an excellent site for studying marine aerosols. It is located at the west coast of Ireland ($53^\circ\,19'\,N,\,9^\circ\,54'\,W$) on a peninsula, which is surrounded by coastline and tidal areas except for a small sector (where there is land mass) ranging from $20^\circ$ to $40^\circ$. The research station is about 70 to 120 m from the shoreline (tide dependent) at 5 m above sea level. Air that arrives at the Mace Head site from the direction between $180^\circ$ and $300^\circ$ is classified as marine or clean air (Jennings et al., 1997).

Most of the instruments are connected via the community air-sampling system of a 10-cm diameter stainless steel pipe, reaching 10 m above ground level, with a flow rate of 150 liter per minute (lpm) to ensure laminar flow. While size fractionation of the aerosol at the sample inlet was not conducted (Kleefeld et al., 2002; Yoon et al., 2007), the whole particle size range was not measured in this work. We estimated the 50% cut-off diameter of the inlet system, using the calculations of the sampling system efficiency of Kleefeld et al. (2002), to be on average about $2\,\mu m$ at a mean wind speed of 13.8 m/s (standard deviation: 6.6 m/s) in January/February 2009.

5.2.2 Instrumentation

Light scattering coefficient under dry conditions and at high RH

Since July 2001 a three-wavelength ($\lambda$=450, 550 and 700 nm) integrating nephelometer (TSI Inc., model 3563) has measured the dry scattering coefficients $\sigma_{sp}$ and dry backscattering coefficients $\sigma_{bsp}$ at Mace Head (O’Connor et al., 2008). The RH in the dry nephelometer was on average $26.7\pm4.5\%$ during our measurement campaign. No drying of the air was needed to achieve this RH, due to the internal heating of the nephelometer to $24.2^\circ C$ (average) and mainly due to the temperature difference between inside and outside the laboratory (campaign average ambient $T=5.95^\circ C$).

We used a humidification system for a second integrating nephelometer to measure the RH dependence of $\sigma_{sp}$ and $\sigma_{bsp}$ at a defined RH in the range of 30-90% RH (described in Fierz-Schmidhauser et al. (2010b)). It consists of a humidifier to raise the RH of the aerosol up to 90% RH, followed by a dryer, which dries the aerosol to the desired RH. This system enables us to measure the hysteresis behavior of deliquescent aerosol particles. The light scattering enhancement factor $f(RH)$ is defined as the ratio of $\sigma_{sp}$ at high and low RH:

$$f(RH) = \frac{\sigma_{sp}(RH)}{\sigma_{sp}(RH = \text{dry})}. \tag{5.1}$$

The light backscattering enhancement factor, $f_b(RH)$, is defined similarly with $\sigma_{bsp}$. There are two different operating conditions for the humidified nephelometer: hydration and dehydration. Hydration is defined when the dryer is turned off and the RH within the instrument is monotonically rising from the humidifier to the entrance of the nephelometer. We define dehydration in a similar manner: at the exit of the humidifier the aerosol particles are exposed to RH>80%. The dryer is then turned on, which results in a monotonic decrease of RH.
in the dryer line. With these two operating conditions it is possible to measure deliquescent aerosol, which can exist in the liquid and solid phases at the same RH, known as hysteresis (Orr Jr. et al., 1958).

The humidified nephelometer measured in parallel with the dry nephelometer of the regular GAW program from 19 January to 15 February 2009. The dry nephelometer measured at a frequency of 5 minutes, whereas the humidified nephelometer detected scattering coefficients every minute. These values were then averaged to 5-min values. In the beginning of the measurement campaign (19 January 15:00 to 21 January 13:00) both nephelometers measured at dry conditions and agreed well with each other, with a slope of 1.054, an intercept of $7.4 \times 10^{-7}$ m$^{-1}$ and a squared correlation coefficient of $R^2=0.97$ (at $\lambda=550$ nm). We corrected $\sigma_{sp}$ of the humidified nephelometer with this linear relationship. During almost 12 days (285 hours) (21 to 26 January and 29 January to 5 February) the humidified nephelometer determined humidity cycles of the scattering enhancement, commonly referred to as humidograms. Measuring one humidogram took two hours. On 26/27 January and from 5 to 15 February the humidified nephelometer measured at 85% RH ($\pm 5\%$ RH). All values between 80% and 90% RH were fitted to 85% with one free parameter $\gamma$, already used in other work on $f(RH)$ (Kotchenruther and Hobbs, 1998; Gasso et al., 2000; Zieger et al., 2010):

$$f(RH) = \left(1 - \frac{RH}{100\%}\right)^{-\gamma}.$$ \hspace{1cm} (5.2)

We fitted $f_b(RH)$ with the same equation using the free parameter $\gamma_b$. We corrected $\sigma_{sp}$ and $\sigma_{bsp}$ for nephelometer non-idealities (angular truncation and non lambertian light source) according to Anderson and Ogren (1998).

The backscatter fraction $b$ is the ratio of $\sigma_{bsp}$ to $\sigma_{sp}$:

$$b = \frac{\sigma_{bsp}}{\sigma_{sp}},$$ \hspace{1cm} (5.3)

and is the percentage of radiation that is scattered back at angles between 90° and 180°. $b$ decreases with increasing particle size. Another intensive property which can be derived from the scattering coefficient is the Ångström exponent $\alpha_s$ of the scattering coefficient:

$$\alpha_s = -\frac{\ln(\sigma_{sp}(\lambda_1)/\sigma_{sp}(\lambda_2))}{\ln(\lambda_1/\lambda_2)}.$$ \hspace{1cm} (5.4)

The Ångström exponent we used is derived from the scattering coefficients at $\lambda_1=450$ and $\lambda_2=700$ nm wavelength.

**Light absorption coefficient**

An AE-16 aethalometer (Magee Scientific, Berkeley, USA) was also operated during this campaign. The instrument features an automatic filter change, and sampling time was kept at 5 minutes. The aethalometer operates on the principle of light attenuation due to absorption by aerosol particles deposited on a pre-fired quartz fiber filter. This instrument is operated with a polychromatic light source (white light). The determination of the absorption coefficient ($\sigma_{ap}$) is a difficult task because of the ill defined spectral sensitivity of the employed instrument. Here, $\sigma_{ap}$ was calculated using the method presented by Weingartner et al. (2003) with the $C$ value (accounting for multiple scattering in the filter) of 3.05 for Mace Head (Collaud Coen et al., 2010). A filter loading dependent correction was not performed.
Absorption coefficients were first calculated for $\lambda=855$ nm, which is the center of the broadband spectral instrumental response. For the calculation of the single scattering albedo, defined as
\[
\omega_0 = \frac{\sigma_{sp}}{\sigma_{sp} + \sigma_{ap}},
\]
the measured absorption coefficients were extrapolated to $\lambda=550$ nm assuming a $\lambda^{-1}$ dependence of the absorption coefficient.

**Particle number size distribution**

The particle number size distribution (size range $20 \text{ nm} < D_p < 500 \text{ nm}$) was determined with a scanning mobility particle sizer (SMPS) which consists of a differential mobility analyzer (DMA) and a condensation particle counter (CPC). The SMPS system at Mace Head uses a Krypton-85 bi-polar charger for the neutralization of aerosols, along with a TSI-Type long DMA in conjunction with a TSI CPC 3010. All aerosol sample flows are dried to 40% or lower. Three sensors monitored the flow in the sample flow, the sheath flow and excess flow. The RH of the sheath flow was also monitored, along with the pressure in the DMA.

In addition, an optical particle counter (OPC, Grimm Dustmonitor 1.108) measured the dry size distribution of the larger particles in the optical diameter range $0.3 \mu m < D_p < 25 \mu m$. In the OPC, the individual particles are classified according to their light scattering intensity, which depends on the particle size, morphology and refractive index. We used the factory calibration of the OPC size bins (polystyrene latex spheres with a refractive index of 1.59 at $\lambda=683$ nm). With the OPC output a coarse mode fraction ($cmf$) is defined as
\[
\text{cmf} = \frac{N_{D_p>1\mu m}}{N_{D_p>0.3\mu m}}.
\]
We only used data from the OPC to calculate the $cmf$, since in this way discrepancies between instruments (SMPS and OPC) did not influence this factor.

The combined SMPS and OPC data were used as input for the Mie calculation, even if they did not exactly match each other (see Fig. 5.2). All data from the OPC were taken, whereas the SMPS data were just used up to $D_p=340$ nm, to avoid the influence of doubly and triply charged particles for larger diameters.

**Hygroscopic growth factor**

The ratio of the wet to the dry diameters is referred to as the particle’s hygroscopic growth factor $g$(RH). The growth factor $g$(RH) was measured with a hygroscopicity tandem differential mobility analyzer (H-TDMA), which is described in a recent review by Swietlicki et al. (2008). The Mace Head H-TDMA follows the recommendations for the design of an H-TDMA by Duplissy et al. (2009). It is composed of two DMAs and a humidifier. The aerosol sample enters the system through a nafion dryer where the RH is lowered to ~5%. Next it passes through a radioactive charger where it obtains a known charge distribution. In the first DMA a narrow distribution of particles with known mobility is selected at a fixed applied voltage. This quasi-monodisperse aerosol sample is then exposed to 90% RH in the humidifier. The humidifier consists of a heated Gore-Tex tube and humidifies the sample and the sheath air for the second DMA. After that, the sample enters the second DMA which together with a CPC acts as a SMPS. Unlike the first DMA, the voltage applied to the second DMA is changing allowing different sizes of particles go through to the CPC where they are counted. From the change in the size the growth factor is calculated using the inversion algorithm by Gysel et al. (2009).
5.2.3 Mie model to calculate \( f(RH) \)

We calculated \( \sigma_{sp} \) at dry and humid conditions and \( f(RH) \) with a model based on Mie theory (Mie, 1908) where the core Mie routine is based on the code of Bohren and Huffman (2004). The particles are assumed to be spherical and homogenously internally mixed. Assuming spherical particles leads to an error of \( \sigma_{sp} \) of less than \( \pm 5\% \) for particles smaller than 1 \( \mu m \) and an underestimation of \( \sigma_{sp} \) of up to 30\% for cubic salt particles larger than 1 \( \mu m \) (Chamaillard et al., 2006). The number size distribution and the complex refractive index \( m \) of the measured aerosol is needed as input. We calculated the complex refractive index using the average chemical composition measurements of other measurement campaigns: For clean marine air we used the mass concentrations of low biological activity (O’Dowd et al., 2004) and January/February values from Yoon et al. (2007). Polluted air in winter consists of about 15\% of organics (O’Dowd et al., 2004), 5\% BC (Jennings et al., 1997) and 80\% of inorganic species. The inorganic chemical composition of non-clean data over a 4-year sampling period (2003 - 2006) shows 71\% of sodium plus chloride ions, 14\% sulfate ions, 10\% nitrate ions and the remaining 5\% ammonium ions (Ceburnis et al., 2010). The refractive index for the two air mass types was then determined by a volume fraction averaging:

\[
m(\lambda) = \sum \frac{m_f_i}{\rho_i} m_i(\lambda),
\]

where \( m_f_i \) is the mass fraction, \( \rho_i \) is the density and \( m_i(\lambda) \) is the wavelength dependent complex refractive index of the compound \( i \). We took the values for \( m_i \) and \( \rho_i \) as listed in Table 5.1. This resulted in a refractive index for clean marine air of \( m_{clean}(\lambda=550 \text{ nm})=1.539+0i \) and \( m_{polluted}(\lambda=550 \text{ nm})=1.529+0.024i \) for polluted air.

Table 5.1: Microphysical properties of selected aerosol compounds used for the model predictions. The imaginary part of the complex refractive index \( m \) was omitted for all components except for black carbon (BC). All values are interpolated to the nephelometer wavelengths.

<table>
<thead>
<tr>
<th>( \lambda )</th>
<th>H(_2)O</th>
<th>Org.</th>
<th>NH(_4)</th>
<th>(NH(_4))(_2)</th>
<th>NH(_4)</th>
<th>H(_2)SO(_4)</th>
<th>NaCl</th>
<th>BC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>450 nm</td>
<td>1.337(^a)</td>
<td>1.559(^c)</td>
<td>1.536(^c)</td>
<td>1.438(^e)</td>
<td>1.560(^g)</td>
<td>1.75+0.46i(^f)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>550 nm</td>
<td>1.333(^a)</td>
<td>1.48(b^j)</td>
<td>1.556(^c)</td>
<td>1.53(^e)</td>
<td>1.473(d^j)</td>
<td>1.434(^e)</td>
<td>1.548(^g)</td>
<td>1.75+0.44i(^f)</td>
</tr>
<tr>
<td>700 nm</td>
<td>1.331(^a)</td>
<td>1.553(^c)</td>
<td>1.524(^c)</td>
<td>1.432(^e)</td>
<td>1.542(^g)</td>
<td>1.75+0.43i(^f)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \rho_i ) (g/cm(^3))</td>
<td>1.0(^k)</td>
<td>1.4(h)</td>
<td>1.72(^k)</td>
<td>1.77(^k)</td>
<td>1.78(^k)</td>
<td>1.83(^k)</td>
<td>2.17(^k)</td>
<td>1.7(^b)</td>
</tr>
</tbody>
</table>

\( ^a \) Hale and Querry (1973); \(^b\) Nessler et al. (2005a); \(^c\) Software from Andrew Lacis (from http://gaci.giss.nasa.gov/data_sets/ last visited on 19 May 2009) based on Toon et al. (1976); Gosse et al. (1997); Tang (1996); Li et al. (2001); \(^d\) Palmer and Williams (1975); \(^e\) Hess et al. (1998); \(^f\) Lide (2008); \(^g\) Alfarra et al. (2006); \(^h\) Dinar et al. (2006); \(^i\) No wavelength dependence assumed.

Hygroscopic growth was accounted for by using the size resolved H-TDMA measurements of diameter growth factors. The H-TDMA growth factor \( g(RH=90\%) \) at a dry diameter \( D_p \) of 165 nm was extrapolated to different RH using Eq.(3) from Gysel et al. (2009), which uses the \( \kappa \)-model introduced by Petters and Kreidenweis (2007). For the wet refractive index a volume weighting between the refractive indices of water and the dry aerosol was chosen (Hale and Querry, 1973).
5.3 Results

5.3.1 Overview

Jennings et al. (2003) classified the air masses arriving at the Mace Head Atmospheric Research Station into two sectors: clean marine when the wind comes from 180° to 300° and polluted when the wind comes from 45° to 135°. We classified the air masses in this study accordingly; the two air mass types are indicated in Fig. 5.1 with different underlying colors. Light blue is for clean marine and light yellow for polluted air masses.

The temporal evolution of a selection of measured and derived aerosol variables is shown in Fig. 5.1. The hourly dry \( \sigma_{sp} \) varied between \( 3.1 \times 10^{-6} \) and \( 1.6 \times 10^{-4} \) m\(^{-1} \) (uncertainties ±10% (Anderson et al., 1996)) within this measurement campaign in January/February 2009 (Fig. 5.1a). The hourly averages of \( \sigma_{ap}(\lambda=550 \text{ nm}) \) varied within this time period between \( 2 \times 10^{-8} \) and \( 1.4 \times 10^{-5} \) m\(^{-1} \) (uncertainties ±30%). This corresponds to equivalent BC (black carbon) mass concentrations (measured at \( \lambda=855 \text{ nm} \)) between 1.8 and 1400 ng m\(^{-3} \) (on average 134 ng m\(^{-3} \)), which is within the range of measurements presented by Jennings et al. (1993). Since intensive aerosol parameters are needed to understand the variability of the light scattering enhancement factor \( f(RH) \) and the hygroscopic growth factor \( g(RH) \), we investigated the dry intensive properties of the following parameters: single scattering albedo \( \omega_0 \), backscatter fraction \( b \), Angström exponent \( \dot{a}_s \) and OPC coarse mode fraction \( cmf \) for the two air mass types. The \( \omega_0 \) (Fig. 5.1b) was high during the entire measurement campaign (mean: 0.95, see Tab. 5.2) with highest values during the beginning of the measured time period until 29 January. Generally the \( \omega_0(\lambda=550 \text{ nm}) \) at Mace Head is very high, with monthly averages between 0.94 and 0.99 in the years 2000 to 2002 (Jennings et al., 2003). During the clean marine air masses observed at the beginning of the campaign the aerosol tended to be dominated by large, primarily scattering aerosol as indicated by high values of \( \omega_0 \) (Fig. 5.1b) and low values of \( b \) (Fig. 5.1d) and \( \dot{a}_s \) (Fig. 5.1e). \( b \) and \( \dot{a}_s \) yield information on the dominant particle sizes contributing to the scattering signal. Low values of \( b \) and \( \dot{a}_s \) correspond to large aerosol particles. A value of \( \dot{a}_s \) of less than about 0.5 indicates the presence of coarse mode sea-salt aerosols (Smirnov et al., 2002), since coarse mode dust particles can be ruled out because the air masses did not originate from dust sources within 7 days before arrival at Mace Head. This contribution of coarse mode aerosol particles in the beginning of the measurement campaign is also consistent with the relatively high coarse mode fraction from the OPC in Fig. 5.1e. Table 5.2 lists averages of all intensive properties for the whole measurement campaign and for the two air mass types.

Table 5.2: Means and standard deviations of the single scattering albedo, backscatter fraction, Angström exponent, and OPC coarse mode fraction, for dry conditions. The light scattering enhancement factor and the hygroscopic growth factor are also shown.

<table>
<thead>
<tr>
<th></th>
<th>campaign mean</th>
<th>clean marine</th>
<th>polluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega_0 )</td>
<td>0.95±0.05</td>
<td>0.99±0.01</td>
<td>0.89±0.04</td>
</tr>
<tr>
<td>( b )</td>
<td>0.108±0.012</td>
<td>0.101±0.005</td>
<td>0.121±0.017</td>
</tr>
<tr>
<td>( \dot{a}_s )</td>
<td>0.413±0.648</td>
<td>0.014±0.083</td>
<td>1.431±0.503</td>
</tr>
<tr>
<td>( cmf )</td>
<td>0.061±0.029</td>
<td>0.078±0.012</td>
<td>0.017±0.016</td>
</tr>
<tr>
<td>( f(RH=85%) )</td>
<td>2.10±0.25</td>
<td>2.22±0.17</td>
<td>1.77±0.31</td>
</tr>
<tr>
<td>( g(RH=90%, D_p=165 \text{ nm}) )</td>
<td>1.64±0.26</td>
<td>1.84±0.14</td>
<td>1.36±0.15</td>
</tr>
</tbody>
</table>

All intensive properties are significantly different for the two air mass types. When the \( \omega_0 \) and the \( cmf \) are high and the \( b \) and \( \dot{a}_s \) are low, we observe a high \( f(RH) \) and \( g(RH) \)
Figure 5.1: Temporal evolution of the dry scattering and absorption coefficients (a), the dry single scattering albedo (b), the hygroscopic growth factor $g(RH)$ at 90% RH with a dry diameter of 165 nm and the light scattering enhancement factor at 85% RH (c), the dry backscatter fraction (d), the dry Ångström exponent and the OPC coarse mode fraction (e) and the clean marine or polluted wind sector according to Jennings et al. (2003) (f). Underlying colors represent clean marine (light blue) and polluted (light yellow) air masses. $\sigma_{sp}$, $\sigma_{ap}$, $\omega_0$, $f(RH)$ and $b$ are shown at 550 nm wavelength.
5.3 Results

(clean marine air masses), most probably due to more hygroscopic aerosol particles (sea salt and other inorganic species). Low $\omega_0$ and $cmf$, $f(RH)$ and $g(RH)$ plus high $b$ and $\hat{a}_s$ correspond to polluted air masses, indicating a higher fraction of light absorbing aerosol with lower hygroscopicity. $b$, $\hat{a}_s$ and $cmf$ are all linked to the aerosol size distribution and give some indication about the mean particle size in the two air mass types. For a closer investigation we calculated the mean number size distribution and mean surface area size distribution for the two air mass types (Fig. 5.2). The discontinuity in the combined number size distribution is likely to result from the difference of the refractive index (and complex morphology) between the ambient particles and the particles that were used to calibrate the OPC, and not due to RH differences between the SMPS and the OPC, which experienced a similar operational range of RH conditions. Similar deviations were also noted in other studies [Hand and Kreidenweis, 2002; Heim et al., 2008].

![Figure 5.2: Mean dry number size distribution (top) and surface area size distribution (bottom) of the clean marine and polluted air masses, originating from the measurements of the SMPS and OPC.](image)

Below $D_p=500$ nm about five times more particles are present in polluted air masses compared to clean marine air masses. In contrast, for particle diameters above 500 nm the particle surface area of the clean marine air masses is more pronounced than the one of the polluted air mass types. This is consistent with the results of $b$, $cmf$ and $\hat{a}_s$ described above.

5.3.2 Measurements at varying relative humidity

The intensive properties $b$, $\hat{a}_s$ and $\omega_0$ change with RH. Since the atmosphere is not generally dry, these values at humid conditions are of higher climate relevance than the dry values (the average ambient RH was 85.3% during the campaign). Therefore we calculated the mean of $b$, $\hat{a}_s$ and $\omega_0$ at 85% RH for the whole measurement campaign and for the clean marine and polluted air masses (see Tab. 5.3). The $\omega_0$ at 85% RH was determined from the dry $\sigma_{sp}$ values and $f(RH=85\%)$ as described above and from the dry measured $\sigma_{ap}$ values assuming that the absorption does not change with RH. This simplification is plausible since even though the humidity effect on absorption can be substantial, its maximum contribution to the humidity effect on the single scattering albedo is only 0.2% for aged aerosol within the wavelength
Table 5.3: Means and standard deviations of the intensive properties at 85% RH (single scattering albedo, backscatter fraction, Ångström exponent) from measured values in January/February 2009 at Mace Head. $\omega_0$ and $b$ are at $\lambda=550$ nm.

<table>
<thead>
<tr>
<th></th>
<th>campaign mean</th>
<th>clean marine</th>
<th>polluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_0$(RH=85%)</td>
<td>0.97±0.03</td>
<td>0.99±0.02</td>
<td>0.93±0.04</td>
</tr>
<tr>
<td>$b$(RH=85%)</td>
<td>0.086±0.010</td>
<td>0.082±0.005</td>
<td>0.098±0.016</td>
</tr>
<tr>
<td>$a_\alpha$(RH=85%)</td>
<td>0.162±0.465</td>
<td>-0.037±0.118</td>
<td>0.931±0.626</td>
</tr>
</tbody>
</table>

range from 450 to 700 nm (Nessler et al., 2005b). The $\omega_0$ increases from between 0.89 and 0.99 under dry conditions to very high values of between 0.93 and 0.99 for RH=85%.

$b$ at RH=85% was determined from $\sigma_{sp}$ and $\sigma_{bsp}$ values at RH between 80 and 90% recalculated to RH=85% using Eq. 5.2. By taking up water, aerosol particles grow and therefore $b$ decreases. We observed a decrease of about 20% for the campaign mean value of $b$ from dry conditions to RH=85%, which results in a backscatter fraction which is smaller than 10% for both clean marine and polluted air masses.

For calculating the Ångström exponent of the scattering coefficient at 85% RH, we used Eq. 5.4 with $\sigma_{sp}$(RH=85%). From all investigated parameters, the $a_\alpha$ changed most with increasing RH, its values decreased by 35-60% compared to those under dry conditions.

We measured humidograms from 21 January to 5 February (with a break between 26 and 29 January). The total of 141 humidograms, each lasting for 2 hours, were allocated to the two clean marine and polluted air masses. We linearly interpolated the dry scattering coefficients to 1-min values and calculated the $f$(RH), then grouped the $f$(RH) of each sector into 5-% RH-bins and calculated the mean $f$(RH) of each RH bin for hydration and dehydration. Since the RH at Mace Head is very high (RH>80% for 71% of the time of the campaign) the values of the hydration measurement are much less important than the values of the dehydration curve. Nevertheless we report both curves, so that measurements from humidified nephelometers that are only capable of measuring hydration could be compared. Figure 5.3 presents all these values including standard deviations of $f$(RH) as y-axis error bars. The x-axis error bars represent the mean change of RH per time interval in the corresponding RH bin. These bars are much larger between 65 and 75% RH for dehydration than for all other RH bins, because of instrumental reasons: when the dryer is on, the RH in the nephelometer changes relatively fast.

In general the humidograms of polluted air show no deliquescence, with $f$(RH) smoothly increasing with RH to a maximum of 1.8 at 85% RH. The $f$(RH) already starts to be slightly enhanced at RH=35% and monotonically rises with RH. In contrast, the aerosol particles of the clean marine air masses do not start to grow until 50% RH in the nephelometer. The humidograms for the clean marine air clearly indicate hysteresis behavior of the aerosol and for certain single humidograms also show a sharp deliquescence, which is however not visible in the mean humidogram presented in Fig. 5.3 as deliquescence occurred at slightly varying RH. We assume that the main components of clean marine aerosol are inorganic salts (like NaCl), which show deliquescence behavior. In the polluted air masses, components with no distinct phase transition like organics are assumed to be the main components. Note that the phase transition appears at the RH in the nephelometer, which is lower than the deliquescence relative humidity, because the highest RH in the system is encountered upstream of the nephelometer (Fierz-Schmidhauser et al., 2010b).

The maximum $f$(RH) at 85% RH is 2.3 for marine air masses. Comparing this result to different studies of marine air masses, our $f$(RH) is in the range of the results of McInnes.
5.3 Results

Figure 5.3: Averaged humidograms for clean marine (top) and polluted air masses (bottom) showing $f(RH)$ vs. RH in the nephelometer under hydrating and dehydrating conditions.

et al. (1998) ($f(RH=85%)=2.7$) and Carrico et al. (1998) ($f(RH=82%)=1.98$). McInnes et al. (1998) also measured anthropogenically influenced $f(RH)$ at 85% RH of 1.7, which compares very well to our measurement of 1.8. The marine aerosol shows a clear hysteresis behavior with $f(RH=55%)$ of 1.66 for the upper branch and 1.23 for the lower branch. This hysteresis behavior is much smaller for polluted aerosol ($f(RH=55%)=1.30$ and 1.19). For conditions with a generally high ambient RH, the values of the upper branch should be used. Efflorescence could not be measured, since we were not able to dry the aerosol to below 50% RH after the humidification to 85% (see above).

It is interesting to note that the $f(RH)$ at Mace Head is much lower than the values reported for laboratory measurements of monodisperse pure sodium chloride (NaCl) particles in the size range of 100 to 300 nm, where the $f(RH)$ at 80% ranged from 15 to 5.5 (Fierz-Schmidhauser et al., 2010b). The reasons for this discrepancy are firstly that in this study the surface area size distribution is dominated by particles that are larger than 300 nm (see Fig. 5.2) and $f(RH)$ decreases with increasing particle size. A second reason for the discrepancy is that the Mace Head aerosol does not consist of pure NaCl. O’Dowd et al. (2004) found that in winter 75% of the mass fraction of the accumulation mode aerosol at Mace Head is sea salt, 10% non-sea salt sulfate and 15% organic compounds.

5.3.3 Model calculation of the scattering coefficients and $f(RH)$

With our model based on Mie theory we calculated $\sigma_{sp}(dry)$ and $\sigma_{sp}(RH)$, which depend on the aerosol size distribution, the chemical composition of the aerosol and the RH in the nephelometer. The chemical composition determines the refractive index and the hygroscopic
growth factor $g(\text{RH})$. We calculated a refractive index for clean marine and polluted air as described in Sect. \ref{s:5.2.3}. Using one fixed dry refractive index per air mass type is not a critical issue, since the refractive index at high RH will be dominated by the one of water. $g(\text{RH})$ was measured by the H-TDMA at 90% RH and $D_p=165$ nm.

For Fig. \ref{fig:5.4} we only used measured $f(\text{RH})$ data points, when at the same time size distribution and H-TDMA data was available and so $f(\text{RH})$ could be calculated. Since there were either missing OPC or SMPS data for appreciable time fractions, we could not calculate the scattering coefficients and $f(\text{RH})$ for 62% of the time when the air masses were polluted (69 h out of total 111 h), therefore the humidograms of Fig. \ref{fig:5.3} and \ref{fig:5.4} do not exactly look alike. The grey and white circles in Fig. \ref{fig:5.4} represent the average of these data points for hydration and dehydration, respectively. The mean calculated $f(\text{RH})$ vs. RH are shown in blue for clean marine air masses and in orange for polluted air masses.

The calculated $f(\text{RH})$ at low RH (30-45%) is much higher than the measured (especially for clean marine air) since the model assumes that particles are hydrated over the full RH range, which is not the case for a deliquescent aerosol like pure NaCl or sea salt or the aerosol we measured in clean marine air. At RH when the measured aerosol shows hysteresis behavior (55%<RH<75%) the calculated $f(\text{RH})$ lies between the values for hydration and dehydration $f(\text{RH})$. For both clean marine and polluted air masses at RH>80% the model either overestimates $f(\text{RH})$ or the humidified nephelometer measures too low values. Below 75% RH the calculated $f(\text{RH})$ humidogram of polluted air masses is consistent with the measured humidogram. A hypothesis for the discrepancy between model and measurement at high RH is losses of largely growing super-$\mu$m sea salt particles in and after the humidification system. We calculated particle losses in the humidification system with the program described by von der Weiden et al. (2009) and found that we have less than 10% losses for particles smaller than 5 $\mu$m and about 33% losses for particles with a diameter of 10 $\mu$m (for a flow of 10 lpm).

Figure \ref{fig:5.5a} shows that the model calculated the $\sigma_{sp}(\text{dry})$ very well, with a slope of 0.99 and a squared correlation coefficient $R^2=0.9$. This supports our choice of the refractive index in the model assumption of the dry aerosol. We did the same calculation for refractive indices of either pure NaCl or pure organics; the resulting slopes ranged from 0.98 to 1.06. The calculation of $\sigma_{sp}(\text{RH})$ is also quite good (Fig. \ref{fig:5.5b}); the difference between measured and calculated $\sigma_{sp}(\text{RH})$ is within about 10%. As a consequence the calculated ratio of $\sigma_{sp}(\text{RH})$ and $\sigma_{sp}(\text{dry})$, the $f(\text{RH})$, correlates quite well with the measured $f(\text{RH})$ (Fig. \ref{fig:5.5c}). Figure \ref{fig:5.5d} shows the same as Fig. \ref{fig:5.5c} but separated into clean marine (blue) and polluted (orange) air.
masses. The calculated $f(RH)$ of clean marine air masses is higher than that of polluted air. In the scatter plot of $f(RH)$ measured vs. $f(RH)$ calculated of clean air masses (Fig. 5.5e) it is also possible to see how the $f(RH)$ is overestimated by the model both at low and high RH. For polluted air masses, we also observe higher values of the calculated $f(RH)$ at low RH but not so much at high RH.

![Figure 5.5: Measured vs. calculated $\sigma_{sp}(dry)$ (a), $\sigma_{sp}(RH)$ (b), $f(RH)$ (c), $f(RH)$ split into clean marine and polluted air masses (d), $f(RH)$ from clean marine air masses (e) and $f(RH)$ from polluted air masses (f). The color code denotes the RH in the humidified nephelometer. Only times where measurements of SMPS, OPC, H-TDMA were available are shown here.](image)

This very good agreement between measurement and calculation of $\sigma_{sp}(dry)$ (Fig. 5.5a) shows that the calculation using the refractive indices of the mean chemical composition of the two air mass types works well even if the size distributions of OPC and SMPS do not agree perfectly. From the good agreement between the measured and calculated $\sigma_{sp}(RH)$ we further conclude that the $g(RH)$ value from the H-TDMA is a good input parameter for the model even if this is a mean $g(RH)$ value (aerosol mixing state is not taken into account) and
Chapter 5 Light scattering enhancement factors in the marine boundary layer

representing particles at only one diameter (165 nm).

We investigated the model sensitivity of \( f(RH) \) on the input parameters hygroscopic growth factor, refractive index, particle number concentration and particle diameter. The model predictions were repeated by keeping all but one of these parameters constant. We used the mean size distribution for both air mass types and added extra supporting points for the OPC size range by fitting a 3-log normal size distribution function to the measured distribution, in order to reduce uncertainties caused by the low resolution of the OPC. For both air mass types we varied the input parameters from -20% to +20% of their mean values and show the resulting error of \( f(RH) \) on Fig. 5.6. The \( f(RH) \) is most sensitive to variations of the hygroscopic growth factor and the refractive index, whereas a comparable percentage of variation in the particle diameter has very little influence on the \( f(RH) \). However, variations in \( g(RH) \) and \( m \) of ±20% are much less likely than variations of ±20% in the particle diameter.

![Figure 5.6: Sensitivity of \( f(RH) \) to variations of the model input parameters: hygroscopic growth factor, number concentration, particle diameter and refractive index, shown as the relative error in \( f(RH) \) vs. percent variation from the mean value for clean (a) and polluted (b) air masses.](image)

### 5.4 Summary and conclusions

With two nephelometers (one operated under dry conditions and one at changing RH) light scattering enhancement factors \( f(RH) \) and other aerosol optical properties were determined at the Mace Head atmospheric research station. Additional instruments provided data on the aerosol light absorption, number size distribution \( (D_p=20 \text{ nm} - 25 \mu \text{m}) \) and hygroscopic properties. From these aerosol measurements we derived the intensive properties \( b, a_s, \) and \( \omega_0 \) for dry and elevated RH conditions.

We analyzed the data for two distinct air mass types, i.e., polluted and clean marine. The \( f(RH=85\%) \) at \( \lambda=550 \text{ nm} \) was on average 1.77 for polluted air and 2.22 for clean marine air, both for winter conditions. The latter values compare well with other measurements in clean marine air \([Carrico et al., 2000, 2003]\). However, the \( f(RH=85\%) \) of marine aerosol is lower than for example the free tropospheric aerosol \([Fierz-Schmidhauser et al., 2010a]\) or the Arctic aerosol \([Zieger et al., 2010]\). This finding can be explained by the influence of relatively large sea salt particles with a relatively high organic mass fraction of about 15% at Mace Head in winter \([O’Dowd et al., 2004]\).

No distinct hysteresis behavior was observed for the polluted aerosol but a distinct hysteresis was encountered during clean marine conditions: Here the \( f(RH=55\%) \) values for
dehydration are on average 35% higher than for hydration. This shows that the hydration state of the marine aerosol needs to be correctly measured and properly included in climate models.

The dry $\omega_0$ (at $\lambda=550$ nm) at Mace Head is high with an average value of 0.99 for clean marine and 0.89 for polluted conditions. At 85% RH the $\omega_0$ increases on average to 0.99 (clean marine) and 0.93 (polluted), as compared to dry conditions (RH<40%). The mean $b$ varied between 0.101 and 0.121 (clean and polluted) and decreased by about 20% at RH=85% compared to RH<40%.

Measured scattering coefficients $\sigma_{sp}(\text{dry})$, $\sigma_{sp}(\text{RH})$ and $f(\text{RH})$ were compared to calculations obtained from a Mie-model using measured time resolved size distributions, hygroscopicity, and a fixed aerosol refractive index for each air mass type as input. The model calculated $\sigma_{sp}(\text{dry})$ very well (slope=0.99, $R^2=0.9$) and $f(\text{RH})$ quite well (0.91, 0.77). For clean marine air masses, the model overestimated the $f(\text{RH})$ at low and moderate RH (30-55%) since it does not account for deliquescence and hysteresis effects and assumes that the aerosol particles are only present in the liquid state. The good results of this closure study demonstrate that measurements with a humidified nephelometer can provide light scattering enhancement factors ($f(\text{RH})$) similar to those retrieved from combined size distribution and $g(\text{RH})$ measurements. The advantage of using the humidified nephelometer in the field is that it is a relatively simple and stable system which does not need a lot of maintenance in operation.

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References


5.4 Summary and conclusions


6 Outlook

The goal of this work was to gain information about the enhancement of aerosol light scattering due to water uptake at different locations. This knowledge will then support climate models to better predict direct influence of aerosols on climate. Remote sensing instruments like e.g. the MAX-DOAS (multi-axis differential optical absorption spectroscopy) or lidar (light detection and ranging) can compare their altitude dependent extinction coefficients with this sensing method. As shown in Chapters 4 and 5 and will be shown by Zieger et al. (2010), achieving this goal can be done by two different approaches (at least for remote sites). Either light scattering enhancement factors \( f(RH) \) are directly measured, or data from other instruments are taken to calculate light scattering enhancement factors. In my opinion in the future all dry scattering coefficient data should be accompanied by scattering coefficient data at ambient or high RH, received either from measurements or from calculation by a model, which fits for the local conditions.

To measure light scattering enhancement factors with the techniques that are available today, one needs a nephelometer measuring at dry conditions and a second nephelometer that varies the RH. Size distribution measurements and measurements of either the chemical composition or the hygroscopic growth factor are at least necessary to derive the dry scattering coefficients \( \sigma_{sp}(\text{dry}) \) and the light scattering enhancement factor by a model. Direct measurements of \( f(RH) \) are for certain more accurate, but the input data for the model calculation can be used otherwise (e.g. size distribution, chemical composition, hygroscopic growth factor). A model deepens the understanding of the involved processes and highlights the sensitivity of the input parameters.

Measurements of dry light scattering and absorption coefficients \( \sigma_{np} \) and size distribution (at least for particle sizes smaller than 1 \( \mu \)m) are standard measurements at many sites. In contrast, there are not many sites with continuous H-TDMA (hygroscopicity tandem differential mobility analyzer) measurements (H-TDMAs running for one year were introduced at about 10 stations in Europe within the European Commission project EUSAAR) and even less or none with continuous AMS (aerosol mass spectrometer) measurements. A few humidified nephelometers are currently used for monitoring activities at the US National Oceanic
and Atmospheric Administration (NOAA). So it is mainly the question which of the two instruments, H-TDMA or humidified nephelometer, if not both, is more useful to be employed. Both measurement techniques and results have advantages and disadvantages:

- For investigation of the direct aerosol effect the humidified nephelometer directly provides the measurement of interest. To receive scattering coefficients from H-TDMA data, size distribution data, calculations and assumptions are necessary.
- The humidified nephelometer yields information about the direction of the scattering (forward, backward), which cannot be retrieved with the H-TDMA.
- The humidified nephelometer measures in the optically relevant size range \((D_p>100\text{ nm})\) and is therefore more representative for optical studies, whereas most H-TDMAs would need to have another set-up to be able to measure particles above \(D_p\text{(dry)}=300\text{ nm}\).
- The H-TDMA measures the hygroscopic growth factor for different particles sizes and therefore gives detailed information about size dependent hygroscopic properties. The humidified nephelometer measures the whole particle size range, and specific size information needs a cyclone or an impactor before the instrument. A cyclone and an impactor determine maximal 3 size classes (e.g. PM1, PM10, TSP).
- No information about the mixing state of hygroscopic aerosols is given by the humidified nephelometer, whereas with the H-TDMA externally mixed aerosol and growth factors of individual particle classes can be detected.
- Less maintenance is necessary for the humidified nephelometer and data analysis is easier and less time consuming.
- H-TDMA measurements can also contribute to further investigate the indirect aerosol effects by predicting CCN number concentrations (additionally using size distribution data).
- Both instruments are rather expensive and large.

To conclude, both instruments have their advantages and the user needs to know which qualities are important to him.

The calculation of \(f(RH)\) from other data requires additional measurements, which pose their own difficulties: First, there are discontinuities of the size distribution data in the transition between SMPS and OPC measurements, creating the question which data should be trusted and how the other data should be adapted. Second, measurements of the chemical composition are highly labor intensive. Measurements with AMS need special care during operation, but are highly time resolved. Filter sampling can be easily done automatically, but with low time resolution and later time consuming analysis. For many institutions it is impossible to have two nephelometers because these instruments are expensive.

To be successful amongst all the different aerosol measurement techniques, which are used to study aerosol properties, the humidified nephelometer must, in my opinion, be able to measure dry and humid scattering coefficients with only one nephelometer. A humidifying box with a bypass should be constructed, which switches between dry and changing RH conditions alternatingly at a frequency of about 5-10 minutes. However, it seems that a construction of such an ideal humidified nephelometer is not so trivial, otherwise our partners in the project EUSAAR would have done that.

So far the analysis of measured data from our humidified nephelometer only covered aerosol from remote areas and only from relatively short time periods (1-3 months). As a contrast it will be very interesting to investigate how the light scattering enhancement factor...
behaved at the rural polluted continental site Melpitz (measurements performed in February/March 2009) and at the site Cabauw (measurements performed from June to October 2009), where the air masses can vary from clean maritime to continental polluted. With addition of an urban site the extremes of possible air masses would be covered. Further it will be interesting if a closure at such sites will be possible. This could be more difficult, since the mixing state of the particles is more variable, and the size distribution and chemical composition will probably change faster such that the variability of $f(RH)$ will be larger.

A future project with a humidified nephelometer could also be a long-term measurement covering different seasons to perform a climatological study. It would need to be at a site where large differences in air types are expected throughout a year. In my opinion the Jungfraujoch would probably not be very well suited for such a project, since the aerosol there is aged, therefore the variability of $f(RH)$ is not expected to be too large, with the exception of Saharan dust events.

Beside a further development of the humidified nephelometer to a future dual-purpose (low and high RH) nephelometer, there are small improvements of the existing instruments which could and should be done:

- A longer dryer enables to measure the dehydration branch of the hysteresis curve to lower RH
- Dry and humid scattering coefficients are combined in the software (or a second Labview program) and the user is able to directly observe the light scattering enhancement factor. Many problems that can occur by using two different instruments could be noticed and solved before a long measurement campaign

To complete the ambient measurements of aerosol properties that are important for the direct aerosol effect, the aerosol light absorption coefficient would also need to be measured at changing or high RH. However, it is not expected that the influence of water uptake strongly influences the absorption coefficient (Nessler et al., 2005), which also results in a small influence on the single scattering albedo. Nevertheless the hypothesis that the RH does not strongly influence the absorption coefficient should be proven. The difficulties of measuring the absorption at high RH relate to the fact, that most instruments that are able to measure $\sigma_{ap}$ at low concentrations ($<10^{-5}$ m$^{-1}$) are filter based. When the aerosol is humid, the filter properties change as well, resulting in a combined RH effect on filter and aerosol. New photoacoustic instruments with lower detection limit are currently developed or new on the market, which would make measurements of RH dependent $\sigma_{ap}$ realizable.

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Rahel Andrea Fierz, born on May 24, 1980 in Kilchberg, Switzerland

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