

Referee #1:

Major comments:

1. Based on Figure 3, all computations were made with ammonium sulfate for summer and ammonium bisulfate for winter. However, later they point out flaws with this assumption/simplification. For example on Page 14314, line 11-12 they state “However, for the end of the campaign the AIM model calculation reached ion balance with ammonium bisulfate in absence of ammonium sulfate. This is in contrast to our original assignment.” As another example, in the conclusions they state that possible reasons for differences between predicted and measured growth factors include ambiguous ion balance calculations. After reading the document I wonder why they have used such a simplification for ion balance? Some other recent papers on a similar topic do not appear to make the same simplification [Hersey et al. ACP, 2009, 9, 2543-2554 and Gysel et al. ACP, 2007, 7, 6131-6144]. Why not use an ion balance that is calculated daily or hourly?

A comparison has been made 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 concentration of NH_4NO_3 always less than 1 % and the resulting growth factor calculated with the assumed masses by the Gysel et al. (2007) ion pairing deviated from our growth factor calculation by 4.7 % in maximum and less than 1 % in the mean value. For the winter and summer campaigns, the deviation in the concentration of NH_4NO_3 is less than 1 %. The resulting growth factor computations differ by 1.3 % in maximum, and less than 1 % for the mean value.

Apparently, the ion-pairing scheme used in this work and the ion pairing scheme provided by Gysel et al. (2007) obtain very convincing and similar results. Therefore, we suggest to keep the general ion-pairing scheme used for our data in the original manuscript.

2. In the conclusions the authors state that a possible reason for differences between predicted and measured growth factors include “evaluation of the descriptive growth factor measurement for a particle diameter of 285 nm in comparison with growth factor calculations using the chemical composition of PM1.” Why didn’t the authors use the chemical composition of 285 nm for the calculations, since I assume this information is available from the AMS. Some other recent papers on a similar topic have used sized resolved chemical composition from the AMS in their calculations [Hersey et al. ACP, 2009, 9, 2543-2554 and Gysel et al. ACP, 2007, 7, 6131-6144 and Aklilu et al. 2006, 40, 2650-26621].

It is true that the AMS can provide size resolved chemical composition that can be used to calculate size resolved HGF. However, this approach was not used due to the following limitations of the data:

- a. no size resolved information are available for black carbon.*
- b. In contrast to the HTDMA, HDMPs is not specifically measuring size selected HGF but the Descriptive hygroscopicity Growth Factor (DGF) based on the estimation of the size distribution difference between dry and wet measurements.*
- c. AMS size resolved data are not available for the summer campaign. Therefore, in order to provide consistent and comparable results for the 2 campaigns, we only consider bulk concentrations in the manuscript.*

3. What size did the authors assume when calculating growth factors? I guess they used a size of 285 nm and used the total mass from the AMS, but this was not absolutely clear from the figures and

tables. For example in Table 1 they indicated a growth factor for 285 nm particles, but in the figure caption for Figure 6 they indicated that the calculated growth factor is for 1 micrometer particles and in the legend for Figure 6 they indicated that the calculation is for PM1, implying < 1 micrometer particles. Please clarify.

The growth factors provided by HDMPS and the summation method were for 285 nm particles, whereas the growth factor calculated from the AMS data used the total mass of the AMS, i.e. approximately the PM1 range. As we had no detailed information about the mass of the chemical compounds at 285 nm, we used the total AMS mass but the theoretical growth factor at 285 nm for each compound for the ZSR computations. We changed the figure caption from 1 μm particles to bulk chemical composition measured by the AMS.

4. On Page 14311, line 10 the authors discussed results for air masses brought from over the Atlantic Ocean to Paris. The modelling/interpretation do not consider NaCl particles. For the uninformed reader, it would be useful to add some discussion on why NaCl particles do not need to be considered.

We have added the following discussion to section 4.4: "When the air masses were brought over the Atlantic Ocean, NaCl is not considered because a minor contribution of sea-salt to PM1 is expected. Moreover, no direct sea-salt measurements in the PM1 range were performed, as the used AMS cannot detect NaCl under normal operating conditions due to vaporization at 600 °C under high vacuum."

5. Page 14313, line 3. "It is remarkable that the measured times series of the DGF shows a much higher variability in winter than in summer. This decreases the correlation coefficient of the wintertime data to $R=0.52$ (Fig.6c)." Is it obvious that a higher variability in the data will lead to a decrease in the correlation coefficient?

We agree, this passage may be unclear to the reader. We try to clarify it by extending the statement: "It is remarkable that the measured time series of the DGF show a much higher variability in winter than in summer. The maximum deviation between the measured and the predicted GF is 37.1 % in winter and 27.1 % in summer. Also, the average value of the deviation of the wintertime data is 8.5 %, and thus higher than in summer with 6.5 %. For the wintertime data, the correlation coefficient is decreased to $R=0.52$ (Fig. 8c)."

6. Page 14310, line 4, "The reason for this is a concentration maximum within the measurement range of the HDMPS directly below a diameter of 300 nm. This maximum becomes obvious in Figure 5." I don't understand this statement, since Figure 5 does not show concentration.

Indeed, Figure 5 does not show concentrations but the DGF. Therefore, we changed the sentence: "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."

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.

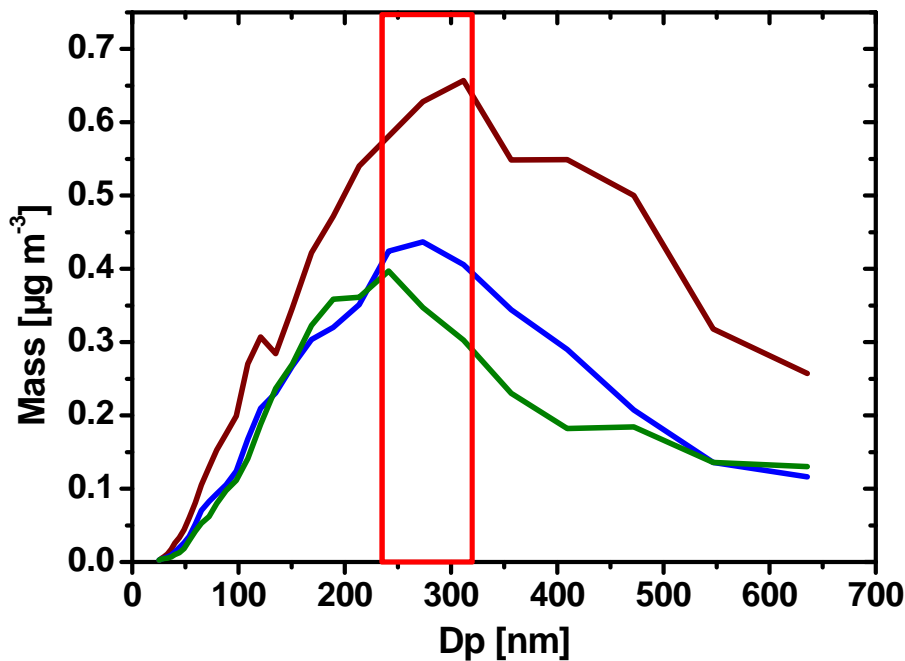


Figure 1: Mass size distributions of humidified samples at an RH of 90 % for a sample day during the summer campaign.

We have also included the figure below in the manuscript and added the following to section 3.1: “One example of 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.”

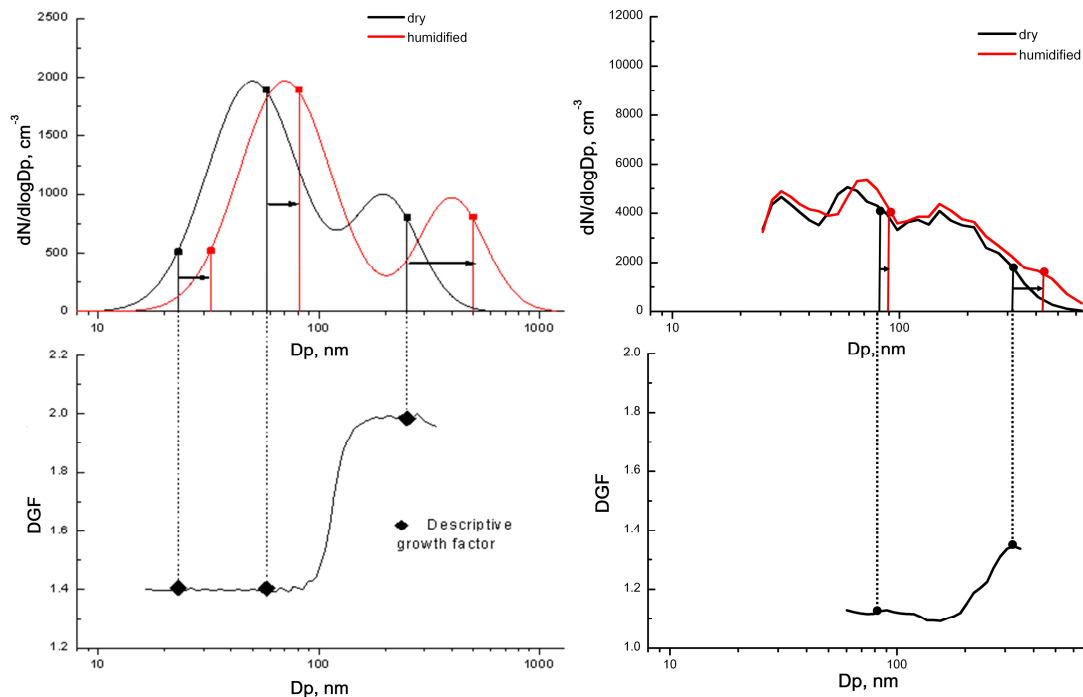


Figure 2 (Figure 1 in manuscript) Dry and humidified size distributions and the corresponding DGF calculated by the summation method. The left side has been adapted from Nowak, 2006. The right side shows data from the Paris summer campaign.

7. It would be very useful to show the size resolved mass spectrum from the AMS so that a reader can see the size distribution for each component.

Unfortunately, there are no size-resolved AMS mass spectra for the summer campaign due to signal problems. Therefore, we chose not to show any size-resolved AMS mass spectra.

8. Page 14312, line 17. "As already mentioned in Section 4.4, the first few days of the summer campaign are different from the rest of the campaign. This is also evident in the DGF measurements of 285 nm particles which show the strongest variation in this time interval (Fig 6a)." When looking at the first few days, I don't see a stronger variation in the data than during other time periods. Please include quantitative statistics.

9. Page 14312, line 18. " Furthermore the deviation of the measured and the calculated DGF is strongest during this period, whereas the rest of the time series fits well if one considers the use of a simplified growth model." Again, when I look at the data the deviation of the measured and calculated DGF doesn't appear to be any worse than the rest of the time series. Please include quantitative statistics.

8./9. We have revised this passage including quantitative statistics: "This is also evident in the strongest deviation of the measured and the calculated DGF during this period (Fig. 8a), which has a mean value of 10.2 % for the beginning of the campaign and 5.4 % when excluding this period. Therefore, the rest of the time series agrees well if one considers the use of a simplified growth model."

10. Figure 2 shows data for the summer. Why not show the same analysis/data for winter?

We have now added a figure for the winter data and expanded the text in 4.2: "As obvious in the temporal patterns of the DGF and the organic mass fraction depicted in Figure 3a and Figure 4a, and the negative regression between the two variables (Fig. 3b, 4b), the DGF and the organic mass fraction are clearly anti-correlated."

"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."

11. The authors state on page 14305, line 26, "as long as no stepwise changes with particle size are observed in the average hygroscopic growth factors, the SM remains valid. In this study stepwise changes were not observed." Please refer to the figure where this is shown (Figure 5?). Also, please give a reference to where it is shown/proven that the assumption is valid as long as no stepwise change with particle size is observed. If this has not been shown/proven in a previous publication (as suggested by the other reviewer) then some proof should be given here.

Actually, our formulation about "stepwise changes" was somewhat misleading. Basically, we assume the summation method to be valid as long as changes in overall hygroscopicity, which includes the two sub-aspects external mixture as well as the absolute value of the growth factor, are modest compared to changes in particle diameter. An extreme case, which would bring the summation method to a certain breakdown, would be a monodisperse particle population on top of a wide size distribution with entirely different hygroscopic properties. Such a breakdown would, in any case, be

seen in a sharp step in the DGF curve resulting from the allocation of number size distribution segments. There are several arguments against such a failure to be relevant in the case of our MEGAPOLI data set:

1) We did not observe sharp steps in any DGF curve resulting from the allocation of number size distribution segments.

2) The overall size-dependent changes in DGF were monotonous, steady, and rather modest during MEGAPOLI, typically increasing from a campaign average 1.1-1.2 at the lower end of the evaluated diameter range around 80 nm to 1.3-1.4 at the upper size distribution end (our Fig. 6).

3) The urban particle number size distributions during MEGAPOLI were flat and without major contours, suggesting the presence of an aerosol mixed from multiple sources, and from sources exhibiting wide particle modes.

4) In a continental aerosol, the particle modes typically exhibit a minimum spread (sigma of 1.4 and larger). In MEGAPOLI, concretely, black carbon was found to exhibit two rather broad modes in the sub- μm range (Healy et al., 2012).

These arguments will hopefully disperse the concerns that have risen during the review of the article.

We accordingly reformulated the text:

“The summation method is assumed to be valid as long as changes in overall hygroscopicity, which includes the two sub-aspects external mixture as well as the absolute value of the growth factor, are modest compared to changes in particle diameter.”

12. At the end of the document they give a few possible explanations for why they have over predicting the growth factor, one possibility being evaporation of ammonium nitrate. Have the authors also considered the possibility of the organic being in a glass state or the possibility of liquid-liquid phase separation?

We did not consider the possibility of the organic being in a glass state or the possibility of liquid-liquid phase. We do not have data to analyze this in detail, and therefore, this is out of the scope of this manuscript

Technical comments:

1. Abstract, line 15. Units are incorrect. Should be m^{-3} .

The fraction bar got lost by the conversion to pdf, but $\mu\text{g m}^{-3}$ is better anyway. We changed that.

2. Page 14299, line 1. “direct and indirect light scattering properties of aerosols” is slightly confusing. Maybe rewrite to “direct and indirect effect of aerosols”?

Agreed. We changed that as recommended.

3. Page 14301, line 21. “well below 30 %” is not precise. It would be more useful to state the range. For example, < 20% RH or < 10% RH.

We changed that to “...kept the relative humidity of the sample flow below 25 %.”

4. Page 14302, line 23. The authors refer to crystalline organics; however, I thought in most cases crystalline organics are not expected. See work by Marcolli et al. JPC, Volume: 108, Issue: 12, Pages: 2216-2224.

Crystalline organics were given as an example for hydrophobic compounds that could be included in the solution droplet after humidification. Sjogren et al. (2007) characterized the hygroscopic growth, in particular, the time required for the aerosol particle phase and the surrounding water vapor to reach equilibrium at high relative humidity, of solid aerosol particles consisting of mixtures of ammonium sulfate and either adipic acid or humic acid sodium salt with a hygroscopicity tandem differential mobility analyzer and an electrodynamic balance.

Adipic acid (AA) was chosen as an organic constituent. AA has a low vapor pressure and is only moderately soluble in water. Pure AA does not show any uptake of water (e.g. $GF = 1.00 \pm 0.02$ up to 96% RH) (Joutsensaari et al., 2001), which was confirmed up to RH 92 % with both HTDMAs and the EDB by Sjogren et al. (2007). AA is considered to be present as a crystalline solid in their study. AA has also been identified in atmospheric samples (Ray & McDow, 2005).

Marcolli et al., 2004 performed solubility and water activity measurements for model systems containing a series of dicarboxylic acids and the inorganic salts. The dicarboxylic acids were divided into the highly soluble malonic, glutaric, malic, maleic, and methylsuccinic acids and the less soluble oxalic, succinic, and adipic acids. Adipic acid was the only exception of these acids that did not partition preferentially into the aqueous phase. Oxalic and succinic acid exhibit low saturation solubilities in water since they form very stable crystalline solids (Marcolli et al., 2004).

So, indeed in most cases organics are not present in crystalline form, but they have been found in atmospheric samples. To prevent misunderstanding we removed the reference to crystalline organics, which was just an example.

5. Figure 6, Panels b and d. In these panels the data are divided into high NO_x and low NO_x, implying the authors have applied a filter to separate ALL high NO_x from ALL low NO_x. But on line 5, page 14313, the authors indicate that that they use the dates Jan 23-29 and Feb 6-15 for high NO_x. I suggest changing the legend slightly to be more consistent with what is plotted. Instead of indicating high NO_x, change to something like Jan 23-29 (high NO_x conditions). Alternatively the authors could include in the figure caption exactly what they mean by high NO_x (i.e. Jan 23-29 and Feb 6-15).

Agreed. The high NO_x periods are now indicated by date in the legend and the figure caption labels read: "Red dots in the scatter plots denote periods under high NO_x conditions."

Also a small supplement on page 14313 has been added: "Just like in summer, the correlation between measured and calculated growth factor improves from $R = 0.52$ to $R = 0.63$ if these periods (indicated in red in Fig. 8d) are not taken into account."

6. Page 14314, line 29. Indicate the RH for the growth factors of the organics.

We included this information: "The median growth factor of organics for a relative humidity of 90 % was 1.06 in summer..."

7. Page 14311, line 18. Typo. "saltsis".

Thanks for that correction.

8. Several of the figures were hard to read due to the small size of the axis labels and annotations.

We revised Figures 2, 3, 6 (Figures 3, 5, 8 appropriate to the new numbering) for better readability.

References:

Joutsensaari, J., Vaattovaara, P., Vesterinen, M., Hämeri, K., & Laaksonen, A.: A novel tandem differential mobility analyzer with organic vapor treatment of aerosol particles. *Atmospheric Chemistry and Physics*, 1, 51–60, 2001.

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Ray, J., & McDow, S. R.: Dicarboxylic acid concentration trends and sampling artifacts. *Atmospheric Environment*, 39(40), 7906–7919, 2005.

Sjogren, S., Gysel, M., Weingartner, E., Baltensperger, U., Cubison, M. J., Coe, H., Zardini, A. A., Marcolli, C., Krieger, U. R., and Peter, T.: Hygroscopic growth and water uptake kinetics of two-phase aerosol particles consisting of ammonium sulphate, adipic and humic acid mixtures, *J. Aerosol Sci.*, 38, 157–171, 2007.