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

Anonymous Referee #1

Received and published: 11 November 2003

General comments:

This paper describes some interesting improvements in methodology for using TDMA measurements for studying the effects of water uptake and loss on aerosol particles. The work appears to be have been done with great care and thoroughness. However, it is difficult to extract the content of the paper since it is unfocussed and not very well written. I can't tell what the major results are supposed to be. The most interesting part to me were the results in section 4.4, but I remain unsure about how significant they might be. And they don't seem to be mentioned in the abstract and conclusions.

Specific comment (scientific):

Only four samples were analyzed. I realize that the TDMA procedure is elaborate and it would be difficult to do a full TDMA analysis of a large number of samples. But surely

there are chemical analyses available for a larger number of samples. Were the ones used for the TDMA typical?

I am a little concerned about the aerosol generation procedure. Milli-Q systems are very good at removing ions, but they tend to contaminate the water with organic material from the exchange resins. Were any blanks or calibration standards done to test for possible contamination?

Comparisons are made to model systems containing "humic acids" and "fulvic acids". I don't know what the reference compounds actually are except that they are relatively high molecular weight species of, I think, biological origen. Either structures or some basic information should be given on them, such as the molecular weights, functional groups present, number of oxygens. To what degree are these reference compunds comparable to the species that might be found in atmospheric particles?

I am puzzled as to the purpose of using the three different models to analyze the data.

The authors include a correction for the Kelvin effect, but then they assume that the particles have the same surface tension as pure water. High molecular weight, oxygenated organic compunds are likley to be surface active. The presence of such compounds can easily lower the surface tension to less than half the value for water. In that case, including the correction would be less accurate than ignoring the Kelvin effect. It seems to me that this effect will not be significant either way. If it is significant, then results should be given both with and without the correction so as to bracket the real effect and to guide future workers as to its possible importance.

Don't the results of section 4.4 (Figures 9&10) imply that the dry particles have a range of shape factors? Should I expect these results to apply to mixed particles in the atmosphere?

Specific comments (editorial):

The paper makes excessive use of acronyms, thus decressing its readability. The

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glossary helps some.

Figures 1, 2, and 3 are of little use. Figure 1 seems to be sorted in order of hygroscopicity; if so, that provides some value to graphic, but the caption does not say that is so. I don't see much value to Figure 2; the image is not very clear and I am willing to take the authors word that the particles were spherical. Figure 3 needs more detail to be useful. In particular, a well designed and captioned figure could be helpful in understanding the different sampling regimes in Figure 4.

The captions to Figures 5, 6, 7, and 9 should identify the samples as "summer" or "winter". The text should also make it clear which samples are being discussed. The use of cryptic codes (8 character computer file names?) for this purpose is not acceptable. The multiple curves on Figures 5, 6, and 7 are confusing. Most don't seem to be discussed.

On page 4894 the authors say "While the initial size decrease at low RH is common for all four WSM extracts, the two winter samples exhibited a more gradual growth characteristic between 40 and 20 80% RH in contrast to the continuous growth of both summer samples (cf. also Figs. 6 and 7)". I don't know what this means. But it looks like Figures 6&7 show weak deliquescence behavior while Figure 5 does not.

Page 4895 and Table 3: Which model is being discussed? The mixed particle model?

The term "excess water" (pgs 4895, 4896) does not seem to be defined.

I got nothing out of the last several paragraphs of section 4.2. I suppose there is a point, but I missed it.

Figure 8 and section 4.3: I found this incomprehensible.

Section 4.4 and figure 9 and 10 are very interesting. One wouldn't know it from the abstract and conclusions. A clear, one paragraph summary of the conculsions of this section is needed in the "conclusions" section.

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