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Atmospheric
Chemistry
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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.

E. Dinar et al.

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Answers to referee 1

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.

Response: There are reliable observations that HULIS and FA particles are spherical

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(Hoffer, et al., 2006). We also have indications of sphericity from hygroscopic growth measurements (Dinar et al, 2006, JGR in press). From that point of view the effective density determined in this paper is the particle density. However, for clarity we now use the term “effective density” throughout the manuscript.

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$_3 5486.asp$).

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 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.

Response: The separation method, its application and limitations are thoroughly discussed in two previous papers from this group (Dinar, et al., 2006a; Dinar, et al., 2006b) hence for the sake of keeping a short and concise paper we do not find it necessary to repeat these discussions in this paper. It is well-known that separation by ultraflirtation is not by the nominal cutoff, but is a convolution of various properties such as charges, hydrophobicity etc. And indeed we find other molecular weight values by the UV absorption method. The obtained molecular weights are n agreement with most previous estimates found in the literature. We have confidence in the separation procedure by molecular weight and the UV correlations for the fulvic acids, as these have been thoroughly validated by others (see Dinar et al ACP 2006 for further details, Schafer et al 2002). In addition, the calculations for the CCN activity of SRFA, which we have performed before (Dinar et al 2006b), scale with the estimated molecular weights derived by the correlations of Schafer et al (Schafer, A. I., Mauch, R., Waite, T. D., and Fane, A. G.: Charge effects in the fractionation of natural organics using ultrafiltration, Environ. Sci. Tech., 36, 2572-2580, 2002). A short section (2.2) has been added to the text.

3) 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.

Response: In principle the reviewer is correct. However, as stated above, we have confidence in the separation procedure and the estimated molecular weights by the UV correlations for the fulvic acids, as the calculation for the CCN activity, which we have performed before, scale with the estimated molecular weights (Dinar, et al., 2006b). This is true for both the fractions and for the bulk. We implicitly assume in our studies that the correlations found for aquatic fulvic acids hold also for the HULIS. This is clearly stated in our manuscript.

4.) 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.

Response: The reviewer is correct, hence we included the word “size” in the abstract and weakened the expression “dominate all” to “affect”.

5.) 7845/19: The error estimate of 1.5

Response: The overall errors discussed by the referee are small and the overall agreement that we obtain in the measurements with literature values for several standards that we used as the system validation procedure is very good. Despite this, we reanalyzed the data and treated the referee’s comments seriously. The difference in time of flight for various m/z detected for the different aerosols introduce a small (<5Following the referee’s advice we now discuss effective densities in the revised manuscript. But by considering effective density, shape does not affect the precision or accuracy of the determined effective densities. This depends only on the systematic errors (such as the mass-dependent transmission of the QMS), on the SMPS calibration and the stability of the pToF calibration in the range 100 - 200 nm. The SMPS was calibrated using PSL of 50, 81, 102, 152, and 199 nm. We performed linear regression of the nominal DMA size measurements and PSL actual sizes and corrected the nominal size. The R2 value for all days was between 0.999 to 0.998 and the deviation of the slope ranged between -0.5The AMS was also calibrated every day using PSL spheres (102, 152 and 199 nm). In addition, between measurements of the samples PSLs were re-run in the system to ensure stability. It is important to note that the density of each sample was determined using three different aerosol sizes (db = 88, 98 and 128nm) and each size was integrated in the pToF-MS for at least three periods, each 5-15 minutes, depending on the signal intensity. During AMS measurements at least 4 SMPS scans were perform for each size. Here we demonstrate the accuracy of the system. If we apply the SMPS calibration and our base pToF calibration (with 7 PSL sizes, ranging from

80 nm to 600 nm) to all PSL measurements (102 - 513 nm) during the entire experiment period, the ratio obtained between the SMPS mode to the peak of the vacuum aerodynamic diameter distribution, yields a PSL density of 1.029 ś 0.0446 (which is 4.3

In addition, the mass dependent transmission times of ions in the QMS are at maximum 40 61549;s between m/z 104 and 44, and 20 61549;s between m/z 104 and 64. These values are in very good agreement with Zhang et al. (JGR, 110, D07S09, 2005). This shift leads to a systematic error, which is less than <5

6) 7838/15: Please clarify what velocity is being referred to.

Response: We specified “terminal velocities under acting forces in viscous media”

7) 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)

Response: We carefully checked all references, and they are now correct. We apologize for overlooking mistyped references.

8) 7841/7-11 There is no reference or material referenced for how the ultrafiltration was performed. Materials and methods need to be described.

Response: There is no need to repeat published material. We use the same samples as we used in other studies and we refer the reader to two papers that describe all of these in details (Dinar, et al., 2006a; Dinar, et al., 2006b). We do not feel that we need to re-describe the procedure in the manuscript as well.

9) 7841/24: Aerodynamic diameter should be listed as da not db.

Response: We thank the referee for the careful reading of the equations. We rephrased the relevant paragraphs and equations to make our point more clear and concise. We use now consequently, da for aerodynamic and db for electromobility diameter.

10) 7842/Eq 1: The equation is incorrect. db should be replaced by da. In addition, The Hinds reference does not give this equation. However, you can derive this from

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Baron and Willeke (2001) Eq. 4-41.

Response: There was indeed inconsistency in the use of “db”, this has been corrected. We changed the reference accordingly.

11) 7842/Eq 2: This equation is incorrect. db should be dve.

Response: We corrected these paragraphs and the equations. However, for the assumption of spherical particles mobility diameter db and dve are identical and equal the geometric diameter dp.

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

Response: The wording “due to internal voids” is unluckily to wrongly chosen. dva decreases for irregular shaped particles with 967;>1, because dve > dStokes, the diameter of the spherical particle made of the same mass at same density 961;p. We wanted to address this “void” volume dve3-dStokes3 and had a corrugated, irregular particle in mind. These voids are not necessarily internal. However, increasing internal void volume will of course also lead to a decrease of dva.

The text was changed: “Ěand dva decreases (since with increasing irregularity the effective density decreases due to the increasing ratio of dve to dStokes of the sphere made of the same mass and the same density 961;p).”

13) 7842/Eq 3: This equation is incorrect. dva should be in the numerator and db in the denominator.

Response: Error corrected.

14) 7843/24: I would suggest that the authors use the phrase “highly reproducible” in place of “100

Response: Replaced as proposed.

15) 7843/25: Replace “error” with “uncertainty”

Response: Modified as proposed.

16) 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.

Response: The word “narrow” is now removed

17) 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 revisedpaper.

Response: We calibrated the pToF with m/z 104 and detected dva of all organics (HS, HULIS and Glucose) at m/z 44, sulfate at m/z 48 and 64. From the PToF distributions we can measure the shift. For m/z=104 to 64: there is a 20 61549;s shift. For 64 to 44 there is a 20 61549;s shift. For 104 to 44 we observe 40 61549;s shift, consistent the observations of Zhang et al. These shifts lead to a systematic underestimation in our HS and HULIS densities of 5

18) 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.

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Response: These are the selected electromobility diameters (db). Since the density for all studied aerosols reported here is 1.4 or larger, the 80 nm particles (ammonium sulfate, 961; 1.77 g/cm3) fall within the everyday calibration range of 102 - 199 nm (aerodynamic sizes). This size range was used for calibration of the FA, HULIS, and HS experiments and for the everyday AS control measurements. The densities quoted in Table 1 (AS, ABS and Glucose) were determined bases on PSL calibrations, which included in addition, larger PSL of 345 nm, 513 nm, and 600 nm (geometric diameters).

19) 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)

Response: We understood already the point of the effective density. According to our understanding, when comparing db and dva only particle density 961;p can be determined, not the material density 961;m. If the particles are spherical, compact and contain no internal voids, 961;p = 961;m. The Jayne factor S, which relates material density 961;m to dva, is for calibration purposes with size selected salt particles. We prefer to define S' similar to Jayne factor which relates 961;eff and 961;p. Equations (compare DeCarlo et al. 2004):

For our case (room temperature and atmospheric pressure at the DMA and particle diameters of 100-200 nm (Knudsen number, Kn of the order of magnitude of 1)), S' is that of the transition regime. We know from Hoffer et al (2006) that HULIS particles are near spherical, i.e. 967; close to 1. Thus, 967;va8776;967;b. This yields 1/S'8776;967;2. For 967;<1.05 this is still a good approximation of 967; to better than 6

The ratio of the Cc's for 100 nm diameter particles and 967;b=1.05 is 1/1.02. 1/S' is still an approximation of 967; good to <8

The referee is still correct though, and this approach is only an approximation. Therefore, we introduce S' in equation 4 and change 967; in the figure to 1/S', with the explanation that 1/S' is somewhere between 967;(3/2) and 967;(2).

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.

20 Response: We changed that, although it is not of relevance in context of this paper.

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

Response: We replaced mass by dva.

20) 7845/18: Use “effective” density as that is what is being measured.

Response: We added “effective”.

22) 7845/23-26: In assuming that the particles are spherical you are assuming that X=1 not that XŸ1.

Response: We changed “ 1” to “1”.

23) 7846/3: density should read effective density.

Response: We added “effective”.

24) 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.

Response: We changed “correlation” to “relationship”, whenever suited.

25) 7846/10: How were the C/O ratios determined? Please, provide a reference (or describe the method in the experimental section).

Response: It was calculated from the elemental analysis of the samples. The results are given in Table 4 with the reference to Dinar et al. (ACP 2006). We added: (C/O, taken from the elemental analysis as given in Table 3).

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26) 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.

Response: Here we disagree with the referee. As we write in the text (7846/14) there is a tendency of increasing density with increasing oxygen content and of decreasing density with increasing acidity. This implies weak relations, as stated by the referee. A linear regression will not be suitable here, since there is no reason to assume linear relationship between these quantities. We show the data in Figure 6 and comment in the caption clearly about the line to guide the eye. We added a comment about the one outlier in Fig. 6b.

27) 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.

Response: We changed to “Harmata and Barnes”, and checked all references with respect of the critics.

28) 7847/2: 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.

Response: Here we do not agree with the referee. Stacking, by definition, requires more than one molecule. So this is a semantic question. Our statement is valid, although only one substance was investigated. To clarify we replaced “stacking of Ĕ complex organic molecules” by “stacking of Ĕ a complex organic substance”.

29) 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.

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Response: We added the reference Dinar et al. 2006b.

30) 7847/14: No correlation is presented here. Use the word relationship, or use statistical techniques to determine a correlation.

Response: We replaced “correlation” with “relationship”.

32) 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.

Response: We modified this sentence: A similar trend in increasing effective density with photochemical aging may partly explain the observation of Pitz et al (2003) who also observed an increase in particles’ effective density from morning to the afternoon, due to change in composition and shape.

32) 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.

Response: We changed “Dynamic shape factor, 967;” to 1/S’ as explained above.

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

Response: We disagree with the referee. Fulvic and humic acids have chemical similarities. We currently do not know which one is chemically more similar to the real atmospheric system. Therefore we studied both materials, to examine what are the differences and similarities. This is also the first time that the effective densities of aerosols composed of these materials are measured. Therefore, we decided to present and keep the data of the PPHA samples. A sentence was added to the text. The humic acid measurements are presented for comparison to fulvic acids. We now combined Tables 2 and 3 to one table (Table 2) and we have added the following text: “Since it is accepted that FA are the products of fragmentation of large HS (HA) [Diallo, 2003 181] we have added for comparison in Table 2 the measured effective densities of three PPHA samples (bulk, F2 and F5)"

34) 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.

Response: This information is important in the context of this manuscript (see also comment by referee 2). Therefore we leave the table in the manuscript.

35) 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.

Response: As explicitly stated in our previous studies (Dinar 2006a.b), we inherently assume in these studies that the correlations for SRFA hold for HULIS, since they are also fulvic acids which have been recovered from the aerosol in the same manner as the SRFA. See our previous studies (Dinar et al., ACP 2006 and Dinar et al., JGR 2006). We have changed 3WKS to 3WSFA.

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

Response: Fixed.

37) 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.

Response: Since we emphasize the relation between sizes to shape we plotted all the measured points as measured without averaging and calculating the error. This allows the reader to get a better perspective of the trend and the error can be seen when the reader will focus on an imaginary line of a certain Voltage/Mobility. As for S values of less than one, the referee is correct, this is a result of the experimental error (max 2

38) Figure 5, 6, and 7: This is not a correlation and should be changed to "Scatter plot ofE711; ". 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.

Response: We replaced the word "correlation" by "relationship". Figures 5 and 6 were separated as suggested. As for figure 7, the x axis is the same parameter (dry diameter in nm) and the aim of this figure is to demonstrate the distinct differences in HULIS and SRFA populations, we did not change the figure.

References

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