

1 Supplementary Information for manuscript

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3 **Hygroscopic properties of the Paris urban aerosol in** 4 **relation to its chemical composition**

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6 **K. A. Kamilli^{1,*}, L. Poulain¹, A. Held^{1*}, A. Nowak^{1,#}, W. Birmili¹ and A.**
7 **Wiedensohler¹**

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9 [1]{Leibniz-Institute for Tropospheric Research, Leipzig, Germany}

10 [*]{now at: University of Bayreuth, Bayreuth Center of Ecology and Environmental
11 Research, Bayreuth, Germany}

12 [#]{now at: Physikalisch-Technische Bundesanstalt, Braunschweig, Germany}

13 Correspondence to: K. Kamilli (katharina.kamilli@uni-bayreuth.de)

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15 Validation of the H-DMPS/summation method:

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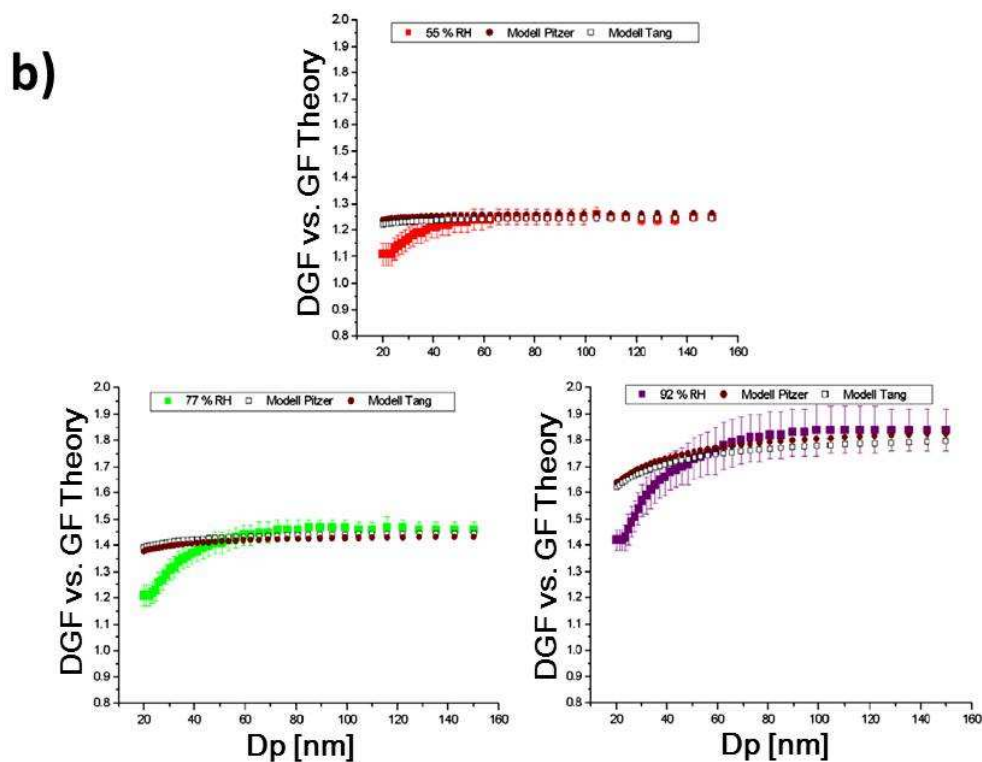
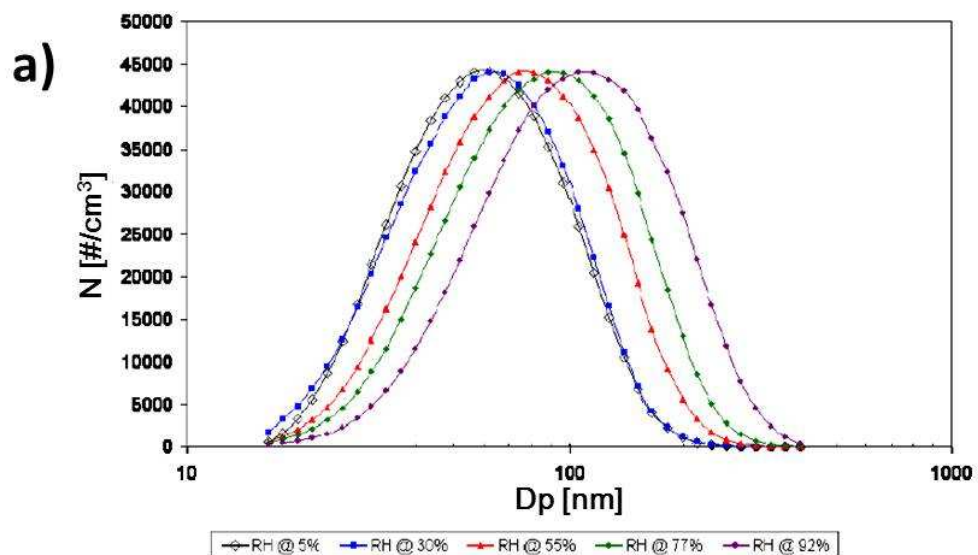
17 Figure S1 and S2 illustrate the verification of the H-DMPS/summation method for ammonium
18 sulphate and sodium chloride. These experiments were conducted in the laboratory. Results
19 obtained by the summation method were compared to calculations from two solubility models
20 (“Pitzer” and “Tang”). – based on Tang and Munkelwitz (1994). As can be seen for RH =
21 92%, the H-DMPS/summation method agrees with the theoretical calculations within +/- 0.05
22 for dry diameters > 50 nm. Below 50 nm, larger deviations were found, most likely due to a
23 mis-balance in particle number concentration between the H-DMPS and the dry DMPS.

24 Figure S3 illustrates a comparison of H-DMPS/summation method vs. H-TDMA growth
25 factors, again using ammonium sulphate test aerosol under laboratory conditions. An inter-
26 instrumental comparison for RH = 88% basically confirmed an agreement of both methods
27 within +/- 0.05 in hygroscopic growth factor.

28 As regards comparisons with the H-TDMA for ambient aerosols, there are rather few data
29 available. Figure S4 shows a comparison of H-DMPS/summation method vs. H-TDMA
30 growth factors using ambient atmospheric aerosols during the FEBUKO field experiment

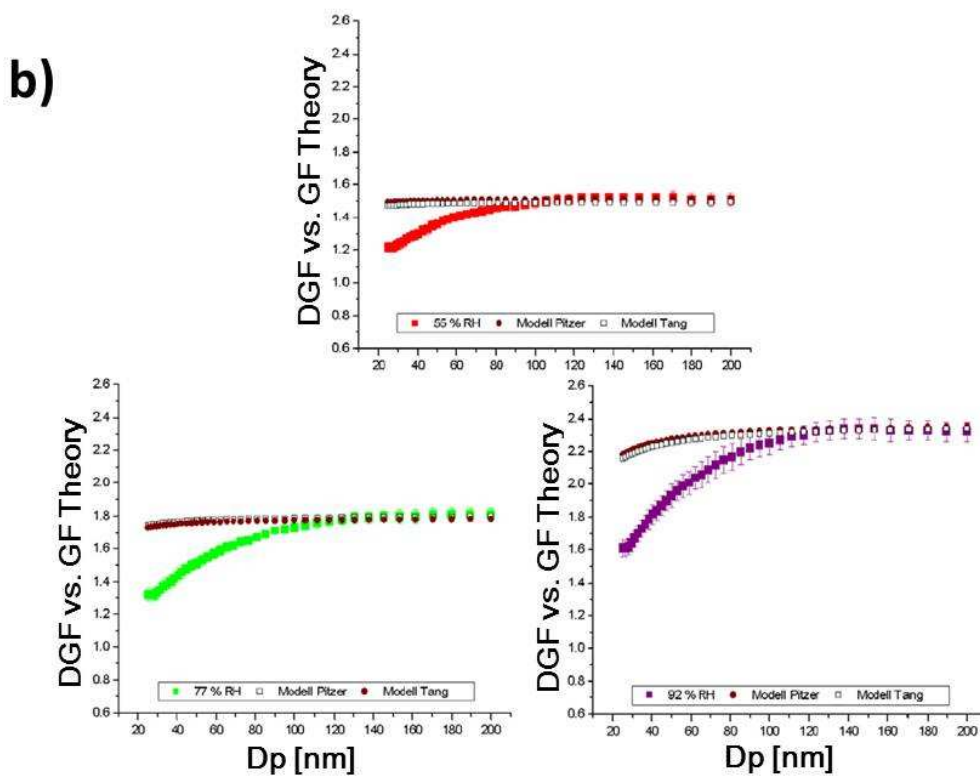
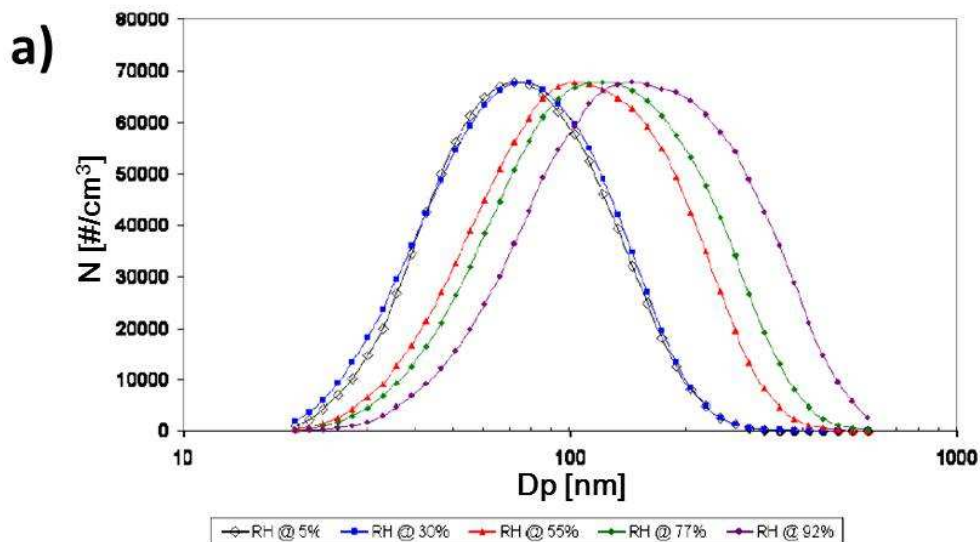
1 (Herrmann et al., 2005). These data are now quite old and still relate to a premature version of
2 the H-DMPS. At the time of measurement, the temperature regulation of the H-DMPS was
3 less accurate, and the instrument was not yet optimized for particle losses. This is likely one
4 of the reasons why Figure S4 showed larger deviations in DGF between the instruments than
5 the previous Figures.

6 In summary, we believe that the H-DMPS/summation method is a valid method, and useful to
7 derive hygroscopic growth factors of ambient aerosols. Nevertheless, we also acknowledge
8 the limited accuracy of the method, particularly in the diameter range below 50 nm.
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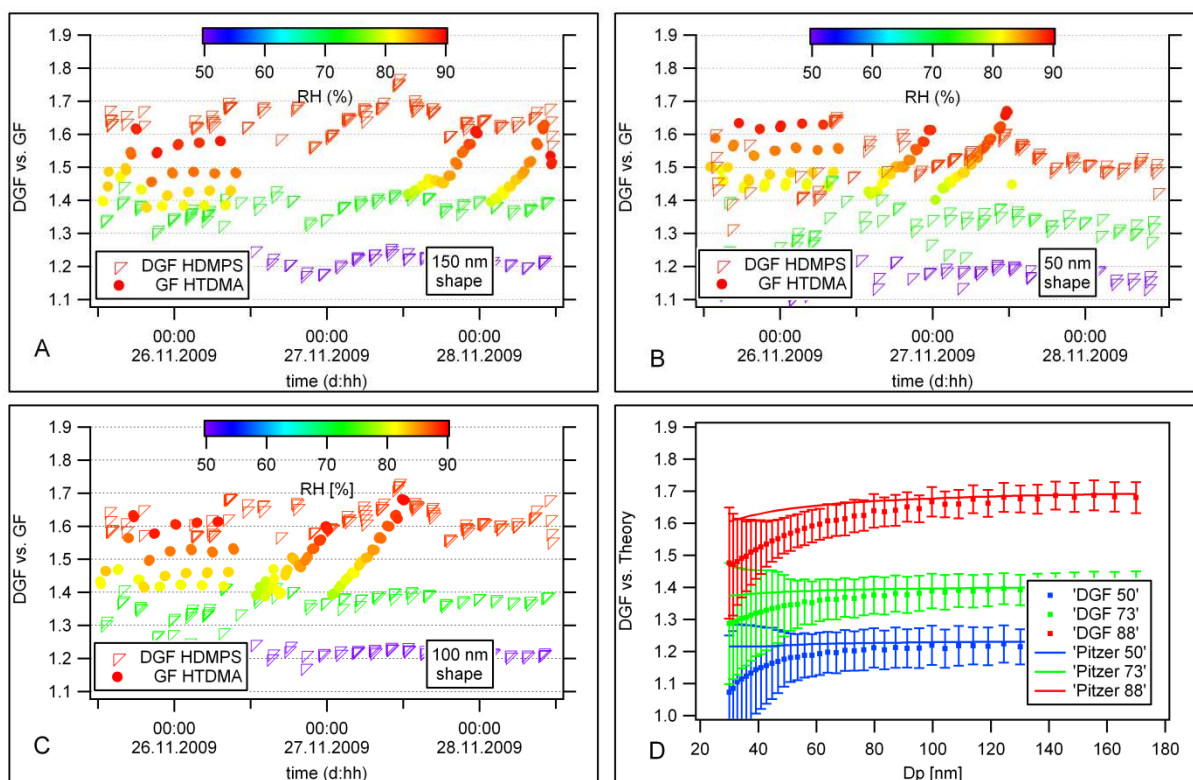
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Figure S1: Verification of the H-DMPS/summation method for ammonium sulphate particles:
 a) Particle number size distributions concentration measured by the dry DMPS (black; RH < 2 %) and the humidifying DMPS (coloured; 30 % < RH < 92 %). b) Size-dependent DGF obtained by using the summation method. Figure S1b includes calculations from two solubility models: “Pitzer” - based on Pitzer et al. (1973) and Pitzer and Mayorga (1973) (see also Brechtel and Kreidenweis, 2000), and “Tang” – based on Tang and Munkelwitz (1994). As can be seen for RH = 92%, the H-DMPS/summation method agrees with the theoretical calculations within +/- 0.05 for dry diameters > 50 nm.



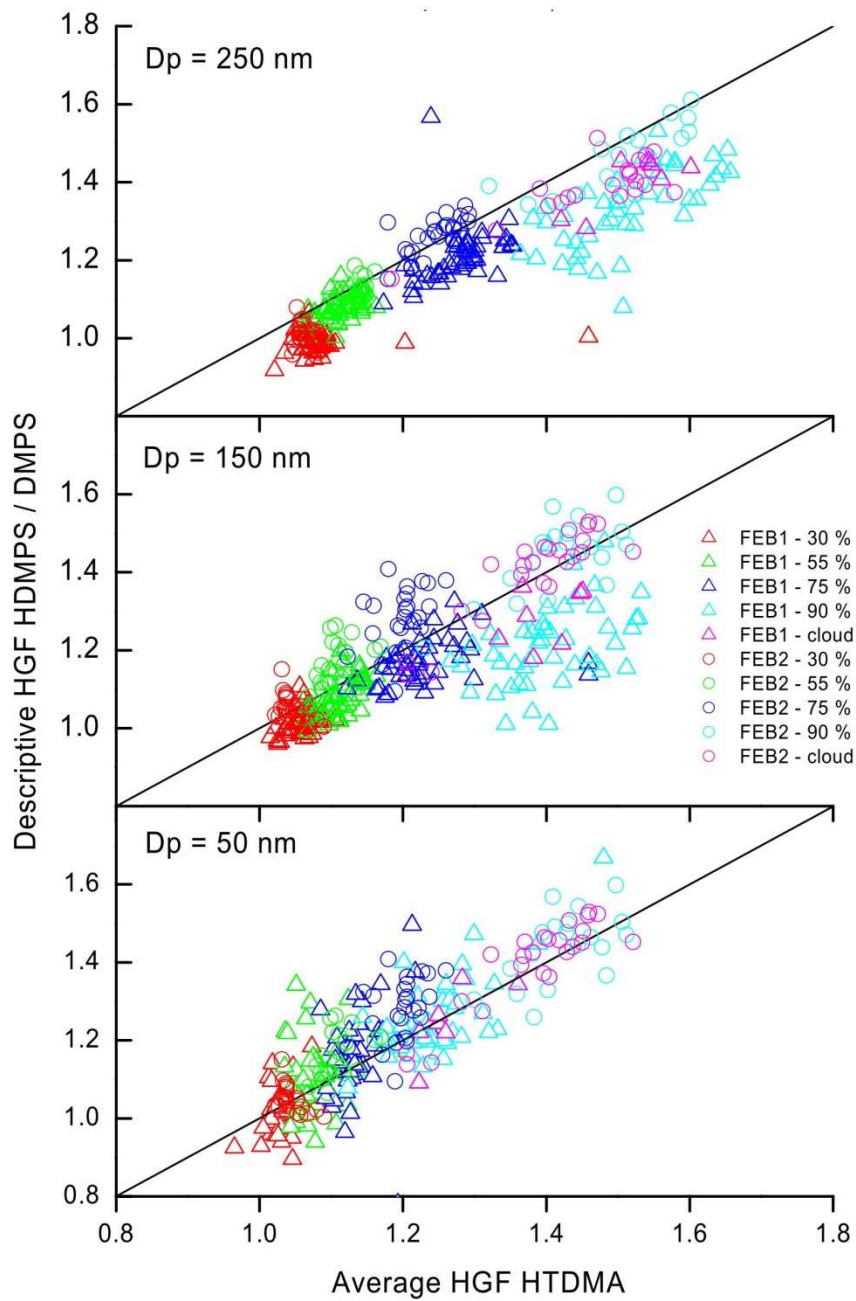
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3 Figure S2: Verification of the H-DMPS/summation method for sodium chloride particles:
 4 a) Particle number size distributions concentration measured by the dry DMPS (black; RH <
 5 2 %) and the humidifying DMPS (coloured; 30 % < RH < 92 %). b) Size-dependent DGF
 6 obtained by using the summation method. Figure S1b includes calculations from two solubility
 7 models: “Pitzer” - based on Pitzer et al. (1973) and Pitzer and Mayorga (1973) (see also
 8 Brechtel and Kreidenweis, 2000), and “Tang” – based on Tang and Munkelwitz (1994).
 9 As can be seen for RH = 92%, the H-DMPS/summation method agrees with the theoretical
 10 calculations within +/- 0.05 for dry diameters > 50 nm.



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Figure S3: Comparison of H-DMPS/summation method vs. H-TDMA growth factors using ammonium sulphate test aerosol. The sub-figures illustrate DGF for a) 150 nm particles, b) 50 nm particles, c) 100 nm particles. Triangles mark DGF by the H-DMPS/summation method, while circles mark average GF derived from the H-TDMA instrument. Inter-instrumental comparison can be made for RH = 88% (red symbols). For the dry diameters 100 and 150 nm, the comparison basically confirms an agreement of ± 0.05 in hygroscopic growth factor. Figure d) shows, as in Fig. S1 and S2, a comparison against the “Pitzer” solubility model.



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3 Figure S4: Comparison of H-DMPS/summation method vs. H-TDMA growth factors when
 4 using ambient aerosol. These unpublished data were measured over the course of the
 5 FEBUKO field experiment (2001 and 2002; Herrmann et al., 2005).

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1 References

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3 Brechtel, F. J. und S. M. Kreidenweis (2000). Predicting particle critical supersaturation from
4 hygroscopic growth measurements in the humidified TDMA. Part I: Theory and sensitivity
5 studies. *Journal of the Atmospheric Sciences*. 57: 1854-1871.

6

7 Herrmann, H., R. Wolke, K. Mueller, E. Brüggemann, T. Gnauk, P. Barzagli, S. Mertes, K.
8 Lehmann, A. Massling, W. Birmili, A. Wiedensohler et al. (2005) FEBUKO and MODMEP:
9 Field measurements and modelling of aerosol and cloud multiphase processes. *Atmos. Env.*
10 39: 4169-4183.

11

12 Pitzer, K. S. (1973). "Thermodynamics of electrolytes. I. Theoretical basis and general
13 equations." *J.Phys.Chem.* 77: 268-277.

14

15 Pitzer, K. S. and G. Mayorga (1973). "Thermodynamics of electrolytes. II. Activity and
16 osmotic coefficients for strong electrolytes with one or both ions univalent." *J.Phys.Chem.* 77:
17 2300-2308.

18

19 Tang, I.N. and Munkelwitz, H.R. (1994): Water activities, densities and refractive indices of
20 aqueous sulfates and sodium nitrate droplets of atmospheric importance, *J. Geophys. Res.*,
21 99, 18 801–18 808.