

# Reply to reviewer: “Effects of relative humidity on aerosol light scattering: results from different European sites” by P. Zieger et al.

## Anonymous Referee #1:

We like to thank Referee # 1 for his or her very detailed review and constructive comments, which helped to improve the quality of the manuscript.

### General comments:

The manuscript is fairly clear though figure 3 and related discussion. After that a lot more detail will be needed to describe the methods use to model and estimate ‘closure’. Much of the latter half of the manuscript is difficult to read and interpret.

[Reply:](#) We have substantially improved the manuscript, by removing unnecessary figures (which were replaced by a table), by adding the missing information and references, by adding two tables, and by adding one figure on the working principle of the main instrument. We have also slightly changed the structure of the paper. A general error analysis using Monte Carlo simulation has been added to the appendix of the manuscript. In general, we still would like to keep the paper short and precise, without too much excessive explanation and annotation, as reviewer # 2 gratefully acknowledged.

Visually there is very little to be gained from figures 7 and 8 even when magnifying them by 300%. A table quantifying the main effects of dust and coarse mode seasalt as described in the text would be adequate.

[Reply:](#) We agree and have removed Fig. 7 and 8 from the revised manuscript. Both figures were replaced by a table. However, both figures can still be found in the supplement on the internet, where they are shown in a landscape format with a better resolution. As suggested, the table focuses on the main effects of the coarse mode (sea salt or dust), the size effect of the fine mode, as well as the fine mode hygroscopicity (see comment below).

A definition of closure and a means of quantifying the closure for each of the modeling parameterizations and locations is needed. Without a definition of closure and inclusion of and propagation of the uncertainties in the parameters that are compared achievement of closure” is a hollow claim.

[Reply:](#) We agree and have improved the definition of closure and have added an error propagation analysis for the closure studies using Monte Carlo simulations. This exercise also shows that most systematic errors cancel out for  $f(\text{RH})$  and that the overall (relative) error of  $f(\text{RH})$  is clearly below 25% for  $\text{RH} < 85\%$ . We have also quantified the agreement between measurement and model (for each site) within the text and by a table in the supplement. See comments and changes below.

The Köhler kappa parameter is often invoked. It is not always clear how that kappa value was determined.

[Reply:](#) This has been changed and improved (see specific comments below).

The OPAC parameters were determined to be inadequate for many atmospheric aerosol types and recent literature values were recommended. A table of the original OPAC values and component types should be compared to values of recent literature values as mentioned but not cited or presented quantitatively in text. This would be of value to the community to adopt or further revise.

[Reply:](#) We have added a table on the original and revised OPAC values and have added further information within the OPAC discussion section (see specific comments below).

I recommend that the manuscript be shortened to cover the observations and analysis thereof or that a major revision of the second half be made to include more detailed explanations of the methods and results and conclusions.

### Specific comments:

Abstract line 2 “...to 3.41 for Arctic aerosol.” Strictly, ‘to 3.41 for Arctic marine aerosol.’

[Reply:](#) This is a mean value for periods without sea salt influence that was observed in the Arctic summer (24h of Sun light) at the Zeppelin station (475 m a.s.l.) when predominantly secondary particles were observed, so the word ‘marine’ will not be added here. Table 2 lists the value for Arctic marine aerosol ( $f(\text{RH}=85\%, 550\text{nm})=2.86$ ).

P 8943, line 15 This period was characterized by very low particle concentrations and distinct sea salt transports transport to the station

[Reply:](#) It is not 100% clear, what the reviewer proposes here. Maybe it is the wording “transports”. We slightly changed the sentence to:

“... and distinct sea salt transport events reaching the station which is located an altitude of 475m a.s.l.”

P 8994 line 14 Henne et al. (2010) categorized the CAB site as agglomeration... This last word doesn’t make sense. Simplify to: Henne et al. (2010) characterized the CAB site as one impacted by large and varied pollution burdens from multiple sources.

[Reply:](#) We agree and have changed the sentence (after contacting Stephan Henne again) to:

“Henne et al. (2010) characterized the CAB site as one impacted by relatively large pollution burdens that may strongly depend on wind direction.”

P 8945 line 5 ....in the humidogram humidograph mode. In the latter one mode .... Humidograph is the proper term for the instrument. Humidogram is the record or graph made by the humidograph. I know this syntax is counterintuitive but there it is. Revise here and throughout the manuscript.

[Reply:](#) We agree and have changed “humidogram mode” to “humidograph mode” within the manuscript.

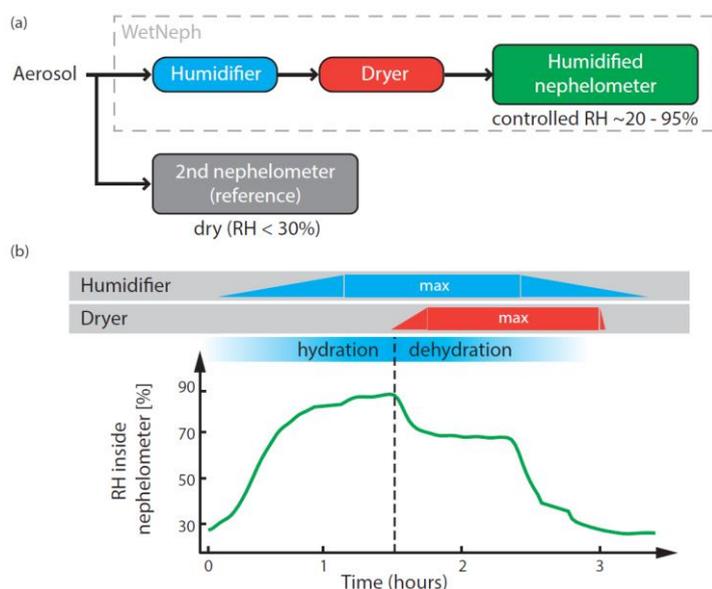
Section 3.1 A block diagram of the humidograph system and an example of the RH time profile through the instrument would be valuable here.

[Reply:](#) A detailed characterization of the humidograph mode is given in our technical paper (Fierz-Schmidhauser et al., 2010), however, we have added a simplified diagram to illustrate the working principle of the WetNeph and have added the sentence in Sect 3.1.:

“A schematic diagram showing the WetNeph set-up is shown in Fig 1a.”

and

“The humidograph mode and the time line of the RH inside the humidified nephelometer is shown schematically in Fig. 1b.”



**New Fig. 1.** (a) Block diagram of the WetNeph set-up consisting of a humidifier, a dryer and a modified nephelometer. A second nephelometer was always operated in parallel as a reference instrument. (b) Schematic time profile of the relative humidity inside the humidified nephelometer. The performance of the humidifier and dryer is shown schematically above the diagram. More technical details can be found in Fierz-Schmidhauser et al. (2010a).

Line 22 Delete “e.g.”, not needed.

[Reply:](#) Done.

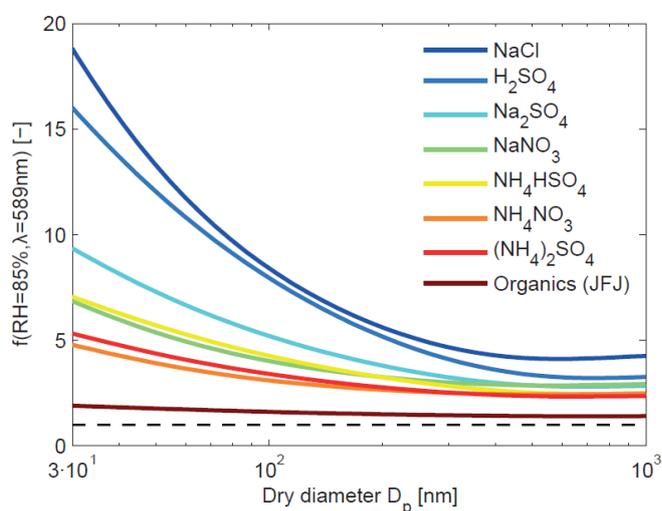
P 8948 line 2 droplet converges to the one that of water.

[Reply:](#) We agree and have changed the sentence to:

“...the refractive index of the aerosol droplet approaches that of water.”

P 8948 paragraph 2 The model  $f(\text{RH})$  results presented in Fig. 1 and described here are of value to the extent they have been used in calibration (QA tests) of the humidograph though that is mentioned only peripherally and has been published already and adequately referenced. The data does not represent the atmospheric  $f(\text{RH})$  data presented in figure 3 or table 1 except in the diameter range 100 to 1000 nm. The plot and discussion should be limited to that range. Your points about chemistry vs. size in the text can still be made without unrepresentative, misleading, high  $f(\text{RH})$  values.

[Reply:](#) It is true that a 10-nm particle is optically not relevant. However, in Fig. 1 the dry particle diameter is shown on a logarithmic axis. As an example, a 40-nm particle (dry diameter) with a hygroscopic growth factor of  $g(85\%) = 2$  will grow to a particle with a wet diameter of  $D=80$  nm and with this being in the optical relevant range. At Spitsbergen, we have measured these small particles at dry mobility diameters of around 30-40 nm (see Zieger et al., 2010). To remove the possible misleading high values for particles below 30 nm, we have changed the x-axis scale starting from 30 nm to 1000 nm. In addition, we have changed the color code of the lines for the most hygroscopic substances (blue) to the less hygroscopic ones (red).



**Modified Fig. 2.** The scattering enhancement  $f(\text{RH})$  at  $\text{RH}=85\%$  and  $\lambda=589$  nm vs. dry particle diameter calculated for different inorganic salts (see legend) and for organics (typically found at the Jungfraujoch, JFJ). A monomodal size distribution is assumed ( $\sigma = 1.8$ ). The hygroscopic growth factors were taken from Topping et al. (2005); Sjogren et al. (2008) and the refractive indices from Seinfeld and Pandis (2006) and Nessler et al. (2005a).

P 8949 line 22 The inverse calculation needs explanation or a reference.

[Reply:](#) Yes, we have added:

“... (see Zieger et al, 2010, for more details).”

line 24 “At MHD, all relevant aerosol measurements except of for chemical measurements ...”

[Reply:](#) Changed accordingly (“... for chemical measurements ...”).

P 8950 line 15 Figures refer to this as SDE. Saharan Dust Events? Mention this acronym here and in figure legends or captions.

[Reply:](#) Yes, we have added in that specific line:

“These air masses transported mineral dust particles up to JFJ which is often also called a Saharan dust event (SDE).”

line 23 “... behavior as one would expect from relatively pure inorganic salts like NaCl.”

[Reply:](#) Changed accordingly.

P 8951 several places. I understand how hysteresis could be measured with the humidograph system as described. I fail to see clear evidence of hysteresis in the data, e.g., Figure 4 where it is mentioned. Clear evidence would be the difference between a humidogram of increasing RH from  $RH < \text{efflorescence}$  and a humidogram of decreasing RH from  $RH > \text{deliquescence}$ .

**Reply:** Figure 4 was meant to display the variety in the measured humidograms. Indeed, the hysteresis is hard to identify, so we have modified Fig. 4 (Fig. 5 in the revised manuscript) and show the example humidograms now in three subpanels. The humidograms are also sorted into maritime, continental/background and pollution influenced. The hysteresis is now seen in the upper panel in a separation of certain curves (e.g. Mace Head) or in a steeper increase at  $RH \sim 70\%$  (Ny-Ålesund). It should be mentioned that the WetNeph can observe the deliquescence of the aerosol (increasing RH), but fails to measure the efflorescence RH (dehydration) due to the limitation of the dryer, which usually was only operated until 50% RH (depending on the temperature condition / instrument settings at the site). We have added a sentence on this fact in the instrumental section.

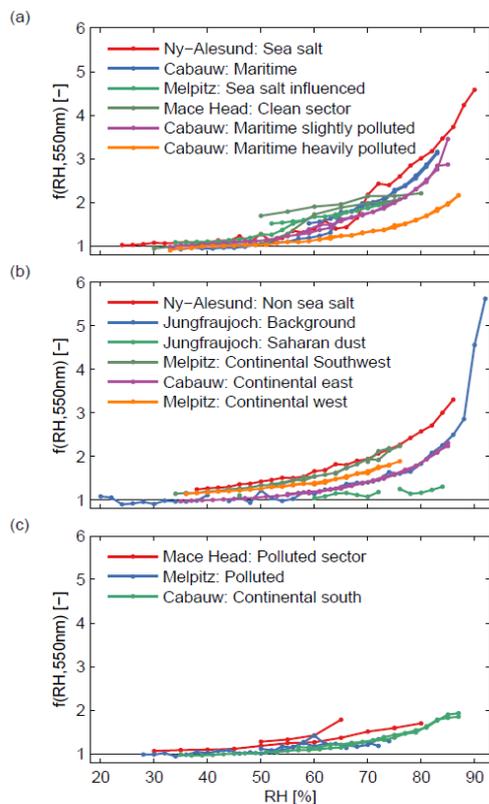
First paragraph of Sect. 3.1:

“It should be mentioned that the deliquescence RH observed in the humidograms is not identical with the thermodynamically deliquescence RH, because the particles have experienced the highest RH within the humidifier, while the RH slightly decreases until the light scattering is measured within the nephelometer. The efflorescence (during the dehydration mode) cannot be observed with the WetNeph due to the limitations of the dryer, which was usually only operated at a minimum of 50% RH.”

Last paragraph of Sect. 6.1.:

“Example humidograms of  $f(RH)$  measured at the five sites are depicted in Fig. 5. They are sorted according to their origin: maritime, continental/background and pollution influenced. These average humidograms show the high variability in curve shape, hysteresis behavior and magnitude. The particles’ deliquescence is seen for the unperturbed sea salt periods (Fig. 5a), in a separation of certain curves (e.g. MHD: green curve or CAB: blue curve) or in a steep increase at  $RH \approx 70\%$  (for NYA: red curve), while the efflorescence cannot be observed due to the limitations of the dryer (see above). The individual humidograms will be separately shown again Sect. 6.4 (Figs. 8 and 9) with a comparison to model data.”

Modified Figure 5 (old: Fig 4):



**Modified Fig. 5.** Example humidograms of  $f(RH)$  at  $\lambda = 550 \text{ nm}$  from the different sites with respect to different air masses: (a) maritime, (b) continental and background, and (c) pollution influenced.

Page 8951 line 10 The main catchment area at NYA was the open oceans and ice shields of the Arctic, bringing, e.g. clean sea salt to ... Catchment is not the right term, geographically it refers to river basins. Use the term 'source area'. What is "clean" seasalt?

Reply: Changed accordingly. "Clean" was meant to be sea salt without the influence of anthropogenic aerosol. We have changed this sentence to:

"The main source area at NYA was the open oceans and ice shields of the Arctic, bringing besides fine mode-dominated secondary aerosol also pure sea salt to the site. No clear long-range transport of pollution to the measurement site was observed during the summer and fall 2008."

P 8952 line 1 "settings"? More properly termed 'limitations', perhaps.

Reply: We replaced "settings" by "characteristics":

"As mentioned in Sect. 5, all closure studies had their individual characteristics due to the site-specific availability of auxiliary aerosol measurements and different instrumentations ..."

line 5 Define optical closure quantitatively and how that was calculated. Is that  $f(\text{RH})$  closure, specifically or optical closure, i.e., the intensive cf. the extensive variable?

Reply: The calculations were first of all performed for  $f(\text{RH})$ , our main observational quantity of interest, so for the intensive variable (as described in the manuscript). Of course, the scattering coefficients had to be calculated first for the dry and humidified (i.e. for  $\text{RH}=85\%$ ) state. At all sites, an optical closure for the scattering coefficients, so for the extensive parameters, was achieved as well, which we now additionally mention in the manuscript. We now also refer to Sect. 4 and 5, where the calculation via Mie theory and the used instrumentation are explained and references are given. We modified the entire section on the closure study results. We also have added the mean ratios of predicted to measured value for the different sites. In addition, we have added a table in the supplementary material summarizing the closure results in addition to Fig. 5 (now 6).

Revised Section 6.3:

### "6.3 Closure studies

As mentioned in Sect. 5, all closure studies had their individual characteristics due to the site-specific availability of auxiliary aerosol measurements and different instrumentations (see Table 1). The optical properties were calculated using Mie theory (see Sect. 4). Figure 6 shows the ratio of the predicted to measured value of  $f(\text{RH})$  as probability density functions for the five sites. An optical closure with respect to the intensive parameter  $f(\text{RH})$  was achieved at all five sites, giving again confidence in the performed in-situ measurements. It should be mentioned, that the optical closure with respect to the dry and wet scattering coefficients (the extensive variables) was a prerequisite for the calculation of  $f(\text{RH})$  and was achieved at all sites as well (see individual publications given in Table 1). However, the focus is here set on  $f(\text{RH})$  our main observational quantity which is an intensive parameter.

At JFJ, the best closure was achieved, if the measured size distribution, the chemical composition (refractive index) and the hygroscopic growth factor (calculated from AMS plus aethalometer or measured by H-TDMA) were used in the Mie model (mean ratio  $\pm$  standard deviation:  $1.08\pm 0.13$  using  $g_{\text{AMS}}$  and  $1.07\pm 0.12$  using  $g_{\text{HTDMA}}$ ). The slightly higher predicted values were probably due to calibration issues of the RH sensor inside the WetNeph. Keeping the chemical composition (refractive index and hygroscopic growth) or the size distribution shape or both constant still delivered reasonable prediction results ( $1.06\pm 0.14$ ,  $1.11\pm 0.12$ , and  $1.11\pm 0.14$  respectively), showing that a mean chemical composition is sufficient to predict  $f(\text{RH})$ . This result is in accordance with findings of Jurányi et al. (2010) who showed that for a prediction of the cloud condensation nuclei (CCN) number concentration, using measured size distribution and hygroscopicity measurements (H-TDMA), a mean submicron chemical composition is sufficient at JFJ. Nessler et al. (2005a) proposed a simplified scheme to predict  $f(\text{RH})$  for the summer and winter periods separately, using the measured Ångström exponent of the dry scattering coefficient. A slightly overestimation with a broader distribution of the PDF of the predicted to measured value of  $f(\text{RH}=85\%)$  is observed due to the simplifications in this model ( $1.07\pm 0.27$ , see orange curve in Fig. 6a). This model is based on the fact that the aerosol coarse mode at JFJ consists mainly of non-hygroscopic mineral dust which is characterized by low Ångström exponents, in contrast to the other four sites where the coarse mode was mainly attributed to sea salt. However, a full seasonal comparison of the model by Nessler et al. (2005a) would be desirable.

At NYA, the measured values of  $f(\text{RH}=85\%)$  were in general higher compared to the other sites (see Fig. 4). The full chemical composition and the hygroscopic growth were not measured directly. Nevertheless, the hygroscopic growth was retrieved from the measured size distribution and the wet and dry scattering properties using Mie theory and by assuming a fixed refractive index (ammonium sulfate). The hygroscopic growth factor as one input of the Mie calculations was varied until it matched the measured  $f(\text{RH})$ -values (see Zieger et al., 2010, for more details). As summarized in Fig. 6b, also a mean hygroscopicity (using a growth factor of  $g(\text{RH}=85\%)=1.6$ ) is sufficient to predict  $f(\text{RH}=85\%)$  at NYA (mean ratio  $\pm$  standard deviation:  $1.07\pm 0.2$ ), although with a higher uncertainty compared to JFJ. Although a mean  $g(\text{RH})$  was partially sufficient for the prediction, it can also lead to large uncertainties in the predicted  $f(\text{RH})$ , as can be seen in Fig. 6b, where the upper and lower bound of the retrieved  $g(\text{RH})$  was used as a constant value for the entire time series ( $1.78\pm 0.41$  and  $0.64\pm 0.11$ , respectively). A parameterization of  $g(\text{RH})$  using the measured volume coarse mode fraction, discussed in Zieger et al. (2010), brought only a slight improvement ( $1.05\pm 0.19$ ).

At MHD (Fig. 6c), the calculations were performed assuming a different refractive index for the polluted (higher imaginary part) and clean sector separately (Fierz-Schmidhauser et al., 2010c). The  $g(\text{RH})$  of the H-TDMA was only available at  $D_{\text{dry}} = 165\text{nm}$ . The closure was achieved for both cases (mean  $\pm$  standard deviation for all cases:  $1.07\pm 0.18$ ; polluted cases:  $1.00\pm 0.20$ ; clean cases:  $1.10\pm 0.16$ ). For the clean case, the agreement was slightly worse, which was attributed to the assumption of the refractive index and problems in combining the two size distribution measurements of coarse and fine mode, which showed discrepancies when comparing the surface size distribution.

For CAB, the situation is more complex, because the aerosol origin showed larger fluctuations (see trajectories in Fig. 3). Besides the continental and urban influence, the close by marine environment also contributed to the aerosol composition. As described in Zieger et al. (2011), the measured hygroscopic growth factor is limited to smaller size ranges starting at CAB with the dry diameter of 35 nm to the largest dry diameter of 165 nm. The larger particles above 165 nm were therefore missed by the H-TDMA. Since larger particles can consist of highly hygroscopic sea salt particles, the ratio of predicted to measured values of  $f(\text{RH}=85\%)$  in Fig. 6d (blue curve) using the growth factor  $g(\text{RH})$  of the H-TDMA is shifted towards an underestimation of the predicted  $f(\text{RH}=85\%)$  with a mean ratio and standard deviation of  $0.91\pm 0.09$ . A proposed parameterization of  $g(\text{RH})$  using the coarse mode volume fraction and black carbon (BC) volume fraction improved the agreement to the measured values (with  $1.00\pm 0.12$ ; see green curve in Fig. 6d). An increased BC volume fraction will by trend decrease  $g(\text{RH})$ , while an increased coarse mode volume fraction is a sign for more sea salt contribution which will by trend increase  $g(\text{RH})$ . Both volume fractions are continuously measured by an OPSS, SMPS and MAAP at that site (see Sect. 3.2). Together with the measured size distributions and an assumption on the refractive index, the  $f(\text{RH})$  can then be estimated (for more details see Zieger et al., 2011). Assuming a constant value of  $g(\text{RH})$ , which can e.g. be done for JFJ and NYA, gives a less precise prediction at CAB as can be seen in Fig. 6d (orange curve with a mean ratio of  $0.92\pm 0.15$ ).

Closure was also achieved at MEL (Fig. 6e). Good result were achieved if the refractive index and growth factor was derived from the AMS (plus MAAP) measurements or if the growth factor was taken from the H-TDMA measurement and the refractive index was derived from AMS and MAAP (mean ratio  $\pm$  standard deviation:  $1.08\pm 0.22$  and  $1.01\pm 0.18$ , respectively). Both instruments were operated successfully during the entire campaign, while the H-TDMA was only partly available. A mean  $g(\text{RH}=90\%)=1.53$  was found to be sufficient for the prediction at MEL, however with exceptions especially during transported sea salt and high anthropogenic pollution events. In addition, the coarse mode composition was varied for the calculation: If a very hygroscopic coarse mode of NaCl was assumed, the  $f(\text{RH})$  was clearly overpredicted ( $1.20\pm 0.25$ ), while an assumed dust coarse mode clearly lead to a good agreement ( $1.02\pm 0.22$ ).

Generally, all the measurements of  $f(\text{RH})$  were predicted on average within 10%, with changing variability among the different sites and assumptions, if the hygroscopic growth factor was measured (or for NYA assumed) correctly. A table summarizing the mean, standard deviation of predicted and measured  $f(\text{RH}=85\%)$  plus the mean ratio of predicted to measured value can be found in the supplementary material.

A general uncertainty analysis for the closure studies was performed using the Monte Carlo Method according to Anderson (1976). It was found that the relative error in the calculated  $f(\text{RH})$  increased for larger hygroscopic growth factors, but was always smaller than 15-25% despite the high uncertainties assumed e.g. for the refractive index. More details can be found in the Appendix (Sect. 8).

In summary, both size and chemical composition mattered when determining  $f(\text{RH})$ , which is schematically depicted in Fig. 7. For the aerosol discussed here, the relative contributions of the fine to the coarse mode and the specific chemical composition were important. At JFJ, the coarse mode was most probably attributed to long-range transported non-hygroscopic mineral dust, whereas at NYA, MEL, MHD, and CAB it was also dominated by hygroscopic sea salt. Sea salt was never observed at JFJ which also explains the absence of hysteresis effects (which was occasionally observed at all other sites). The fine mode was dominated either by organic substances with low hygroscopicity, non-hygroscopic BC, or by hygroscopic inorganic salts. As seen in Fig. 1, the interaction between size and hygroscopicity can lead to compensation effects for  $f(\text{RH})$ , as observed at NYA, where smaller and less hygroscopic particles had the same magnitude of  $f(\text{RH})$  as larger and more hygroscopic particles (Zieger et al., 2010)."

line 7 At JFJ, the best closure was achieved, if the...

Reply: It is not clear to us, what the reviewer explicitly suggests here, since this is the original stated beginning of the sentence, so we keep the sentence as it is.

line 8 and fig 5 The  $g$  factors in the legend are not explained other than in cursory fashion here; please expand and add to figure captions perhaps only by reference to text section.

Reply: This has been improved. In addition, we have added to the figure caption:

" $g_{\text{HTDMA}}$  denotes the hygroscopic growth factor measured by the H-TDMA, while  $g_{\text{AMS}}$  is the calculated value from the chemical composition measurement of AMS and aethalometer or MAAP.  $g(V_{\text{opc}}/V_{\text{tot}})$  shows the result for a parameterization site-specifically derived for Ny-Ålesund (NYA; see Zieger et al., 2010), while  $g(V_{\text{APS}}/V_{\text{tot}}, V_{\text{BC}}/V_{\text{tot}})$  is a site-specific parameterization for Cabauw (CAB; see Zieger et al., 2011).  $m_{\text{AMS}}$  denotes the particles' complex refractive index derived from AMS and MAAP or aethalometer measurements. CM denotes the coarse mode."

line 12 "showing that a mean chemical composition is sufficient to predict  $f(\text{RH})$ . This result is in accordance with findings of Jurányi, et al. (2010) who showed that for a prediction of the cloud condensation nuclei (CCN) number concentration, using measured size distribution and hygroscopicity measurements (H-TDMA), a mean chemical composition is sufficient." The accordance you mention is not strictly relevant since CCN activation occurs at a much higher RH and water content per particle. The more relevant reason, briefly, is that the integral (over size) chemical composition is dominated by the majority of the particulate mass being in the accumulation mode to lower coarse modes, the size ranges that contribute most to light scattering and control  $f(\text{RH})$ . You should define the size range of your mean chemical composition, total mass, sub10, sub-2.5, sub-1 $\mu\text{m}$ ; filter, AMS.

Reply: Yes, we agree. All CCNC measurements were performed on an inlet without a size cut, while the AMS and/or HTDMA used in Jurányi et al. (2010) only measured submicron particles. So we have modified the above mentioned sentence:

"... a mean submicron chemical composition is sufficient."

line 19 The modal value of the Nessler-based predicted to measured is an overestimate, i.e.,  $>1$ . But there is a significant tail of underestimates in the PDF. How do both of these relate to Ångström and dust? "Validation" is the wrong term. 'A seasonal comparison' would be better. So far Nessler's model is not validated for the aerosol at this location

Reply: The underestimation is mainly during periods with large or moderate Ångström exponents (so not dust influenced). The dust influence is well captured by the Nessler model. The Nessler model is a simplified model using the Ångström exponent which might not capture the real aerosol characteristics found in the atmosphere. We agree that this is no real validation. We have modified this part:

"A slightly overestimation with a broader distribution of the PDF of the predicted to measured value of  $f(\text{RH}=85\%)$  is observed due to the simplifications in this model (see orange curve in Fig. 5a). This model is based on the fact that the aerosol coarse mode at JFJ consists mainly of non-hygroscopic mineral dust which is characterized by low Ångström exponents, in contrast to the other four sites where the coarse mode was mainly attributed to sea salt. However, a full seasonal comparison of the model by Nessler et al. (2005a) would be desirable."

Page 8953 line 1 and following Its not clear how these  $g$  values were obtained from size distribution, scattering, absorption and volume ratios.

Reply: The  $g(\text{RH})$ -values were retrieved by taking the measured wet and dry scattering coefficients, the measured size distribution, by assuming a refractive index (ammonium sulfate) and by varying the growth factor within the Mie calculation until the calculated  $f(\text{RH})$  agreed with the measured value. The assumption on the refractive index

was not critical, first of all, because no long-range transported pollution was observed during the campaign (very low imaginary part) and secondly, because the dry calculated scattering coefficients agreed well with the measured ones if the refractive index of ammonium sulfate was taken. The absorption coefficients were actually not used for the  $g(\text{RH})$ -retrieval, this has been corrected. We stated in the original paper (Zieger et al., 2010) that this retrieval is based on strong simplifications (spherical particles, internal homogeneous mixture, and a fixed dry refractive index for the entire period), but that it gives useful insights to the apparent physical growth of the measured aerosol.

For clarification, we have changed the sentence

“Nevertheless, the hygroscopic growth was retrieved from the measured size distribution, and the absorption and scattering properties using again Mie theory.”

to:

“Nevertheless, the hygroscopic growth was retrieved from the measured size distribution and the wet and dry scattering properties using Mie theory and by assuming internally mixed spherical particles with a fixed refractive index (ammonium sulfate). The hygroscopic growth factor as one input of the Mie calculations was varied until it matched the measured  $f(\text{RH})$ -values (see Zieger et al., 2010, for more details).”

line 17 “...because the aerosol origin showed larger fluctuations.” ...because the back trajectories showed a large fluctuation in transport vectors and likely aerosol sources.

Reply: Yes, we agree and have added a reference (at the end of this sentence) to Fig. 2 (now Fig. 3) which shows the air mass trajectories. “... (see trajectories in Fig. 3).”

line 21 “...largest dry diameter of the deployed H-TDMA was 165 nm. The larger particles in the coarse mode accumulation and coarse modes were therefore missed by the H-TDMA.” Its not just the coarse mode that was not sampled.

Reply: Yes, we agree. The HTDMA at Cabauw additionally measured at the dry diameters of 35, 50, 75, and 110 nm. We have modified the sentence to:

“As described in Zieger et al. (2011), the measured hygroscopic growth factor is limited to smaller size ranges starting at CAB with the dry diameter of 35 nm to the largest dry diameter of 165 nm. The larger particles above 165 nm were therefore missed by the H-TDMA. Since larger particles can consist of highly hygroscopic sea salt particles, the ratio of ...”

Line 25 Again, what is the proposed parameterization?

Reply: One research question of our measurements was always to find out whether other continuously measured aerosol properties can be used as a proxy to estimate  $f(\text{RH})$ , when no direct hygroscopicity measurements are available. For Cabauw, we retrieved an empirical equation, which estimates  $g(\text{RH})$ . It is based on the black carbon (BC) and coarse mode volume fraction (higher black carbon content will decrease  $g(\text{RH})$ , while an increased coarse mode is an indicator for sea salt at Cabauw and therefore will increase  $g(\text{RH})$ ). For the BC volume fraction, a density had to be assumed. The  $g(\text{RH})$  can then be used together with the measured size distribution and an assumption on a fixed refractive index (here we used one for polluted air masses). The latter assumption did not significantly affect the agreement within the closure study.

For clarification, we have modified this part:

“A proposed parameterization of  $g(\text{RH})$  using the coarse mode volume fraction and black carbon (BC) volume fraction improved the agreement to the measured values (see green curve in Fig. 5d). An increased BC volume fraction will tend to decrease  $g(\text{RH})$ , while an increased coarse mode volume fraction is a sign for more sea salt contribution which will increase  $g(\text{RH})$ . Both volume fractions are continuously measured by an OPSS, SMPS and MAAP at that site (see Sect. 3.2). Together with the measured size distributions and an assumption on the refractive index, the  $f(\text{RH})$  can then be estimated (for more details see Zieger et al., 2011). Assuming a constant value of  $g(\text{RH})$ , which can be done for JFJ and NYA, is not sufficient at CAB as can be seen in Fig. 5d (orange curve).”

6.3 “recipe” ‘formula’ or ‘analytical method’ would be better here. This is basically a sensitivity study.

Reply: We agree and have replaced “recipe” by “analytical method” and have changed the first sentence of Sect 6.3. to:

“To show the difficulty in retrieving a simple analytical formula for an accurate  $f(\text{RH})$ -prediction, we have performed a sensitivity study by varying the main input parameters of the Mie calculations in the typical encountered ranges.”

P 8955 line 11 “width” is OK but standard deviation is the more scientific, statistical term.

Reply: We agree, different terms are used in the literature (“width” is actually used by the OPAC authors). We have changed it to “standard deviation” within the manuscript.

line 16 It hard to put these number ratios in context given the steep slope of the number distribution and where the fine-coarse size cut is made. A volume ratio would be more intuitive and comprehensible.

Reply: A volume ratio cannot be given, since the fine mode diameter is being varied, while the number concentration is kept constant. As mentioned above, we have moved the two figures to the supplementary material (where they are now shown in a better resolution) and have added as suggested a table describing the main effects. We have adapted this paragraph accordingly:

“The result for a constant refractive index ( $m = 1.54$ ) and a standard deviation of  $\sigma = 1.8$  for coarse and fine mode is shown in Tab. 3 for four different coarse mode number fractions (CM frac = 0.02, 0.01, 0.00001, 0) and alternating for a very hygroscopic ( $\kappa_{\text{CM}} = 1$ , e.g. sea salt) or non-hygroscopic ( $\kappa_{\text{CM}} = 0$ , e.g. mineral dust) coarse mode. The hygroscopicity of the fine mode is also varied ( $\kappa_{\text{FH}}=0, 0.25, 0.75, 1$ ). The figures of the entire sensitivity study can be found in the supplementary material.

The dominance of even small amounts of coarse mode particles on the overall  $f(\text{RH})$  can be seen. Coarse mode particles suppress  $f(\text{RH})$  in case of dust particles or enhance the overall  $f(\text{RH})$  in case of very hygroscopic particles (e.g. pure NaCl). The mode diameter of the fine mode (in Tab. 3 exemplary at 50, 100 and 250 nm) determines if the mode at enhanced RH (here 85 %) is moving into the optically relevant size range. This separate growth into the optical active size range also explains the wave-like structures seen in Fig. 1 and 2 of the supplementary material. Under the full absence of coarse mode particles, the  $f(\text{RH})$ -values can reach high values similar to the calculation of the monodisperse substances shown in Fig. 2.

The dependence of  $f(\text{RH})$  on the standard deviation of the fine mode ( $\sigma$ ) and the imaginary part has been investigated as well (see Fig. 2 in the supplementary material). The dependence of  $f(\text{RH})$  with respect to a varying  $\sigma$  or imaginary part of  $m$  is less pronounced than the parameters discussed above. The strong influence of the coarse mode number fraction is seen in a similar way as in Tab. 3.”

Page 8956 lines 19 through 21 Terms such as “predominantly”, “will fail”, “reliable” are not useful in this discussion. The discussion needs to be quantified.

Reply: To our knowledge, there are no observations of sea salt transport to Jungfraujoch, however it cannot be totally excluded. Cozic et al. (2008) showed that the coarse mode particles are “predominantly” composed of mineral dust. Unfortunately, we cannot quantify this statement further.

Page 8957 The OPAC model often used as a basis for hygroscopic growth in global chemistry models but other aerosol classes are added and/ or heavily modified. I’m not convinced this exercise is relevant. It could be improved by a table of original and modified OPAC parameters.

Reply: A high number of users from many different communities use OPAC because of its simplicity, which is the strength of OPAC. The user hereby does not always question every detail or modify components within the database due to the different scientific backgrounds and knowledge of the user. These exercises are needed to prevent the propagation of errors and to improve a model in general. We agree that a table will help the reader to easily improve its OPAC database with respect to the particle water uptake in a simple way. The possible needed update of the dry size distribution or refractive index is beyond the scope of our work and has to be done in a future work. We have added Tab. 4 with the original and modified hygroscopic growth factors. In addition, we have added the following sentences:

Sect 6.4 (2<sup>nd</sup> last paragraph):

“The original and modified  $g(\text{RH})$ -values are shown in Tab. 3 for the relative humidities used in OPAC.”

Sect 6.4 (last paragraph):

“As a first step to improve the OPAC components, we propose to use the modified  $g(\text{RH})$ -values (see Tab. 3). Equation 5 and Eq. 6 can then be used to obtain the wet size distribution and wet refractive index together with the original OPAC component values given at  $\text{RH}=0\%$ . Values at other RH values can be calculated using Eq. 3.

This has to be followed by a re-calculation of the optical properties e.g. by using Mie theory (Bohren and Huffman, 2004)."

And in the recommendations (last point):

"The hygroscopic growth within the OPAC (Hess et al., 1998) components should be replaced by current literature values (see Tab. 4). The RH-dependency of  $g(\text{RH})$  can be approximated for the upper branch using the  $\kappa$ -equation (Eq. 3)."

Page 8958 Modal terminology here and elsewhere is not consistent or defined, accumulation, fine, coarse.

Reply: Yes, we agree. Fine ( $D < 1\mu\text{m}$ ) and coarse ( $D > 1\mu\text{m}$ ) mode are defined at their first appearance in Sect. 3.2. To be consistent, we have replaced 'accumulation mode' in the last paragraph of the discussion on the closure study and in Fig. 6 (now 7) by 'fine mode', which includes the accumulation mode. OPAC, however, uses for its components additionally the differentiation between nucleation (approx.  $D < 100\text{ nm}$ ) and accumulation (approx.  $100\text{ nm} < D < 1\mu\text{m}$ ) mode. We have added in the OPAC Section a definition at the first appearance:

"The *sea salt* components are given for the accumulation ( $100\text{ nm} < D < 1\mu\text{m}$ ) and the coarse mode ( $D > 1\mu\text{m}$ ) separately and both are dependent on RH."

Page 8961 line 15 and following The modifications that were made to OPAC components is not clear.

Reply: As described in the paragraph before line 15, only the hygroscopic growth factors were replaced by current literature values. To clarify this part, we have rewritten this paragraph and have added a table on the modified parameters (see comment above and comment of reviewer 2). In addition, we have modified the sentence (line 20)

"Modifying the *water-soluble* and *sea salt (acc. and coarse mode)* components leads to an improved agreement between calculated and observed  $f(\text{RH})$  (see Fig. 13b)."

to

"Modifying the *water-soluble* and *sea salt (acc. and coarse mode)* components with hygroscopic growth factors based on current literature leads to an improved agreement between calculated and observed  $f(\text{RH})$  (see Fig. 12b)."

Page 8962 The first recommendation (and the earlier description of the data reduction process for the nephelometer) does not mention the illumination, truncation correction also needed for a precise measurement. The internal, Ångström-based correction has large uncertainty when coarse particles are present. A better correction requires size distribution measurements, ideally at the sensing volume RH of the nephelometer.

Reply: Yes, we agree. We have added to this point the sentence:

"Standard nephelometer truncation and illumination correction should be applied (Anderson et al., 1996)."

In addition, we have added to the experimental part (Sect 3.1):

"To retrieve the full hemispheric scattering coefficients and to correct for the non-ideal light source, the recorded nephelometer data has to be corrected e.g. by using the proposed scheme by Anderson et al. (1996). This correction scheme is based on the measured Ångström exponent. The increasing uncertainties for coarse mode dominated aerosol can be reduced if the measured size distribution (ideally as a function of RH) is taken into account, which has not been done within this study due to the predominant fine mode aerosol."

For a given aerosol,  $\kappa$  changes depending on the RH range over which it is applied. Specify recommended range limits.

Reply: Yes, we agree. The  $\kappa$ -equation only considers the deliquescent aerosol, which we measured with the WetNeph on average between approx. 50 and 95% RH. The  $g(\text{RH})$ -values extrapolated with the  $\kappa$ -formula and  $\text{RH}=85\%$  differed within this RH range (50-95%) by maximal 6% compared to the thermodynamically calculated values i.e. by Topping et al. (2005). However, we think that the error induced by the RH-dependency of  $\kappa$  is small compared to overall model uncertainties due to the model assumptions (homogeneously internal mixture, spherical particles, etc.).

We have therefore added this information to the sentence:

"The  $\kappa$ -equation (Eq. 3) should be used to describe the RH-dependency of  $g(\text{RH})$  for the deliquescent aerosol (for the RH range of 55% to 95%)."

Strictly speaking the third fourth and fifth points are not recommendations but only observations or conclusions.

Reply: Yes, we agree. We have merged the third point with the second point (where it makes more sense) and have rephrased the fourth and fifth point:

“ ...

- If no direct measurements of  $f(\text{RH})$  are available,  $f(\text{RH})$  can be approximated using the measured particle number size distribution, the hygroscopic growth factor and chemical composition measurements and Mie theory. The  $\kappa$ -equation (Eq.3) should be used to describe the RH-dependency of  $g(\text{RH})$ . However, the user should be aware that the hygroscopic growth measurements with a standard H-TDMA may miss the important coarse mode contribution to  $f(\text{RH})$  and therefore may under- or overestimate the overall  $f(\text{RH})$  (see Tab. 3 but also Fig. 6 in Zieger et al., 2011).
- The humidograph mode should be used to identify hysteresis behavior and thus can be used to further identify air mass origin (e.g. sea salt).
- Optical closure studies should be performed to identify measurement errors, possible model weaknesses and to constrain the obtained measurement results.

... ”

Fig 4 The color coding is not different enough to distinguish the traces for individual locations.

Reply: Yes, we agree. We have modified this figure and now show the example humidograms in three subpanels (see comment above).

Fig. 8. “Same as Fig. 7 but for varying imaginary parts of the refractive index and varying width of the fine mode.” Add that” Indicated values of  $\sigma$  and  $m_{\text{imag}}$  as indicated in the legend are compared to the reference case given in figure 7.

Reply: This figure has been moved to the supplement. We have added a detailed caption:

“The scattering enhancement  $f(\text{RH})$  at  $\text{RH}=85\%$  and  $\lambda=550$  nm modeled for different imaginary parts of the refractive index ( $m_{\text{imag}}$ ) and different standard deviations of the fine mode ( $\sigma$ ). The fine mode hygroscopicity is assumed to be constant with  $\kappa_{\text{FM}}=0.5$ , while the real part of the refractive index is  $m_{\text{real}}=1.54$ . The mode diameter of the coarse mode is assumed to be constant at  $D=2$   $\mu\text{m}$ . Note the different scale of the z-axis for the monomodal case (blue axis).”

Fig 10 Not all parameters in the legend are evident in the plots, e.g., Melpitz. Are they overplotted or not in the data set? If the latter delete from legend.

Reply: Yes, sorry, there were some not needed legend entries in the Melpitz subpanels. This has been corrected. In addition, the titles of the subpanels were improved (same for Fig. 5 and Fig. 8 - 10).

Fig 11 Several of the measured distributions look unreasonable. Is this due to poor sampling statistics.

Reply: The three “unreasonable” size distributions are all periods where the coarse mode had an increased influence due to the presence of sea salt or dust. This part of the size distribution was measured using an OPSS (see Tab 1), which is limited by the amount of channels. In addition, it is a very simple instrument, which uses a single laser wavelength to discriminate the particle diameter (although with good counting statistics) and thus is influenced by Mie oscillations. These can be responsible for the fact that the distributions look unreasonable (e.g. the local minima at approx. 1.3  $\mu\text{m}$  can be reproduced using Mie calculations) and are usually observed, when plotting the volume or surface size distributions of an OPSS.

Fig 13 This includes a range of uncertainties in OPAC-based  $f(\text{RH})$ . What is the range of uncertainty in measured  $f(\text{RH})$ ?

Reply: This figure shows the ratio of all OPAC predictions to the measured  $f(\text{RH})$  for the Cabauw site (entire available time series) and does not include any uncertainties. We have added the information on the measurement uncertainty in the instrumental section (see also comments from reviewer 2).

“Two main factors contribute to the uncertainty of the measured  $f(\text{RH})$ : the uncertainty of the particle scattering coefficient measurement by the two nephelometers (approx. 10%, Anderson et al., 1996) and the uncertainty of the RH inside the humidified nephelometer (1.5-2 percent point of RH, see Fierz-Schmidhauser et al., 2010a). The uncertainty of the RH sensor can be included to the total  $f(\text{RH})$ -uncertainty at a given RH if an empirical course of  $f(\text{RH})$  is being assumed (see e.g. Eq. 8 in Zieger et al., 2010). The resulting relative uncertainty then increases

with the increasing hygroscopicity and increasing RH (and vice versa). At RH = 85%, the relative error in  $f(\text{RH})$  due to the RH sensor error is smaller than 14% for very hygroscopic aerosol like sea salt. Both main error sources propagate to a total relative uncertainty of  $f(\text{RH}=85\%)$  smaller than 20%.”

## Anonymous Referee #2

We like to thank Referee # 2 for his or her very detailed review and constructive comments, which helped to substantially improve the quality of the manuscript.

General comments:

The article ‘Effects of relative humidity on aerosol light scattering’ by Paul Zieger et al. provides an overview of measured humidity scattering enhancement factors in Central Europe. The available data set, although limited to intensive campaigns at only five European stations, gives a valuable insight into the situation in Central Europe.

The reviewer appreciates that the authors aimed to present their work without too many excessively explanation and unnecessary annotation. However, at some points the given information is not sufficient. The main criticism of the reviewer is that a description of the used instrumentation and measurement uncertainties is too short or even missing. Measurement uncertainties and systematic errors of the used instrumentation and derived parameters are important to judge if a closure is successful. This is a necessary prerequisite for a comparison with the OPAC database.

Data were measured with an up-to-date instrumentation and the principle approach of data evaluation is sound. The comparison with the OPAC database could be an important scientific contribution when considering the measurement uncertainties.

Reply: Yes, we agree. We have added the information on the WetNeph uncertainty in the instrumental section and also have added a new figure showing the main working principle of the WetNeph (see specific comment below). More information can be found in the technical paper, which we have referenced. In addition, Tab. 2 includes the measured standard deviations and percentile values for different aerosol types. The instrumental part of the auxiliary aerosol instrumentation used for the closure studies has been expanded (giving the instrument type, brand and uncertainty). In addition, we have performed a general Monte Carlo based error propagation analysis (see also comments of reviewer 1) and have added the missing information and discussion in the according section (see specific comments below).

The OPAC derived  $f(\text{RH})$  values are still significantly larger and lie clearly outside the measurement uncertainty. The too high hygroscopic growth factors implemented in OPAC are most probably the main reason for this finding. The OPAC hygroscopic growth factors of the hygroscopic components are clearly above recent literature values (see Fig. 11). As suggested, we have added a table on the modified growth factors in the revised manuscript, so the user can continue using OPAC but with modified values. For a future work, it would be desirable to further improve OPAC, e.g. by including findings of recent long-term SMPS size distribution measurements (see e.g. Asmi et al., 2011), non-sphericity effects of mineral dust or volcanic ash (see e.g. Nousiainen et al., 2009; Gasteiger et al., 2011) and by including new measurements on hygroscopicity (see e.g. Swietlicki et al., 2008).

Specific Comments:

Page 8942 lines 16 to 18: Can the authors give references for pure mineral dust

Reply: Within the literature, only  $f(\text{RH})$ -values for long-range transported mineral dust have been reported e.g. measured at the Jungfraujoch (Fierz-Schmidhauser et al., 2010, Zieger et al., 2012), on cruise ships (Carrico et al., 2003) or e.g. at Barbados (Li-Jones et al, 1998). To our knowledge, there are no  $f(\text{RH})$ -values for pure mineral dust. However, we would speculate that the  $f(\text{RH})$ -values should be closer to 1 compared to the long-range transported values, since atmospheric aging will increase the hygroscopicity of the particles (see e.g. Jimenez et al, 2009). We have added the Li-Jones reference to the manuscript.

Section 3.2 : The description of the additional aerosol measurements is too short. What are the size ranges of the size spectrometers SMPS, APS, OPSS? It should be mentioned that these size spectrometers measure different diameters. These are the mobility, aerodynamic and optical diameters. Similar for the H-TDMA and AMS, at what diameters the hygroscopic growth factor and chemical composition were measured? For each instrument the manufacturer and references to the working principle should be given. In this section the reader would expect information on the measurement uncertainties.

Reply: We have rewritten Sect. 3.2 and have extended it by more technical information (instrument type, main working principle, size ranges, and uncertainties) and references. We have tried to keep it as short as possible and like to refer the reader to the individual publications of the instrument or the different campaigns, where the full technical details as well as the set up (e.g. flow rates, inlet properties, etc.) are being discussed in further detail. The uncertainties on the  $f(\text{RH})$  measurements are of course important and are now added in Sect. 3.1. We have added a general uncertainty analysis for this section to the appendix. For the hygroscopic growth factor (H-TDMA) and the fine mode particle number size distribution (SMPS or DMPSS) the error from the individual instrument was taken, while for the coarse mode particle number size distribution (OPSS) and refractive index (AMS, MAAP or aethalometer) assumptions on the uncertainty had to be taken. Especially for the refractive index, we cannot provide an exact uncertainty. Therefore we used a broad distribution within the Monte Carlo error analysis which covered all the observation and reasonable literature values. However, it will be shown that most uncertainties mainly cancel out in the calculation of the intensive property  $f(\text{RH})$ , since they are systematic and appear in both the wet and dry scattering coefficient.

We have added to Sect. 3.1 (Particle light scattering measurements at elevated relative humidity):

“Two main factors contribute to the uncertainty of the measured  $f(\text{RH})$ : the uncertainty of the particle scattering coefficient measurement by the two nephelometers (approx. 10%, Anderson et al. 1996) and the uncertainty of the RH inside the humidified nephelometer (1.5-2 percent points in RH, see Fierz-Schmidhauser et al., 2010). The uncertainty of the RH sensor can be included to the total  $f(\text{RH})$ -uncertainty at a given RH if an empirical course of  $f(\text{RH})$  is being assumed (see e.g. Eq. 8 in Zieger et al., 2010). The resulting relative uncertainty then increases with the increasing hygroscopicity and increasing RH (and vice versa). At RH = 85%, the relative error in  $f(\text{RH})$  due to the RH sensor error is smaller than 14% for very hygroscopic aerosol like sea salt. Both main error sources propagate to a total relative uncertainty of  $f(\text{RH}=85\%)$  smaller than 20%.”

We have modified and expanded Sect. 3.2 (Additional aerosol measurements):

“A large variety of further aerosol parameters was measured in parallel during all field campaigns. The data was needed to describe the physical and chemical properties responsible for the encountered scattering enhancement, to search for other proxies to predict  $f(\text{RH})$  and was used for relevant closure studies. Table 1 gives an overview of the instrumentation employed at the different sites. Here, only a brief description will be given and more details can be found in the individual publication and the in the references therein.

The particle light absorption coefficient was measured using either a multi-wavelength aethalometer (Magee Scientific, Model AE-31) or a single-wavelength multi-angle absorption photometer (MAAP; Thermo Scientific Inc., Model 5012). The MAAP measures the light attenuation and light scattered back from aerosol particles which are deposited on a filter. A radiative transfer scheme is applied to retrieve the fraction of light absorbed by the deposited aerosol (with a 12% rel. uncertainty; Petzold and Schönlinner, 2004). The aerosol absorption coefficient  $\sigma_{\text{ap}}$  is obtained by multiplying the measured black carbon (BC) mass concentration with the instrumental set value of the mass absorption cross section of  $6.6\text{m}^2\text{g}^{-1}$ . The aethalometer measures the light attenuation by the aerosol particles (also deposited on a filter) at 7 wavelengths. The aerosol absorption coefficients were derived by a formula given by Weingartner et al. (2003) and site-specifically corrected for filter effects using values given by Collaud Coen et al. (2010).

The particle number size distribution of the fine mode particles (diameter  $D < 1\mu\text{m}$ ) was either characterized using a scanning mobility particle sizer (SMPS) or a dual mobility particle size spectrometer (DMPSS), while the coarse mode particles ( $D > 1\mu\text{m}$ ) were measured using either an aerodynamic particle sizer (APS) or an optical particle size spectrometer (OPSS). The SMPS (at CAB: TSI Inc., Model 3034 (modified); at JFJ, NYA, MHD: custom build instrument, see references in Tab. 1) and DMPSS (custom build instrument) measure an electrical mobility diameter between 10 and approx. 800nm. For both instrument types, the particles are charged and then size selected by a differential mobility analyzer (DMA) before they are counted by condensation particle counter (CPC). The DMPSS at MEL consists of two DMA for an extended size range starting already from 4 nm (Birmili et al., 2009). A correction for multiple charged particles has to be applied for all measurements of DMPSS and SMPS. These uncertainties for the fine mode particles measured by the SMPS or DMPSS lie within the findings of Wiedensohler et al. (2012) and are clearly below 10% for particles between 20-200nm, while the uncertainties can increase up to 30% for particles  $>200\text{nm}$ . The APS (TSI Inc., 3321) measures the particle number size distribution with an aerodynamic particle diameter between approx. 0.5 and 20  $\mu\text{m}$ . It uses a time-of-flight method by using two laser beams to measure the time and to count the particles. The measured distributions have to be corrected for non-sphericity and the density of the ambient aerosol (Marshall et al., 1991), since the APS is being

calibrated with standardized spherical polystyrene latex particles. The counting and sizing uncertainty of the APS for particles with diameters  $> 1\mu\text{m}$  is below 10% (5-8% as e.g. reported by Putaud et al., 2000), while the counting uncertainty may significantly increase for smaller particles. The OPSS (Grimm GmbH, Dust Monitor 1.108) measures an optical diameter between 0.3 and 25  $\mu\text{m}$ . The instrument uses the light intensity that is scattered by the particles from the light emitted by a laser diode. The counting efficiency of the OPSS is believed to be within 90-100% (Heim et al., 2008). The optical particle diameter, however, depends on the refractive index of the particles, which has to be corrected for (see e.g. Bukowiecki et al., 2011) as it is important especially for the surface, volume or mass determination. Here, we assume an uncertainty of 20% in the OPSS particle sizing (see appendix for more details).

The hygroscopic growth factor, defined as the ratio of the particle diameter at high RH to its dry value (see Eq. (2) below), was added to the analysis using measurements of a hygroscopic tandem differential mobility analyzer (H-TDMA; see e.g. Liu et al., 1978). The aerosol sample is first dried in the H-TDMA and then charged by a bipolar charger. A dry size class of particles with the diameter of  $D_{\text{dry}}$  is then selected by a DMA, before the particles are exposed to controlled RH (90%) and temperature. The wet particles go through the second DMA and are followed being counted by a CPC. A humidified size distribution for a certain  $D_{\text{dry}}$  is then obtained. The hygroscopic growth factors were inverted from the humidified distributions using the procedure described by Gysel et al. (2009). All instruments were set to measure the hygroscopic growth factors of  $D_{\text{dry}} = 35, 50, 75, 110, 165$  and 265 nm (265 nm was not measured at CAB, at MHD only 165 nm was used as dry diameter). The growth factors in these studies were determined within  $\pm 0.05$ , which is typical for a well-maintained TDMA system (Swietlicki et al., 2008). All H-TDMA instruments were custom build instruments and more technical details can be found in the references given in Tab. 1.

The Aerodyne high resolution time-of-flight aerosol mass spectrometer (AMS; Aerodyne Research) measured the chemical composition of non-refractory particles with diameters smaller than 1  $\mu\text{m}$  (vacuum aerodynamic particle diameter). The aerosol is introduced into the instrument via an aerodynamic lens which focuses the aerosol into a tight beam. The particle beam impacts on a heated tungsten plate, where the components are flash vaporized. The resulting gas plume is ionized and the mass spectra is being recorded using a high mass resolution spectrometer. Because soot, crustal material and sea-salts cannot be detected, the AMS is commonly considered to provide non-refractory  $\text{PM}_{10}$  (particulate matter with a particle diameter  $< 1\mu\text{m}$ ) aerosol particle chemical composition. Only mass fractions were used in our data analysis, which avoids a systematic error due to the collection efficiency of the AMS. The relative ionization efficiency would result in an error of the mass ratios of approx. 10%. The AMS has been characterized in detail e.g. by DeCarlo et al. (2006); Canagaratna et al. (2007).

At MEL and NYA, aerosol particles were also collected on daily  $\text{PM}_{10}$  high volume filter samples. The results were only needed to identify sea salt transport events to the station.

..."

**Page 8949 lines 17 to 19: How were the hygroscopic growth factors and refractive indices derived from AMS?**

**Reply:** The complex refractive index as well as the hygroscopic growth factor were calculated at Jungfraujoch using the chemical composition measurements of the AMS and the aethalometer (determining the black carbon contribution). A time resolved mean refractive index was then determined by averaging the respective volume fractions using literature values for the organics,  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$ ,  $\text{H}_2\text{SO}_4$  and for BC (see Table 1 in Fierz-Schmidhauser et al, 2010b). It should be mentioned that these calculations were only performed for the mineral dust free episode, because the H-TDMA was only measuring for this period (May 2008). Mie calculations for mineral dust lead to large discrepancies due to non-sphericity and unknown refractive index (as e.g. has been discussed for the Jungfraujoch in Zieger et al, 2012).

For clarification, we have modified this sentence:

"The AMS measurements were used together with aethalometer measurements to calculate (a) the hygroscopic growth factor (in addition to the direct measurement of the H-TDMA) and (b) the complex refractive index which is needed as an input parameter for the Mie calculations (details can be found in Fierz-Schmidhauser et al., 2010b)."

**Page 8949 lines 21 to 24: The authors should explain the inversion calculation of the hygroscopic growth factor in more detail. What refractive index was assumed? How do the inverse calculation and assumption of refractive index affect the error of the hygroscopic growth factor?**

Reply: As mentioned above for the comment of reviewer 1, the  $g(\text{RH})$ -values were retrieved by taking the measured wet and dry scattering coefficients, the measured size distribution, by assuming a refractive index (ammonium sulfate) and by varying the growth factor within the Mie calculation until the calculated  $f(\text{RH})$  agreed with the measured value. The assumption on the refractive index was not critical, first of all, because no long-range transported pollution was observed during the campaign (negligible imaginary part) and secondly, because the dry calculated scattering coefficients agreed well with the measured ones if the refractive index of ammonium sulfate was taken. The absorption coefficients were actually not used for the  $g(\text{RH})$ -retrieval, this has been corrected. We stated in the original paper (Zieger et al., 2010) that this retrieval was based on strong simplifications (spherical particles, internal homogeneous mixture, and a fixed dry refractive index for the entire period), but that it gave useful insights to the apparent physical growth of the measured aerosol. At that time, we also tested different assumptions on the refractive index (e.g. by taking the inverse calculated one, which should be the perfect one to reproduce the optical data), but the influence of the refractive index was only minor.

For clarification, we have modified and added to the sentence

“Nevertheless, the hygroscopic growth was retrieved from the measured size distribution, and the absorption and scattering properties using again Mie theory.”

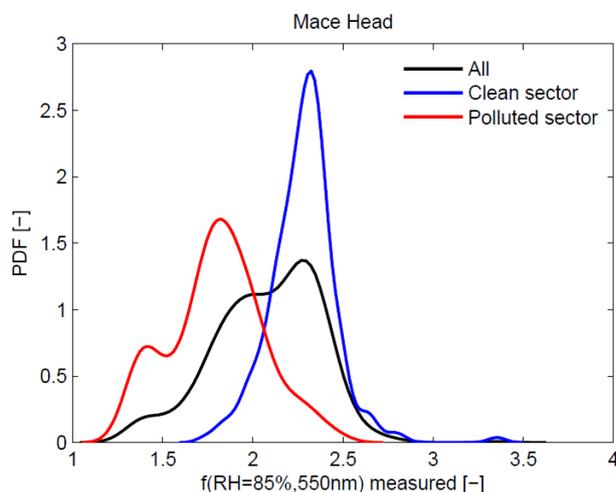
the following:

“Nevertheless, the hygroscopic growth was retrieved from the measured size distribution and the wet and dry scattering properties using Mie theory and by assuming a fixed refractive index (ammonium sulfate). The hygroscopic growth factor as one input of the Mie calculations was varied until it matched the measured  $f(\text{RH})$ -values (see Zieger et al., 2010, for more details).”

Page 8951 line 17: The reviewer can't see a two sector discrimination in Fig. 3.

Reply: The area below the two first local maxima are values mainly from the polluted sector and the area below last maxima stands for the clean sector (see graph below for clarification). For clarification, we have added to this sentence:

“The two-sector discrimination of MHD can be clearly seen (area below first two local maxima of the PDF is representative for air masses from the polluted sector, the area below last maxima at approx.  $f(\text{RH}=85\%, 550\text{nm}) = 2.1$  are mainly values originating from the clean sector).”



**Figure:** Probability density function (PDF) of measured scattering enhancement  $f(\text{RH}=85\%, 550\text{nm})$  at Mace Head. The values for the clean and polluted sector are shown separately (all curves are normalized to the area of one). This figure is just for illustration purposes to reviewer 2, it will not be shown in the revised manuscript.

Page 8952 line 5: What are the criteria for achieving a closure?

Reply: A closure is achieved, if an appropriate model (based on physical principles) can be used to reproduce the observation of interest by applying a different set of observational data. This exercise can assess the consistency of aerosol properties measured with various techniques using different measurement platforms. If the reproduced values (including the model uncertainty) lie within the measurement uncertainty, the closure can be regarded as achieved. We have performed Monte Carlo simulations to determine the model uncertainty which consider the input parameter uncertainty. See comments above.

To clarify, we have added to the Sect. 5:

“The first task was to check for consistency within the in-situ measurements performing so called closure studies. A closure is achieved, if an appropriate model (here a model based on Mie theory, see Sect. 4) can be used to reproduce the observation of interest by applying a different set of observational data. If the reproduced values (including the model uncertainty) lie within the measurement uncertainty, the closure can be regarded as achieved.

In a next step, sensitivity studies were performed to search for independently measured parameters that can be used to predict  $f(\text{RH})$ . ...”

Page 8953, lines 10 to 12: How much varied the imaginary part of the refractive index between the clean and the polluted case?

Reply: The imaginary part of the clean sector was negligible, while the imaginary part of the polluted sector was resulting in a value of  $0.024i$  (see Fierz-Schmidhauser et al., 2010c).

Page 8953, lines 25 to 27: Can the authors explain the ‘proposed parameterization’.

Reply: One research question of our measurements was always to find out whether other continuously measured aerosol properties can be used as a proxy to estimate  $f(\text{RH})$ , when no direct hygroscopicity measurements are available. For Cabauw, we retrieved an empirical equation, which estimates  $g(\text{RH})$ . It is based on the black carbon (BC) and coarse mode volume fraction (higher black carbon content will decrease  $g(\text{RH})$ , while an increased coarse mode is an indicator for sea salt at Cabauw and therefore will increase  $g(\text{RH})$ ). For the BC volume fraction, a density had to be assumed. The  $g(\text{RH})$  can then be used together with the measured size distribution and an assumption on a fixed refractive index (here we used one for polluted air masses). The latter assumption did not significantly change the agreement within the closure study. For clarification, we have modified this part:

“A proposed parametrization of  $g(\text{RH})$  using the coarse mode volume fraction and black carbon (BC) volume fraction improved the agreement to the measured values (with  $1.00 \pm 0.12$ ; see green curve in Fig. 6d). An increased BC volume fraction will tend to decrease  $g(\text{RH})$ , while an increased coarse mode volume fraction is a sign for more sea salt contribution which will increase  $g(\text{RH})$ . Both volume fractions are continuously measured by an OPSS, SMPS and MAAP at that site (see Sect. 3.2). Together with the measured size distributions and an assumption on the refractive index, the  $f(\text{RH})$  can then be estimated (for more details see Zieger et al., 2011). Assuming a constant value of  $g(\text{RH})$ , which can e.g. be done for JFJ and NYA, gives a less precise prediction at CAB as can be seen in Fig. 6d (orange curve with a mean ratio of  $0.92 \pm 0.15$ ).”

Page 8969, line 29: Curve for constant  $g=1.48$  should be orange curve?

Reply: Yes, it should be the orange curve. This has been corrected.

Page 8955, line 16 ff: The reviewer thinks that it would be better to present the results as function of the coarse mode surface fraction instead of the coarse mode number fraction, since the surface size distribution is a better representation for optical properties (see page 8959 line 26ff)

Reply: The surface is indeed a better representation for the particle scattering properties, however, a surface or volume ratio of fine to coarse mode cannot be given as one number, since the fine mode diameter is being varied while the number concentration is being kept constant.

Page 8959 line 10 to 14: Generally one would expect an overlap between the two modes. Is it valid to split the size distribution using a sharp cut diameter since the scattering enhancement is sensitive to the size as discussed before?

Reply: The sharp cut diameter has just been used to retrieve the optimal new mixing ratios for the available OPAC components (in the figures called OPAC mix) which are based on the measured size distribution (see Eq. 8). The optical properties were then calculated as an external mixture (in the identical way as in OPAC) also using the same original microphysical input data. In this way, the overlap between the two modes is taken into account.

Page 8959 line 20: The influence of the refractive index could not be checked because of missing measurement. Can the authors estimate the influence by a sensitivity study?

Reply: The influence of the refractive index on the calculated  $f(\text{RH})$  is now shown in the general uncertainty analysis of the closure studies (see appendix). Here, the Monte Carlo simulations were repeated by only varying the refractive index (real and imaginary part separately) while keeping the other input parameters fixed at their mean

value. We have chosen a very broad range of the uncertainty of refractive index within the Monte Carlo simulation. One can observe that the contribution of the uncertainty of the refractive index (especially the real part -> scattering) becomes more dominant for large hygroscopic growth factors (or large RH). This is due to the fact that the uncertainty of the refractive index for the wet scattering decreases (it converges more towards the known value of water), while the uncertainty of the dry scattering coefficient stays unchanged.

Page 8961 line 15 to 24: Can the authors explain what the modifications of the 'OPAC components' are.

Reply: Only the hygroscopic growth ( $g(\text{RH})=D_{\text{wet}}/D_{\text{dry}}$ ) have been modified by using current literature values. We have added a table on the original and modified  $g(\text{RH})$ -values for the RH-dependent OPAC components and have slightly adapted the text (see comment of reviewer 1).

## Further Changes

- Moved Section 6.4 ( $f(\text{RH})$  sensitivity study) in front of Sect. 6.3. (Closure studies).
- Improved colors in Fig. 3 (now Fig. 4).
- Changed the sentence in Sect 3.1.: "A reference nephelometer is usually operated in parallel at dry conditions (DryNeph)." to "A reference nephelometer (TSI Inc., Model 3563) was always operated in parallel at dry conditions (DryNeph)."
- We have added the networks to Sect. 2.4:
  - o "The JFJ is a GAW monitoring site (Global Atmosphere Watch program by the World Meteorological Organization), and is part of ACTRIS (Aerosols, Clouds, and Trace gases Research Infrastructure Network), EMEP (European Monitoring and Evaluation Programme) and the Swiss Air Quality Monitoring Network (NABEL)."
  - o "NYA is also a GAW site and participates in the EMEP program."
  - o "MHD is a GAW site and as well joins the ACTRIS and EMEP programs."
  - o "MEL is an observation site within EMEP, GAW, and GUAN (German Ultrafine Aerosol Network Birmili et al., 2009)."
  - o "CAB participates in the ACTRIS and EMEP program."
- Corrected some minor spelling mistakes.
- Appendix added:

### **"Appendix: Model uncertainty analysis**

A general uncertainty analysis on the on the predicted or calculated value of  $f(\text{RH})$  was performed using the Monte Carlo Method (Anderson, 1976). Here, the error propagation is being done by repeated Mie calculations where each time the input parameters are randomly varied. 10000 iterations were used, although the results were already converging at less iterations (approx. 1000). The calculations were done for  $\lambda=550\text{nm}$ . For the hygroscopic growth factor (H-TDMA) and the fine mode particle number size distribution (SMPS or DMPSS) the error from the individual instrument was taken, while for the coarse mode particle number size distribution (OPSS) and refractive index (AMS, MAAP or aethalometer) assumptions on the uncertainty had to be taken (see below). To test the sensitivity of the several input parameters, the Monte Carlo simulations were repeated each time varying only one input parameter and keeping the other values with their mean value as constant. In addition, the simulations were repeated for different hygroscopic growth factors (between 1 and 2) and coarse mode number fractions. For the hygroscopic growth factor a normal error distribution with a standard deviation of 0.05 was assumed (Swietlicki et al., 2008). A bimodal size distribution was assumed with  $N_{\text{FM}} = 10000$  and  $N_{\text{CM}} = 200, 100, 50, 1$  and 0 and  $D_{\text{mod}}^{\text{FM}} = 100\text{nm}$  and  $D_{\text{mod}}^{\text{CM}} = 1 \mu\text{m}$  (with FM: fine mode and CM: coarse mode, see Eq. 7). The standard deviation of the mode was taken as  $\sigma = 2$  and assumed not to influence the error in  $f(\text{RH})$ , since it will be included in the systematic error of the diameter sizing. For N we assumed an error of 30% for the fine (SMPS and DMPSS) and 10% for the coarse mode (OPSS and APS), while for  $D_{\text{mod}}$ , we took a 10% uncertainty for the fine mode and 20% for the coarse mode (assuming a normal error distribution with the relative uncertainties recalculated to standard deviations). These uncertainties for the fine mode particles measured by the SMPS or DMPSS lie within the findings of Wiedensohler et al. (2012), while the uncertainties on the coarse mode sizing are assumptions based on our own measure-

ments using the OPSS (Bukowiecki et al., 2011) and literature findings for the APS (Marshall et al., 1991; Putaud et al., 2000). However, it will be shown, that the uncertainties within the absolute size distribution measurements are systematic uncertainties and will finally cancel out when calculating the ratio of  $f(\text{RH})$ . The error of the refractive index cannot be accurately derived, so we have assumed a uniform (rectangular) distributed of refractive index. The real part was randomly chosen from 1.4 to 1.8, the imaginary part from 0 to 0.1. Both ranges cover the observations e.g. of the inversely calculated values at Cabauw (Zieger et al., 2011) or the values given in Hess et al. (1998). The upper limit of 0.1 for the imaginary part is justified in our case because no pure absorbing substances were observed at the sites. The result is depicted in Fig. 13 as the relative error  $\Delta f(\text{RH})$ , which is calculated from the standard deviation divided by the mean value, for different  $g(\text{RH})$ -values and different coarse mode fractions. The overall relative uncertainty within the calculated  $f(\text{RH})$  are clearly below 15-25%, which can be regarded as a very conservative estimation and is still sufficient despite the other strong simplifications that had to be made (spherical particles, homogeneous internally mixed particles, etc.).

The relative error increases with increasing  $g(\text{RH})$  (or increasing RH) because the uncertainty due to the refractive index becomes less important for the wet scattering coefficient, which will approach the refractive index of water, while the wet scattering coefficient itself (in Eq. 1 in the denominator) will increase with increasing  $g(\text{RH})$ . On the other hand, the dry scattering coefficient (in Eq. 1 in the numerator) and its high uncertainty will stay unchanged and thus the overall uncertainty in  $f(\text{RH})$  will increase. The contribution of the real and imaginary part to the relative error also increases with  $g(\text{RH})$  as can be seen by the cyan and violet curves in Fig. 13, while the contribution of the uncertainty in  $g(\text{RH})$  itself concurrently decreases. The particle number size distribution shows almost no effect because the uncertainty can be seen as a systematic error, which cancels out (only a minor effect of the diameter sizing can be expected, especially when no coarse mode is present). The relative error increases with decreasing coarse mode number fraction because the wet scattering coefficient increases stronger for pure fine particles (having a larger  $f(\text{RH})$ ) compared to an aerosol with an existing coarse mode. However, a non-existing or a negligible coarse mode number fraction is probably not relevant for the ambient (tropospheric) atmosphere and was also not observed within the here presented studies.

The relative error in the calculated  $\Delta f(\text{RH})$  decreases below 20% if a normally distributed uncertainty of the refractive index of  $1.5 \pm 0.1$  (mean  $\pm$  standard deviation) for the real part and  $0.02 \pm 0.002$  for the imaginary part are assumed for the refractive index uncertainty, which could be a more realistic assumption on the refractive index uncertainty instead of a rectangular distribution as used above. On the hand,  $\Delta f(\text{RH})$  can rise up to 35%, if the uncertainty of  $g(\text{RH})$  is assumed to be 10%, while the other input parameters have the uncertainty as mention above (both uncertainties refer to size distributions without coarse mode). This is a more reasonable uncertainty assumption for the cases when the  $g(\text{RH})$  was predicted from AMS and MAAP or aethalometer measurements for cases without very strong sea salt, dust or BC influence (Gysel et al., 2007)."

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