

Referee #3:

Major points:

1. The advantages of using a combination of an HDMPS (humidified particle sizer) and a TDMPS (dry particle sizer) instead of the more established HTDMA method are not very clear. The equipment (i.e., number of DMAs, CPCs, driers, humidifiers, etc.) necessary for either of these two methods is very similar, but the accuracy and temporal resolution of HTDMAs is much higher (the 2.5 to 3 hours cycle used in this work is a long time for urban measurements). A good justification for the selection of the methodology would be valuable in the manuscript. Also, what was the reason for taking measurements at different RH values? The discussion is centered around the measurements obtained at 90% RH only.

*The difference between the HDMPS and HTDMA is that the HDMPS scans the whole dry and humidified size distribution in four target humidities which are increased stepwise. So we receive growth factors for a broad diameter range applying the summation method in contrast to the HTDMA, where only specific diameters are humidified to one target humidity. The conditioning of the RH to four intervals in the HDMPS is to get extensive information about the hygroscopic growth in the entire atmospheric humidity spectrum. The temporal resolution of the HDMPS can be increased if only one target humidity (for example 90 %) is used. In our case the measurement cycle would be reduced to less than one hour.*

*In an earlier version, all other RHs were also included for the representation of time series, but to get more straight, the focus was set at a RH of 90 %, exclusively. At a relative humidity of 90 % the aerosol size distribution changes notably and it is the most adequate value for comparisons, for example with HTDMA measurements.*

2. Section 2.3.1: would benefit from some more information and some references for the methodology followed to invert the mobility measurements. For instance was the humidity measured continuously in the TDMPS? Was there a neutralizer upstream of the DMAs? If so, what type?

3. Lines 7-9 on page 14302: *The authors could give a more detailed description of the inversion algorithm used or refer to a published paper with more details.*

*We have now included these information in section 2.3.1: "The particles were charged and brought into charge equilibrium as described by Wiedensohler et al. (2012; Table 3 IFT-TDMPS composition)."*

*"... typical conditions were between 5 and 26 % relative humidity (RH) of the aerosol inlet flow, which was continuously monitored."*

*"The measured raw mobility concentration was inverted ..., as described by Wiedensohler et al. (2012; Table A2)."*

4. In my opinion, the ion-pairing of the HR-AMS measurements needs further investigation (section 3.2, on pages 14396, 14307). The comparison with the AIM model II described Clegg et al. (1998) (cf. page 14313, lines 20 – 29, and page 14314, lines 1-17), indicates that at least in one time period (i.e. at the end of the campaign) their initial assumption (i.e. assign SO<sub>4</sub>-2 to (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) is incorrect. In almost all cases the AIM algorithm resulted in a combination of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>HSO<sub>4</sub> at various fractions.

Inaccurate quantification of  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{NH}_4\text{HSO}_4$ , seems to affect the volume fraction of  $\text{NH}_4\text{NO}_3$ , as indicated by Eq. (2) and (3). I would encourage the authors to compare their results with the simplified ion-pairing scheme provided by Gysel et al., (2007).

*We compared the simplified ion-pairing scheme provided by Gysel et al. (2007) and the AIM for selected dates chosen for the comparison between AIM and our computation. Between the two approaches, the calculated  $\text{NH}_4\text{NO}_3$  deviates by a maximum of 0.5 % for the beginning of the summer campaign until the end of July; afterwards the deviation reaches values typically around 10 % and up to 25 %. For the winter data the computation with both models exhibits a maximum deviation of 0.5 %. We also made a comparison between our ion pairing scheme and the one provided by Gysel et al. (2007). The results for the summer campaign showed a deviation in the amount of  $\text{NH}_4\text{NO}_3$  always less than 1 % and the resulting growth factor calculated with the assumed masses by the Gysel et al. (2007) ion pairing scheme deviated from our growth factor calculation by 4.7 % in maximum and less than 1 % on average. For the winter campaign the deviation in the amount of  $\text{NH}_4\text{NO}_3$  was less than 1 %. The resulting growth factor computations differ by 1.3 % in maximum, and less than 1 % on average.*

*Apparently, the ion-pairing scheme used in this work and the ion pairing scheme provided by Gysel et al. (2007) yield similar results. Therefore, we suggest keeping the ion-pairing of the HR-AMS measurements used for our data.*

5. The chloride mass concentration is too low, possibly below the noise level of the HR-AMS, for the total period of the campaign. If it is indeed below the noise level, it doesn't make sense to take into account the formation of  $\text{NH}_4\text{Cl}$ . Also some uncertainty ranges should be included in the rest of the estimate mass fractions.

*We calculated the chloride detection limit for both campaigns as 3 times the standard deviation of the chloride concentration during filter measurements. The detection limits were  $10 \text{ ng m}^{-3}$  in summer and  $30 \text{ ng m}^{-3}$  in winter. The average chloride concentrations are  $207 \text{ ng m}^{-3}$  in summer and  $33 \text{ ng m}^{-3}$  in winter. While the average chloride concentration is just above the detection limit for the winter campaign it is well above the detection limit for the summer campaign. Therefore, it seems reasonable to include chloride in the model both for the summer and winter campaigns.*

*It is hard to give a rigorous treatment of all the uncertainties, as they are composed of many parts. The mass fraction estimation is directly related to uncertainties of the mass concentration determination by the AMS plus MAAP. Uncertainties of the MAAP are less than 5 % (Müller et al., 2011). Intercomparison measurements between the AMS have been conducted during the MEGAPOLI campaigns (see Crippa et al., 2013, Figure SI-3 for the winter campaign and Freutel et al., 2013 Table S3 for the summer campaign). For both campaigns, a total uncertainty within 30 % is assumed, including uncertainties of the Ionization Efficiency, the Relative Ionization Efficiency and the Collection Efficiency.*

*These uncertainties are representative of the AMS mass measurements. Moreover, the conversion into a volume fraction adds uncertainties of the density estimates.*

*Additional uncertainties arise from dealing with bulk AMS, MAAP, DMPS concentrations, three different size cut-offs (near-PM1, PM10 and PM0.8) and three different diameter definitions (vacuum aerodynamic diameter, aerodynamic diameter and mobility diameter).*

6. In paragraph 4.2, on page 14308 the authors refer to the correlation between DGF and the mass fractions of the organic and inorganic matter for both seasons (i.e. summer and winter), but in figure 2 they show only the correlation for the summer period. It would be interesting to see the respective correlations for winter as well.

*We included a figure for the winter data and expanded the text in 4.2: "For the winter campaign the linear regression with the equation  $y = -0.36x + 1.47$  yields a value of  $DGF = 1.11$  (Fig. 4b) for the organic fraction." ... "For the winter data we obtained a similar correlation (Fig 4c,d), however, the correlation coefficient  $R=0.57$  was lower than in summer."*

7. Section 4.4: the authors mention here that they evaluate the DGFs of particles having diameter 285 nm because the HDMPS (i.e., the humidified DMPS) scans show a peak around that region. What confuses me is that at 90% RH, this peak corresponds to the droplets already. I would expect that the particle diameter selected to calculate the growth factor would come from the "dry" DMPS (the TDMPS) and not the humidified one. In any case, it would be useful to show some HDMPS and TDMPS scans together so that the readers get a better feeling of what's been measured and how this is translated to DGF.

*We tried to make it clearer and changed the sentence in the manuscript: "The reason for this is a maximum of the growth factor within the measurement range of the HDMPS directly below a diameter of 300 nm. Thus, this diameter range is most representative for the growth factor of submicron particles. The maximum becomes obvious in Fig. 6." - The diameters shown in figure 6 are related to the dry size distribution and the figure signifies with the DGF for which value a particle in this size range grows with humidification.*

*The humidified mass distributions depicted below also underline the choice of 285 nm. Looking at different mass distributions during one sample day the peak of aerosol mass is located around the chosen range. Therefore, 285 nm particles are representative for the growth factor of PM1. Additionally, at larger diameters uncertainties associated with the growth factors are higher due to the evaluation method.*

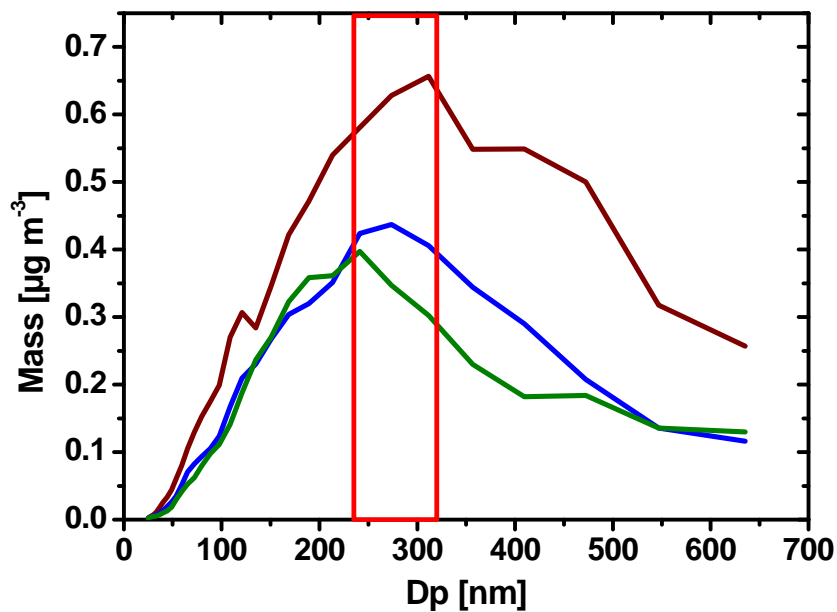


Figure 1: Mass size distributions of humidified samples at a RH of 90 % for a sample day during the summer campaign.

We have also included the figure below in the manuscript and added the following to section 3.1: “One example how the dry and humidified size distributions look like is depicted in Fig. 1. The left side shows theoretical values taken from Nowak (2006). The TDMPS and HDMPs size distributions on the right side are original data measured during the Paris summer campaign.”

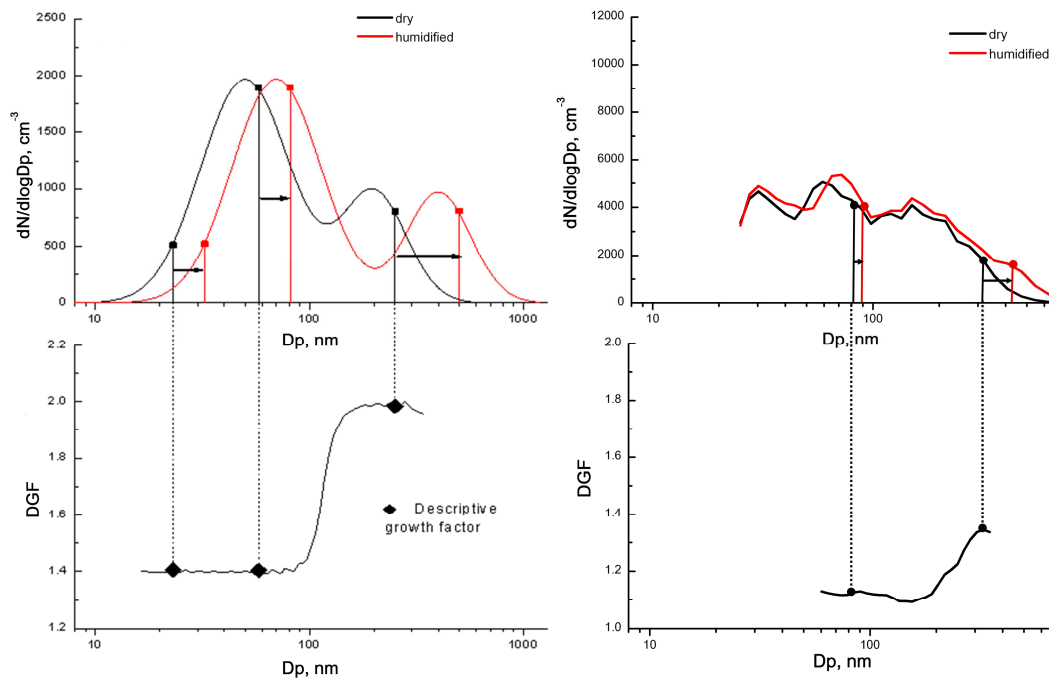


Figure 2 (Figure 1 in manuscript) Dry and humidified size distributions and the corresponding DGF calculated by the summation method. The left side has been adapted from Nowak, 2006. The right side shows data from the Paris summer campaign.

8./ 9. In section 4.5, the authors try to explain the possible causes of the deviations observed between the measured and the predicted (i.e. using the chemical measurements of the HR-AMS) DGFs. While this discussion provides some useful information on the possible causes, it could benefit from a quantitative approach. For example, the effect of having volatile ammonium nitrate could be quantified. In the same section (i.e. 4.5), on page 14314 authors try to approximate the growth factor of the organic fraction. While, the main idea is correct, they end up with an organic growth factor less than unity for the winter period, indicating, that the organic species volatilize inside their experimental setup. I believe, the main cause for this observation is the presence of increased ammonium nitrate volume fractions. The authors should first try to estimate the shrinkage factor due to the presence of ammonium nitrate (or exclude periods with significant fractions of it) before estimating the hygroscopicity of the organic fraction.

*It is hard to quantify how much of the ammonium nitrate gets lost in the system. When the AMS was directly connected to the HDMPs inlet for a short-term measurement, the nitrate concentration dropped by a factor of about 1.5. However, this was just a onetime measurement and does not yield a reliable estimate of potential ammonium nitrate volatilization. As the amount of ammonium nitrate remaining in the particulate phase has such strong temperature dependence and we got no constant difference in temperature between the ambient air and the air in the measuring container or the instruments, the amount of evaporated  $\text{NO}_3$  can vary significantly. As also stated in Wu et al. (2013) who used the same system in their study, the evaporation loss of  $\text{NH}_4\text{NO}_3$  is not known in our system. They excluded data when the volume fraction of  $\text{NH}_4\text{NO}_3$  was above 40 %.*

*To evaluate the potential influence of volatilization of ammonium nitrate, we computed the results of the ZSR under the assumption that all of the  $\text{NH}_4\text{NO}_3$  evaporates in the system, and then compared the time series of the measured and predicted growth factor. The deviation between the two time series decreased from 37.1 % to 25.1 % in maximum for winter and from 27.1 to 16.8 % in summer. The average deviation changed from 8.5 % to 6.7 % for the winter campaign and from 6.5 % to 4.5 % for the summer campaign.*

*We also tried to correlate the absolute  $\text{NO}_3$  mass and the computed growth factor of the organic fraction. For both campaigns it is to say that for higher values of the  $\text{NO}_3$  mass ( $> 3 \mu\text{g m}^{-3}$  for summer and  $> 8 \mu\text{g m}^{-3}$  for winter) the values of the organic growth factor calculated from this correlation are clearly smaller than unity, in some cases even negative. However, this correlation made clear that high nitrate is not the only factor for the discrepancy between measured and predicted growth factor. In some rare cases, the organic GF required to compensate for the difference between measured and computed growth factor is smaller than unity also when the nitrate mass is low.*

Minor points:

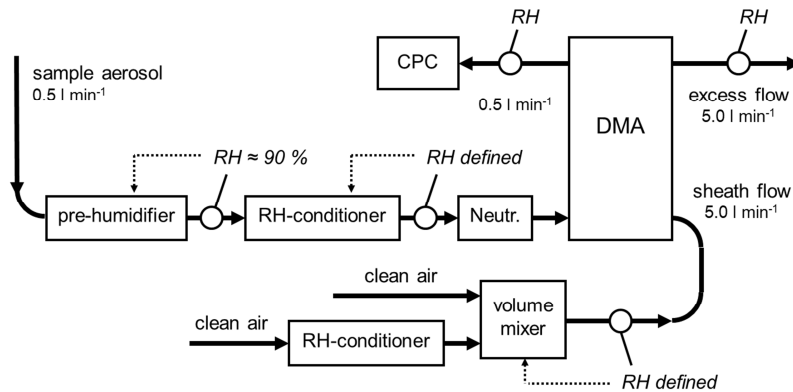
1. Section 2.2: include information of the elevation.

*We included this information in the first sentence of section 2.2:*

*“The measurements were carried out in ... the 13<sup>th</sup> quarter of Paris, a residential and business district in the south-eastern part of the city of Paris, at an elevation of approximately 60 meters above sea level.”*

2. Section 2.3.2 would benefit from a schematic of the experimental apparatus.

We did not include a schematic of the experimental apparatus, but refer to Fig. 2 in Birmili et al. (2009).



3. On page 14310, lines 20 to 26, the authors could provide (if available) the height of the boundary layer above Paris.

We have no detailed information about the boundary layer height, but climatological heights are typically < 1 km during daytime and < 0.5 km at night over Europe and the continental U.S. (Seidel et al., 2012).

4. On page 14311, lines 10 - 12 that read to: "The particles mass concentration which varied from 3 to 18  $\mu\text{g m}^{-3}$  and the concentration of the chemical compound were lower in the first period." needs to be clarified. Mass concentration provided is based on HR-AMS measurements?

The provided mass concentration is based on the TDMPS as a sum of particle mass from particles ranging from 3-700 nm. We included this on page 14311 with: "The particle mass concentration, which is based on TDMPS data applying a density of  $1.6 \text{ g cm}^{-3}$ ,..."

5. Figures 2 and 5, lack of RH information. Authors should mention the RH at which the DGFs, shown in the figures, were measured.

The figures show results at an RH of 90%. We included this in the figure captions.

6. Figures 4 and 5 should be swapped to follow the discussion in the text. Are the DGF shown in fig 5 are estimated by the HDMPs/TDMPS measurements or estimated based on the AMS data? Make this point clear so that confusion is avoided.

You are right, figure 5 has been mentioned before figure 4, so we swapped it. As DGF is always obtained from the coupled TDMPS/HDMPs measurements, the growth factors depicted in Figure 5 are obtained at a relative humidity of 90% by the physical measurement instruments. We added this information in the figure caption: "Growth factor distributions with the mean DGF and 0.1 and 0.9 quantiles in four periods in summer (a,b) and winter (c,d) obtained by TDMPS/HDMPs measurements at an RH of 90%."

7. On page 14311, lines 19 -21, the authors speculate that the organic fraction observed during the second period of the measurements is more hygroscopic than the one observed during the first one. One

reason explaining higher particles hygroscopicity during this period could be also the presence of NaCl, as the winds originated from the Atlantic Ocean.

*It is a possibility that NaCl increases the particle hygroscopicity, however, the influence decreases with distance to the ocean. In a study in Sweden by Gustafsson and Franzen (2000), the sea-salt concentration has generally decreased to approximately 20 % of the coastal concentration 50 km inland. The closest distance from Paris to the coast line is approximately 200 km. In the period of interest the trajectories travelled over the Atlantic Ocean and reached the continent in the North West at a point with a distance of about 600 km to Paris. Therefore, the influence of NaCl is considered to be very small.*

8. On page 14311 line 18, a space is missing between the words “salt” and “is”.

*We changed that, thanks.*

9. In section 4.5, on page 14312, lines 20-28 and on page 14313, lines 1-8 the paper could be benefit if some median or average values of the measured and the predicted DGFs were reported together with the correlation coefficients.

*We follow this suggestion and modified the text: “The correlation coefficient of the two time series of measured DGF and calculated GF at 90 % RH is  $R = 0.66$  for the total of the summer campaign (Fig. 8a). The median of the measured DGF has a value of 1.36 and the median of the calculated GF is 1.28.”*

*“The median of the two time series differs for the whole winter campaign by 0.09. While the measured DGF is 1.35, the calculated GF is 1.44.”*

10. Ln 11-13 p 14312: The authors suggest here that the small variability in the estimated DFG is due to the averaging they perform. One could imagine that it is also due to the technique they use which compared to the classical HTDMA method provides more crude results.

*We do not agree. In the 70-350 nm diameter range that we refer to, reliable results are obtained by the summation method. The averaging over long time periods is expected to have the main influence.*

11. Correlation between the measured DGFs and the Black Carbon concentrations would be interesting to include as well.

*As the correlation between the mass of black carbon and the DGF did not add much information (see figure below), except that the DGF and the BC mass are anti-correlated during the summer campaign and that no clear trend is identifiable for the winter campaign, we did not include this figure in the manuscript.*

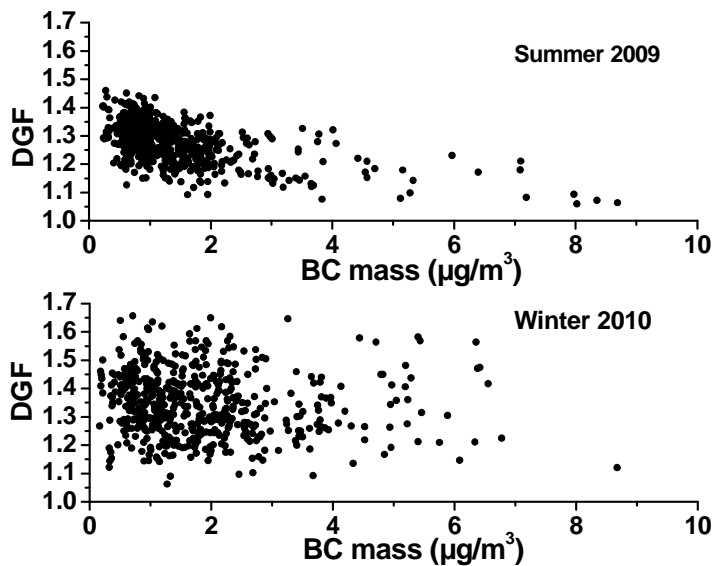


Figure: Correlation between the black carbon (BC) mass and the measured DGF at a relative humidity of 90 %. Linear regression results in  $y=-0.03x+1.32$ ,  $R=-0.55$  for summer and  $y=-0.01x+1.36$ ,  $R=-0.10$  in winter.

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