

Interactive comment on “Hygroscopic properties of the Paris urban aerosol in relation to its chemical composition” by K. A. Kamilli et al.

Anonymous Referee #3

Received and published: 26 July 2013

This manuscript reports hygroscopicity and chemical composition measurements for particles having diameters from 25 to 350 nm observed in the city of Paris. The hygroscopic behavior of the particles was investigated at 30, 55, 75 and 90% relative humidity (RH) using a Humidified Differential Mobility Particle Sizer (HDMPS), while their chemical composition was measured by a High Resolution Aerosol Mass Spectrometer (HR-AMS). Below are some major and minor points that need further clarification in my opinion.

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

C5185

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.

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.

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 SO₄-2 to (NH₄)₂SO₄) is incorrect. In almost all cases the AIM algorithm resulted in a combination of (NH₄)₂SO₄ and NH₄HSO₄ at various fractions. Inaccurate quantification of (NH₄)₂SO₄ or NH₄HSO₄, seems to affect the volume fraction of NH₄NO₃, 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).

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 NH₄Cl. Also some uncertainty ranges should be included in the rest of the estimate mass fractions.

C5186

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.

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.

8. 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.

9. 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.

Minor points

1. Section 2.2: include information of the elevation.

C5187

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

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

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 compounds were lower in the first period." needs to be clarified. Mass concentration provided is based on HR-AMS measurements?

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

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.

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.

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

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.

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.

C5188

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

Reference: Gysel, M., Crosier, J., Topping, D.O., Whitehead, J.D., Bower, K.N., Cubison, J.M., Williams, P.I., Flynn, M.J., McFiggans, G.B., Coe, H.: Closure study between chemical composition and hygroscopic growth of aerosol particles during TORCH2, *Atmospheric Chemistry and Physics*, 7, 6131-6144, 2007. (www.atmos-chem-phys.net/7/6131/2007/)

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 13, 14297, 2013.