

Interactive comment on “Hygroscopic properties of water-soluble matter and humic-like organics in atmospheric fine aerosol” by M. Gysel et al.

M. Gysel et al.

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First of all, we would like to thank the two anonymous referees and U. Pöschl for their valuable comments on our ACPD manuscript. We believe that their comments have helped substantially to improve the quality of the revised manuscript. Below we first provide general answers to issues addressed by both referees and U. Pöschl, and the specific remarks/comments will be answered on a point by point basis afterwards.

Seasonal representativity of investigated samples:

A detailed discussion of the meteorological conditions during sampling and the chemical properties of these samples compared to earlier measurements will be provided by Galambos et al. (2003). The sampling time was 7–9 days for each sample, during which air masses of different origin reached the station. The regional whether was also

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typical for the seasons in terms of temperature, relative humidity, solar radiation, etc. Samples from January to September were previously collected and analysed by Kiss et al. (2002). These samples showed significant chemical similarity in terms of UV absorption spectra, fluorescence spectra, FTIR spectra and elemental composition, although the ratio of isolated and non-isolated organic matter varied throughout the year. The present samples showed also a high degree of similarity to the earlier samples in many aspects. In summary, the present samples are considered to be representative in terms of chemical properties. However, small differences observed between investigated summer and winter samples cannot be definitely attributed to the seasonal influence based on the number of investigated samples. The paper has been completed with corresponding statements, whereas a detailed discussion of chemical analysis results will be presented by Galambos et al. (2003).

Clarity of results section:

When reading the results section again with the reviewer's comments in mind, it is understandable that the relevance of results with respect to the atmosphere and experimental issues was sometimes not emphasized, and that not all results presented in figures and tables were discussed in enough detail. Mainly Sect. 4.2 has been completely revised in order to eliminate these deficiencies. This includes among other things an extra section for the hygroscopicity closure, removal of some curves in Figures 6 and 7, and declaration of the calculation of the numbers in Table 3 in more detail.

Anonymous Referee #1

General comments referee #1:

See above and answers to specific comments.

Specific comments (scientific) referee #1:

1.
See general answer about the representativity of investigated samples above.

2.
Pure MilliQ-water was nebulized in order to investigate possible contamination. These tests revealed that there was no significant contamination from the MilliQ-water:
- There were no particles of the size (100 nm) selected for the H-TDMA measurements.
- There were some small particles ($D < 20$ nm) but less than 1% and 0.1% in terms of number and volume, respectively, compared to the aerosol generated from sample solution.

3.
Details about isolation procedures and chemical properties of humic substances may be found on IHSS's homepage (<http://www.ihss.gatech.edu/>). Previous studies by Krivácsy et al. (2001), Varga et al. (2001) and Kiss et al. (2002) at different sampling sites revealed that the isolated organic matter mainly consists of humic-like substances (see Introduction).

4.
The purpose of these three models is given in the first paragraph of the section "Theory".

5.
We agree that the organic compounds are likely to lower the surface tension of the solution droplets (e.g. Kiss et al., 2003b). However, we do not know whether the solution surface tension is more or less than half the value of pure water. We decided

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to use the value of pure water, but the sensitivity to a 50% surface tension reduction is discussed in Sect. 4.6.

6.

Yes, the dry particles most probably have a range of shape factors. This fact is also supposed to be responsible for the broadening during deliquescence where all particles end up with the same shape factor. The shape factors of dry particles depend on the conditions during particle dehydration in the diffusion dryer (see Sect. 3.4; detailed studies on this topic may be found in the recent paper by Mikhailov et al., Atmos. Chem. Phys. Discuss., 3, 4755-4832, 2003), and hence they may be different in the ambient aerosol. That is why we consider these uncommon hysteresis and shape effects to be only a side result of this study. Nevertheless we present them, because they are needed for two different reasons: First, to find the best possible reference diameter for the growth factors and to identify the deliquescence transition, which is of much greater atmospheric importance. Second these effects are a potential source of discrepancies between different measurement techniques.

Specific comments (editorial) referee #1:

1.

We are aware of the fact that lot's of acronyms are used. The major reason for that is that not the whole water-soluble organic matter may be isolated from the inorganic ions and hence the water-soluble organic matter splits further in the so-called isolated organic matter and the most hydrophilic organic matter, according to available experimental techniques. Whenever possible we tried to use standard acronyms, but we used e.g. WSOM instead of WSOC in order to emphasize the difference between water-soluble organic matter and water-soluble organic carbon. The main purpose of Fig. 1 is to provide a visualization of all compound classes and subclasses, which should help for the reader's guidance. We did not write out the words in full since we

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believe that the use of acronyms marks more clearly which compound class is meant.

2.

Figure 1 is sorted with respect to compound classes but not in order of hygroscopicity. It is mainly intended as a guidance for the reader (see comment above), and it shows the average chemical composition of all investigated samples. The figure caption has been updated.

We will, according to the reviewer's suggestion, remove Fig. 2 from the revised paper. Figure 3 is intended to be a sketch of the H-TDMA showing only the major instrument parts, since a detailed instrument illustration and description may be found in Weingartner et al. (2002). The instrument modes shown in Fig. 4 are discussed in detail in the text (p. 4886, line 9 and following). However, Figs. 3 and 4 including their captions have been modified.

3.

The sample labels are not cryptic 8-character computer codes. They indicate the sampling site and sampling date (\Rightarrow it should be clear which are summer and winter samples) as defined in both Sect. 2.1 and the glossary. Section 4.2 will be completely revised, and some curves from Figs. 6 and 7 will be removed from the revised manuscript in order to emphasize the major results and to improve the readability of this section.

4.

The growth curves in Figs. 5 and 7 (summer) show nearly continuous water uptake starting at low RH, whereas a more pronounced deliquescence transition can be seen in Fig. 6 (winter). The references to the Figures were not well-placed in the original sentence. This has been improved in the revised paper.

5.

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Which model is used, is mentioned one sentence above.

6.

The term “excess water” is defined in the introduction, but we will repeat it at this position.

7.

Main results of this study like the hygroscopic behaviour of atmospheric WSM and ISOM samples, the hygroscopicity closure for the WSM samples, and possible effects of the organics on the deliquescence behaviour of mixed particles are discussed in Sect. 4.2. An extra section for the hygroscopicity closure will be introduced and the text will be revised in order to make that more clear.

8.

Figure 8a–d (discussed in Sect.4.3) shows that there are qualitative similarities between the hygroscopic behaviour (growth factors and deliquescence) of ISOM and humic reference substances, but that there are quantitative differences. The interpretation of the σ values and of the restructuring (Fig. 8e–h) is discussed in Sects. 4.4 and 4.5, respectively.

9.

A brief summary of Sect. 4.4 and our rating in terms of experimental and atmospheric importance is already given in the conclusions section (p. 4904, lines 22–25).

Anonymous Referee #2

General comments referee #2:

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1.

The major reason for the high accuracy of mobility growth factors obtained with this instrument is the use of critical orifices to control the sheath air flow rates. We are confident that the accuracy in terms of electrical mobility diameters is as indicated (± 0.003) and that the effects discussed in sections 4.4 and 4.5 are not an instrument artefact for several reasons:

- Measurements of the sheath/excess air flow rate indicate stability better than $\pm 0.5\%$, which translates into a growth factor accuracy better than ± 0.003 .
- Measurements of the dry diameter (i.e. no humidification) confirm the instrument stability over days.

It can also be excluded that observed deliquescence and restructuring effects are a humidification artefact for the following reasons:

- The growth curves for these samples were highly reproducible.
- The effects differ from sample to sample.
- Measurements during other campaigns with non-hygroscopic soot particles revealed growth factors equal to 1.000 ± 0.001 up to high RH.

The accuracy as provided here is only valid for growth factors in terms of electrical mobility diameters. Larger uncertainty arising from particle shape effects is introduced as soon as electrical mobility diameters are converted to volume equivalent diameters, as the results discussed in Sects. 4.4 and 4.5 showed. A more precise statement will be included in the experimental section.

2.

Measurements with pure inorganic salts conducted at $T = 20$ and -10 °C showed good agreement with theory (Gysel et al., *Env. Sci. Technol.*, 36, 63-68, 2002). A corresponding statement will be included in the experimental section. As mentioned above, the major uncertainty is the relationship between electrical mobility diameter (measured) and volume equivalent diameter (theory).

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3.
See general answer about the representativity of investigated samples above.

Specific comments referee #2:

1.
The aerosol was dried to $RH < 5\%$. This is a typing error which crepted in with the proof corrections.

2.
Approximate residence times in the instrument are 3 s after the prehumidifier, 5 s after the RH-conditioner, and 8 s in DMA2. These numbers are provided in the revised paper.

3.
See general answer about the representativity of investigated samples above.

4.
We agree with the referee, that the size reduction at low RH is probably caused by microstructural rearrangement of the particles as observed in earlier studies for e.g. pure NaCl. However, the presence of organics with low deliquescence RH in the mixed particles might induce this rearrangement at lower RH compared to pure NaCl particles. The corresponding statement will be revised.

5.
Yes, the investigated WSM particles have an average composition of the water-soluble matter of the K-pusztá fine aerosol (see e.g. experimental section). The original ambient aerosol might have been externally mixed containing particles with varying organic/inorganic composition, and hence also varying hygroscopic behaviour. How-

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ever, measurements at the research station Jungfraujoch revealed, that the aged free tropospheric aerosol encountered at this high-alpine station is internally mixed regarding its hygroscopic properties (Weingartner et al., 2002). This point has been highlighted in the revised paper. Possible effects of these ambient organics are nevertheless of interest, since the knowledge about substances that might hinder deliquescence/efflorescence in ambient particles is still poor.

6.

First of all we can rule out insufficient instrument accuracy (see reply to first general comment). Residence time effects could explain too small growth factors in case of particles with delayed growth, but not decreasing growth factors with increasing RH.

The question remains if this size decrease at intermediate RH values is just caused by microstructural rearrangement or by deliquescence (including microstructural rearrangement)? There are mainly two reasons making us believe that it is deliquescence:

- Concluding from the continuous evaporation under decreasing RH conditions, particles are most probably liquid solution droplets once they were exposed to high RH. Accordingly, the size decrease is attributed to deliquescence.

- The size decrease of these particles occurs at a relatively well defined RH, as it is typical for deliquescence transitions, whereas the microstructural rearrangement of pure NaCl particles occurs over a wide RH range.

Section 4.4 will be rearranged, i.e. the arguments which make us believe that it is deliquescence are explained before this transition is called deliquescence.

7.

Details on the humidification may be found in the technical paper about this instrument by Weingartner et al. (2002). It is well possible that individual particles see slightly different RH in the humidifier (aerosol flows through Gore-Tex tubing with external humidification flow in opposite direction), but after that the sample flow is slightly cooled resulting in a slight RH increase. This guarantees that (in the increasing

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RH mode) the particles are exposed to highest RH values in DMA2 were the size measurement is done. The humidification process can be ruled out as a source of the stepwise broadening since:

- the RH where broadening occurs is reproducible for each sample, but different between individual samples, and
- σ is constant above and below deliquescence under increasing RH conditions, and over the whole RH range under decreasing RH conditions.

Larger particles with multiple charges could indeed cause a broadening. However, the dry diameter was selected above the maximum of the number size distribution produced by the nebulizer in order to minimise these effects. In addition, a broadening caused by particles with multiple charges would mainly occur with increasing growth factors and not stepwise at a certain RH.

8.

The γ values obtained in this study for the WSM samples are slightly smaller than values reported by Weingartner et al. (2000) for the free tropospheric aerosol encountered at the high alpine research station Jungfraujoch (Switzerland, 3580 m above sea level), in agreement with the fact, that atmospheric ageing processes tend to increase particle hygroscopicity. Swietlicki et al. (2000) and Massling et al. (2003) reported considerably larger γ values for clean marine aerosol, which is known to be strongly hygroscopic. However, one has to keep in mind that γ values reported here describe the hygroscopicity of the mean water-soluble aerosol fraction of $PM_{1.5}$, i.e. the original aerosol including the water-insoluble aerosol fraction was somewhat less hygroscopic. γ values for the original ambient aerosol should better be determined with direct in situ measurements. We do not include this comparison since the main goal of this paper was to characterise the hygroscopicity of the organic aerosol fraction and to determine its contribution to hygroscopic growth.

9.

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The sampling period was 7–9 days for each sample. Details about the meteorological situation etc. will be provided by Galambos et al. (2003). See also general answer about the representativity of the samples.

Technical corrections referee #2:

1.

In fact, Figures 6 and 7 are already mentioned in Sect. 3. However, Figure 5 is discussed before Figures 6 and 7 in the Results section.

2.

Equation 9 should read:

$$f = g_{decr}(RH_{DMA2} \leq 5\%) \equiv g_{restr}(RH_P \geq 95\%)$$

We missed this error in the proofs.

3.

The Figures will be converted to multicolour.

4.

There are two options for Fig. 8: Either one figure showing the results for all four samples or individual figures for each sample. Despite the drawback of a very compact design we chose the first option since it makes the direct comparison of similarities and differences between samples possible. Figure 8 will be made as large as possible and colouring should also improve the clarity.

Comment by U. Pöschl

Specific comments:

1.

See general reply above.

2.

After submission of our manuscript we realized by our own that the terms “hydration” and “dehydration” are more concise than “increasing RH” and “decreasing RH” and hence we will replace them throughout the whole paper. We also use the terms “effective molar volume of solute molecules” and “effective molar mass” since we agree that they are more appropriate.

3.

Models for hygroscopic growth: Meanwhile we have compared the growth of ISOM, fulvic acid and humic acid with model calculations using the osmotic coefficient parameterisation for globular macromolecules (Mikhailov et al., 2003) according to the suggestion by U. Pöschl. Growth curves obtained with this model (effective molar mass as a free parameter) did not match experimentally observed growth curves over the whole RH range. Resulting effective molar mass estimates hence depend considerably on the RH range chosen for the fitting process. Obtained effective molar mass estimates are about a factor of 1.5 higher for ISOM and nearly an order of magnitude higher for NRHA compared to estimates from the ideal solution model. These findings indicate that effective molar mass estimates obtained with the ideal solution model are possibly biased towards low values, whereas this effect becomes more important for large molecules, in particular for NRHA. An extra paragraph will be included in Sect. 4.6.

Restructuring effects: While restructuring effects have to be considered for data analysis, it was not a goal of this study to investigate the influence of particle generation on restructuring effects during particle hydration in detail.

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4.

We fully agree with U. Pöschl that it would be desirable to investigate hygroscopic properties of the MHOM in order to complete the hygroscopicity closure and to learn more about the suitability of the ZSR-relation for mixed inorganic/organic aerosols. However, the MHOM was not available for this study. The isolation of the whole water-soluble organic matter from the inorganic aerosol fraction should hence be a goal of further developments in chemical isolation techniques.

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