**Atmospheric
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and Physics
Discussions**

Interactive comment on "The density of humic acids and humic like substances (HULIS) from fresh and aged wood burning and pollution aerosol particles" *by* E. Dinar et al.

Anonymous Referee #1

Received and published: 3 October 2006

Review of "The density of humic acids and humic like substances (HULIS) from fresh and aged wood burning and pollution aerosol particles" Dinar et al. ACPD

GENERAL COMMENTS: This paper reports measurements of the effective density of Suwannee River Fulvic Acid, which has been proposed as a model of humic-like substances (HULIS) in atmospheric aerosols. In addition the paper also reports the effective density of the HULIS material of 3 atmospheric aerosol samples, one of night biomass burning, one of mildly processed biomass burning during the day, and one of typical local photochemically processed aerosol particles. These topics are of high current interest and are certainly appropriate for ACP.

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However, beyond the measurement of effective density the paper falls short of supporting its other conclusions. Major revisions are required before this paper can be accepted for publication in ACP.

Note: some comments below will have the following form. Page/Line: Comment

SPECIFIC COMMENTS:

1.) EFFECTIVE density is what is being measured in the paper. In some cases the paper correctly identifies this. In other cases only the term "density" is used. Proof of sphericity would be needed to actually infer the material density. This could be easily done with the AMS by using the beam width probe method of Huffman et al. 2005. We encourage the authors to carry out these additional experiments which will greatly reduce the uncertainties in the reported results. Otherwise "effective density" must be used in place of "density" EVERY TIME this term is used in the paper.

2.) The use of ultrafiltration by the authors as a method of separation is unique in the atmospheric aerosol field (to my knowledge), but it is used in this paper without any acknowledgement of its limitations potential problems, which are considerable. This is especially important since the separation of molecules using ultrafiltration can be affected by molecular shape, electrical charge, sample concentration, and other factors. (http://www.pall.com/34696_35486.asp). If the ultrafiltration was performed in a similar manner to Dinar et al. (2006b) then certain questions must be addressed. In particular the membranes used in Dinar et al. 2006b span from 0.5 kDa to 30kDa, almost 2 orders of magnitude in the molecular weights that should be separated. The measured number molecular weights in Table 2 of this paper do not differ by even a factor of 2. According to the web page above "Ultrafiltration will not accomplish a sharp separation of two molecules with similar molecular weights. The molecules to be separated should differ by at least one order of magnitude (10X) in size for effective separation."

Since in this case the separation is much smaller than one order of magnitude, is it

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possible that ultrafiltration used on these samples is not separating molecules based on molecular size (or weight), but rather on some other axis, for example hydrophobicity. As the authors state on page 7846 line 17 the "higher molecular weight fractions are less hygroscopic, more aromatic, and better packed." As the UV correlation measure of molecular weight is based on absorbance and as a general rule of thumb the more aromatic a molecule the more UV light is absorbed, conceivably you would have a situation in which molecules of the same molecular weight but different amounts or aromatic moieties would have different measured molecular weights with this method. As these issues are not addressed by the authors and can potentially change some of the conclusions of the paper, it is important that this be discussed thoroughly in the revised paper.

3.) In the abstract and the text of the paper, density is said to "dominate" the fluid dynamic properties of the particles. This is an overstatement. Size of a particle dictates transport. As an example: a factor of 2 increase in density is a factor of 2 increase in mass, whereas a factor of 2 increase in diameter is a factor of 8 increase in mass. Since the deposition or settling velocity is proportional to the mass, diameter is 4x more important than density. In addition, for fractal or soot particles the shape of the particle plays more of a role in the fluid dynamic properties than does the material density.

4.) 7845/19: The error estimate of 1.5% is given with no error analysis presented and is extremely (if not wildly) optimistic based on other studies using the AMS (15% would be a more realistic value). This is especially glaring since there is no direct evidence that the particles sampled in this study are actually spherical. The factors controlling phase/shape of organic particles are poorly understood, and it is not clear that the shape of the particles in a previous study can be extrapolated here. A detailed uncertainty analysis involving propagation of errors is need to arrive at a more realistic estimate of the error of this method. This should include the uncertainties in the AMS size measurement, including those from the different flight times of different m/z's.

TECHNICAL COMMENTS:

7838/15: Please clarify what velocity is being referred to.

7839/3 and many other instances: some papers with multiple authors are cited as if they had only one author (eg DeCarlo, 2004 should read DeCarlo et al., 2004)

7841/7-11 There is no reference or material referenced for how the ultrafiltration was performed. Materials and methods need to be described.

7841/24: Aerodynamic diameter should be listed as d_a not d_b.

7842/Eq 1: The equation is incorrect. d_b should be replaced by d_a. In addition, The Hinds reference does not give this equation. However, you can derive this from Baron and Willeke (2001) Eq. 4-41.

7842/Eq 2: This equation is incorrect. d_b should be d_{ve}.

7842/12: X does not increase due to internal voids since it is referenced to the volume equivalent diameter. X increases from non-sphericity.

7842/Eq 3: This equation is incorrect. d_{va} should be in the numerator and d_b in the denominator.

7843/24: I would suggest that the authors use the phrase "highly reproducible" in place of "100% reproducible".

7843/25: Replace "error" with "uncertainty"

7844/2: Figure 4 suggests that with all of the multiply charged particles in the PToF spectrum that the particle population was not "narrow" as is stated in this line. I suggest removing the word.

7844/2: there is a shift in the calibration of the TOF mode in the AMS with m/z due to the increased flight time of ions through the quadrupole as m/z increases (Zhang et al. JGR, 110, D07S09, 2005). This is typically minor for ambient particle distributions

because the distributions are broad and most of the m/z's used are in the lower part of the spectrum. However it can be important for experiments with narrow size distributions and potentially a wide range of m/z's used to monitor the particles. In addition the size calibration of the AMS will depend on which m/z from PSLs has been used to determine the TOF of each PSL standard. Otherwise this type of effect may show up in small "shape factors", since X is where all systematic deviations piles up in this analysis. Has this effect been taken into account? If not, it should be in the revised paper.

7844/13-14: It should be noted that the 60 nm and 230 nm sized particles fall outside of the calibration range. This is of particular importance to the smaller particle which are on a nonlinear part of the calibration curve.

7844/13: Table 1 summarizes EFFECTIVE density and includes a shape correction which is NOT equivalent to X. The shape correction is in fact the inverse of the Jayne shape factor (see Jayne et al. 2000 and DeCarlo et al. 2004)

7845/4: It is recommended that PToF be used in place of TOF to avoid potential confusion of "TOF" with the newer versions of the AMS instrument which now use a TOF mass spectrometer.

7845/6: particles are separated by dva and not mass

7845/18: Use "effective" density as that is what is being measured.

7845/23-26: In assuming that the particles are spherical you are assuming that X=1 not that X~1.

7846/3: density should read effective density.

7846/6: Figure 5 is a plot of SRFA fraction effective densities versus average molecular weight. A correlation is a statistical relationship between independent variables, and requires statistical analysis. Numerous other uses of correlation in the paper should be changed as well in the text and figure captions.

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7846/10: How were the C/O ratios determined? Please provide a reference (or describe the method in the experimental section).

7846/15-16: If one ignores the "lines to guide the eye" the trend of increasing density with increasing oxygen content and the trend of decreasing density to with increasing acidity are weak at best. A statistical analysis is needed which at the minimum requires a linear regression and correlation coefficient USING ALL THE DATA POINTS if these statements are to be made. The "lines to guide the eye" should be removed from the graphs and replaced by regression lines.

7847/2: Harmate should be Harmata, In addition when citing a study by 2 authors it is customary to use both names and not use et al. for the second author.

847/2: The Harmata reference given is the study of one molecule not many. So the use of the plural when describing the molecule Harmata studied is not valid, and the statement should be changed to reflect this.

7847/12: The CCN results are presented without any information on to how they were obtained. A reference is needed or a description in the "Experiment" section.

7847/14: No correlation is presented here. Use the word relationship, or use statistical techniques to determine a correlation.

7847/23-24: Pitz et al measured EFFECTIVE density. The change in the effective density of the particle is likely due to shape (as noted in the paper) as much as it is due to chemistry.

Figures and Tables:

Table 1: Shape Correction is not equal to X. It is equal to 1/S, with S being the Jayne Shape Factor (Jayne et al. 2000 and DeCarlo et al. 2004). This needs to be fixed in the table legend and in the table itself.

Table 3: This table is added as somewhat of a sidenote, and very little text is devoted

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to the analysis of the PPHA sample. Either more explanation as to why this is included should be added, or the table should be removed.

Table 4: This table is a duplicate of the table published in Dinar et al. 2006b, with the addition of error bars. This table should be removed and readers should be directed to the 2006b reference.

Table 5: 3WKS should be 3WSFA. In the caption of Table 3, the authors note that the UV correlation is suited only for Fulvic Acid samples, and that is why this information was not included in Table 3, yet the authors include this information for non Fulvic Acid samples in Table 5 and do not provide any justification for doing so. This is not acceptable.

Figure 1: Synthetic is misspelled. Quadrupole is misspelled. For consistency with the text diameter abbreviations should be in lowercase.

Figure 2: The right axis value is incorrect. The reciprocal of the Jayne Shape Factor is the proper value, and the axis label should be changed to reflect this. Dynamic shape factors of less than one are reported and this is physically impossible, unless there is some measurement artifact such as alignment in the DMA column. Error bars should be added to these measurements.

Figure 5, 6, and 7: This is not a correlation and should be changed to "Scatter plot ofĚ". In addition the "a" and "b" plots should be separated physically since they are on different axis and having them in the same box is confusing to the reader.

Figures 6 and 7: The lines to guide the eye are misleading and should be removed. A linear regression would be appropriate.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7835, 2006.

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