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Atmospheric
Chemistry
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Discussions

Interactive comment on "Measured and modeled humidification factors of fresh smoke particles from biomass burning: role of inorganic constituents" *by* J. L. Hand et al.

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Comments: I am concerned that the authors did not address the possibility that some fraction of the POM is hydrophilic. When I read p. 4227, lines 12-15 or p. 4251, lines 20-24, for example, the logic sounds circular. There is evidence of water soluble organic aerosol from burning of woody savanna in southern Africa described by Gao et al (JGR, 108(D13), 8491, doi:10.1029/2002JD002324, 2003), and a lab analysis of the hygroscopicity of organic species by Chan et al (Environ. Sci. Technol., 39, 1555-1562, 2005) which offers evidence supporting analysis of fRH measurements from SAFARI-2000 described by Magi and Hobbs (J. Geophys. Res., 108(D13), 8495, doi:10.1029/2002JD002144, 2003). Based on Figure 9, the effect of POM on fRH in your study is probably small, but it would be interesting to know just how much POM could be modeled as hydrophilic and have the modeled growth curves still agree with measured growth curves. The reason I think this would be useful is that many chemical transport models and general circulation models simulate POM as partly hydrophilic. Since you are modeling hygroscopic behavior, I think you need to quantitatively comment on the possibility of hygroscopic organic aerosol, rather than assuming POM is hydrophobic, especially given statements like p. 4238, lines 13-15.

Response: We appreciate the reviewer's time and helpful comments on the manuscript. The intention of this manuscript was to examine the role of inorganic species on the hygroscopic response of smoke aerosols. The modeling aspect of this work was intended to investigate whether the hygroscopic response of inorganic species was sufficient to account for the measured water uptake, and we found that we did not need to assume any hygroscopic properties for organics to account for the measured f(RH) within the uncertainty of the measurement. It is possible that organics were weakly hygroscopic but the agreement between measured and modeled f(RH) suggest that this possible effect was within experimental uncertainty in that we did not systematically observe f(RH) values higher than what we predicted. The measurements presented in Figure 9 are compelling evidence that the role of organic species in the hygroscopic response was limited. These results are consistent with those reported by Carrico et al. (2010) and Petters et al. (2009) for the other FLAME measurements. In addition, the contribution to f(RH) from organics would have to be less than ±0.08 (experimental uncertainty) because for most cases the measured and modeled f(RH) agreed within this range, therefore we would not be able to state with any significance the contribution of organic aerosols to water uptake. It is certainly possible that organics are contributing, but the data in Figure 9 suggest that this contribution is likely small.

Comment: More comparisons with previous work should also be included. Day et al. 2006 (already cited) Table 2 lists mean fRH (RH = 71-94%) for sage brush and ponderosa pine of 1.39-1.76 and 1.25-1.95, respectively. Values listed in your Table 2 for sage brush and ponderosa pine are markedly different. Quinn et al. (GRL, 32, L22809, doi:10.1029/2005GL024322, 2005) showed how POM impacts hygroscopicity during 3 major field campaigns. The SCAR-B study of fRH by Kotchenruther and Hobbs (J. Geophys. Res., 103(D24), 32081-32089, 1998) suggested much less hygroscopic growth for biomass burning in South America than the SAFARI-2000 values discussed by Magi C2389 and Hobbs 2003 (above). Perhaps this was a result of higher percentage contribution of POM and LAC to the overall aerosol composition in South America as compared to Southern Africa (eg. compare Table 6 by Reid et al., J. Geophys. Res., 103(D24), 32059-32080, 1998, to Figure 2 by Magi, Atmos. Chem. Phys., 9, 7643-7655, 2009). Semeniuk et al 2007 (cited in your study) limited the analysis of hygroscopic behavior of SAFARI-2000 organics to organics mixed with inorganics.

Response: We did not include a detailed review of previous measurements of smoke f(RH) in this manuscript because it was provided by our earlier paper (Day et al., 2006), but we have added some discussion to this paper [page 4247, line 6]:

“The range of f(RH) values we report (0.99 to 1.81) is consistent with previous observations, both in the laboratory and in the ambient atmosphere. Aircraft measurements of f(RH) during the dry season in Brazil were reported by Kotchenruther and Hobbs (1998) and ranged from 1.01-1.51 (humid/dry RH of 80/30%). Higher values occurred under aged conditions, suggesting the importance of atmospheric processing on aerosol hygroscopicity. However, Magi and Hobbs (2003) found similar values of f(RH) for young (∼hr old) smoke (1.42) compared to heavily aged smoke (1.44) during aircraft measurements in southern Africa. The importance of fuel composition on hygroscopic properties was suggested by Gras et al. (1999) based on aircraft measurements of smoke f(RH) from north Australian savannah fires (1.37) compared to sulfur-rich peat fires in Indonesia (1.65). Laboratory chamber measurements of f(RH) during a preliminary FLAME study ranged from 1.10 to 1.51 (humid/dry RH of 92/10%) (Day et al., 2006). Values of f(RH) for Alaskan duff were comparable between the earlier study and this one (1.10 at RH=92% compared to 1.07 at RH=80-85, respectively). However, lower estimates of f(RH) corresponding to smoke from burns of sage were reported during the earlier study compared to this one (1.30 at RH=92% compared to 1.81 at RH=80-85%, respectively). Petters et al. (2009) also observed a wide range of hygroscopicity of sage from multiple burns, even within the same experiment. Apparently the source location of sage brush can have a significant effect on the hygroscopic response (Carrico et al., 2010). Measurements of f(RH) by Lewis et al. (2009) during the 2006 FLAME experiment were comparable to our estimates for two available fuels (chamise and ponderosa pine). Values of f(RH) for chamise varied between 1.45-1.8 as reported by Lewis et al. (2009) and 1.58 reported here. Results for ponderosa pine were f(RH)=1 for both studies."

Comment from above: Table 2 lists mean fRH (RH = 71-94%) for sage brush and ponderosa pine of 1.39-1.76 and 1.25-1.95, respectively. Values listed in your Table 2 for sage brush and ponderosa pine are markedly different.

Response: These values of f(RH) for sage and ponderosa pine as reported by Day et al. (2006) were obtained under much different experimental conditions as those reported here. These particular values reported by Day et al. were for biomass that was burned on a platform under a stack. Unfiltered air from outside was blown into the chamber, creating a slight overpressure inside the chamber. Smoke from the burns was entrained into the stack flow and the instruments sampled directly from the stack. The stack burns generally lasted around 4-8 minutes and the platforms could be angled, resulting in a heading or backing fire. The results reported for sage and ponderosa pine were for both heading and backing fires. These situations can result in much different flaming conditions. For example, heading fires correspond to a quickly moving flame front that engulfs the entire pile of biomass. In contrast, during backing fires a narrower flame zone moves downhill more slowly, resulting in different parts of the biomass being burned simultaneously. For comparable conditions (chamber burns), Day et al. (2006) reported an f(RH) of 1.3 (92% RH) for sage brush. We measured a much higher value of 2.15 (85-90%) during this experiment. Petters et al. (2009) also observed a wide range of hygroscopicity of sage from multiple burns, even within the same experiment. Apparently the source location of sage brush can have a significant effect on the hygroscopic response (Carrico et al., 2010).

Comment: 1. p. 4227, lines 3-4: Somewhere in the Abstract, you should include the caveat that the fuels were limited to species from W and SE USA only (per line 24).

Response: We changed the abstract [page 4227, line 7-8] to read "Results from burns of several biomass fuels from the west and southeast United States showed large variability in the humidification factor (f(RH) = bsp(RH)/bsp(dry))"

Comment: 2. p. 4230, line 23: Delete 'a'.

Response: Done.

Comment: 3. p. 4233, lines 13-24, Figure 1: I suggest that you delete Figure 1 and relevant text in this paragraph. There is nothing unusual in the comparison.

Response: We believe the data in Figure 1 and the discussion on page 4233 (lines 13-24) are important because they show agreement between the two instruments within experimental uncertainty during dry periods. Agreement between the two data sets is necessary, otherwise the derived f(RH) values are questionable. We also think it is necessary to state uncertainties and describe how they were derived, especially because we are comparing measured f(RH) to modeled estimates. It is also important to understand how contributions from background aerosols in the chamber could effect f(RH) during burn periods.

Comment: 4. p. 4235, Section 2.3: Can you comment on how you overcame the limitation of DMPS size distribution being for diameters between 0.04-0.65 um and scattering measured for particles less than 2.5 um diameter? More to the point, when you integrate the DMPS size distribution with a refractive index to derive scattering using Equation 6, how closely does this match nephelometer scattering at low RH?

Response: Dry (RH$\sim$25%) light scattering coefficients (bsp) were derived using the DMPS data and compared to measured dry bsp from a nephelometer. The same size distributions and refractive indices were used as were reported in the manuscript. The results are shown in Figures (1a) and (1b). Figure 1a shows a scatter plot for the DMPS-derived bsp compared to the measured values. Figure 1b presents bsp as a function of fuel for the two methods. For the fifteen fuels presented here, 10 of them were within a 25% difference. The largest percent differences corresponded to ceanothus (83%, DMPS higher), Puerto Rico fern (61%, nephelometer higher), manzanita (57%, nephelometer higher), lodge pole pine (53%, DMPS higher) and sage/rabbit brush (42%, nephelometer higher). There was no clear distinguishing trait as to why these fuels corresponded to a larger discrepancy in bsp. Shape factors ranged from 0.9-1.8. SEM images showed large agglomerated soot chains as well as round liquid particles and oily liquid films. Geometric mean volume diameters for these fuels were around 0.2-0.3 μm. Because f(RH) is a ratio of humidified to dry bsp, the discrepancies canceled.

Comment: 5. p. 4235, line 18: Do you mean ‘underestimation’?

Response: No, we mean overestimation. Because of the effects of the shape factor on the DMPS measurements, the DMPS-derived mass was actually much larger than the PM2.5 gravimetric mass for some cases.

Comment: 6. p. 4238, line 14: Can you get your deliquescence and/or metastable curves to still agree with the measurements if some fraction of POM is hydrophilic?

Response: See earlier response.

Comment: 7. Table 1: Thank you for stating your assumptions in this table. Please add ‘at a wavelength of 530 nm’ after ‘refractive index’ in the caption. A study worth noting is the recent review of LAC properties by Bond and Bergstrom (Aerosol Science and Technology,40, 27-67, 2006), who suggest LAC refractive index is 1.95-0.79i and density is 1.7-1.9 g/cc. The Stelson (1990) study cited in your Table is more relevant to urban aerosol.

Response: The values of refractive index and density we applied for light absorbing carbon are frequently used in the literature (Seinfeld and Pandis, 1998), and have been applied successfully in closure studies of optical properties of biomass smoke (McMeeking et al.,2005a,b). These values are not significantly different than those proposed by Bond and Bergstrom (2006). The density we used was 2 g cm-3, compared to the range of 1.7-1.9 g cm-3 they suggest. The real part of the complex refractive index we used was 1.96, compared to 1.95, and the imaginary part we used was 0.66i, compared to 0.79i.

Comment: 8. Table 2: Entries 2, 3, 13, 14 all have inorganic/organic ratios of exactly 0.02. Is this correct?

Response: The values in the original paper were correct. The uncertainties in the ratio of inorganic to total carbon were 0.02, so the ratios were reported with the same significant digits. We now report the inorganic/carbon ratios in terms of OC instead of POM, so they have changed slightly (0.03 instead of 0.02).

Comment: 9. Figures 2-6:I suggest that you change the scales on the y-axes – it is hard to glean anything from Figure 4, for example. I would also suggest changing the scales on the x-axes so that you are presenting the measured range of RH (roughly 20-90% seems adequate) Is it meaningful to show modeled fRH and GF beyond the measurement range?

Response: We have changed the scales on the figures.

Comment: 10. Figure 9: I like this figure, but I would change the scale to 0-0.6 on x-axis, and 0.8-2.3 on y-axis to more effectively highlight the data points. How much would the best fit line change if you plotted fRH vs IMPROVE inorganics/POM instead of inorganics/(POM+BC)?

Response: We have changed the scale of the figure. The linear regression was performed assuming only OC and assuming only POM in the denominator. We used f(RH) at 80-85%, based on the suggestion of reviewer #1.

If only OC is used (inorganics/OC): Slope: 0.30 ± 0.03 Intercept: 1.03 ± 0.03 R2 = 0.94

If only POM is used (inorganics/POM): Slope: 0.55 ± 0.04 Intercept: 1.03 ± 0.02 R2 = 0.91 The slope decreased and intercept increased slightly but did not change the interpretation of the results.

References:

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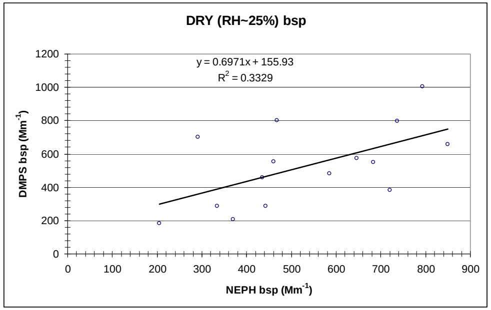

Figure 1a. Dry b_{sp} (Mm^{-1}) derived from DMPS data and dry nephelometer measurements for fifteen fuels.

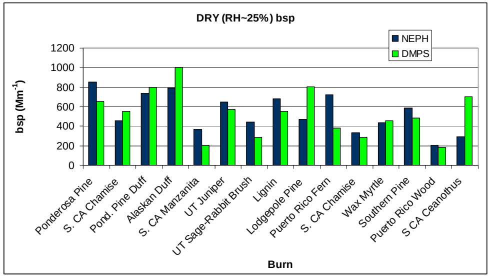

Figure 1b. Dry b_{sp} (Mm^{-1}) as a function of fuel type for estimates derived from DMPS and measured by nephelometry

Fig. 1.

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