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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Optical properties of humic-like substances (HULIS) in biomass-burning aerosols" *by* A. Hoffer et al.

A. Hoffer et al.

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Comment by reviewer: Abstract, line 17: "causing a relatively high (up to 50%) contribution to the absorption at this wavelength." % of which absorption? Absorption by the biomass burning aerosol? Please add.

Reply: Done. "causing a relatively high (up to 50%) contribution to the light absorption of our Amazonian aerosol at 300 nm".

Comment by reviewer: Section 2.1: how many samples in total were collected? When combining all daytime and nighttime samples, how much mass of HULIS was obtained? How large was the contribution of HULIS to the TC aerosol mass concentration on average during the sampling period (on p 7350, you state an "assumption" that 35% of TC are HULIS)? As diel variations are mentioned at several points: was there a

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variation of HULIS / TC between daytime and nighttime samples?

Reply: During the SMOCC campaign 77 samples were collected. At the beginning of the campaign the site was affected by heavy biomass burning. For the present study 26 samples were used from the biomass burning period and about 3/8 of each filter was extracted for the HULIS isolation. After the isolation procedure we obtained 6 daytime (labelled as A1, B1, C1 and A2, B2, C2) and 6 night-time HULIS samples (labelled as D1,E1,F1, D2 E2 F2). For the combined daytime (A1, B1, C1) and nighttime (D1, E1, F1) samples 10.8 mg and 20.3mg HULIS were obtained, respectively. (This information is now included in Section 2.1)

As mention in the MS, the assumption, that 35% of the TC is HULIS-C was based on preliminary results obtained from impactor samples collected parallel with the HI-VOL samples.

Diel variations are mentioned at several points in the manuscript, since the relative amount of the more refractory water soluble carbon (oxidized above 280°C) was higher in the daytime samples than in the nighttime ones (Hoffer et al, 2005). Since the fire properties between day and night were different (more smoldering type during night and more flaming type during daytime) different optical properties were expected for daytime and nighttime HULIS.

Comment by reviewer: Section 2.2: The only information on the size distribution of the HULIS aerosol is that the particle size is between 50 and 100 nm. Please give a plot of the size distribution. Was the bulk density of the aerosol calculated from the integrate number size distribution an the TEOM measurement? Please specify in the text. If the TEOM data were used: what evaporative losses are expected because of the heated inlet? Do HULIS evaporate (at lest slightly) at this temperature?

Reply: A plot is included and more detailed information on the size distributions is provided in the revised manuscript.

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We have included the following information in Section 2.2: The densities of the generated HULIS aerosol particles were calculated from the size distribution and the TEOM measurements. The number concentration of the aerosol was determined for each size bin, and the volume of the aerosols in the size bins was calculated. The calculated volumes were summed up and divided by the mass measured by the TEOM. At the temperature used in the TEOM no evaporative losses were expected for the aged (at least slightly aged) HULIS that was collected at ambient temperatures near or above 30C.

Comment by reviewer: How were the truncation errors of the nephelometer calculated? For such a calculation,the refractive index and the size distribution of the aerosol are needed, but as the refractive index of the HULIS aerosol was derived from measurements of the scattering coefficient, there had to be some iterative procedure?

Reply: As stated in the text the index of refraction (m) was determined iteratively using a Mie code. For each of these iterative steps a certain m was assumed and the phase function of a spherical particle was integrated over the viewing angle of the nephelometer, i.e. the angular truncation error (here $<$0.5%) was taken into account.

Comment by reviewer: The measurements of absorption and scattering coefficient as well as bulk density were performed on an aerosol generated from a solution of HULIS in acetonitrile. The measurements of spectral absorption, however, were made on aqueous solutions of HULIS. It is not quite clear from the text how measurements of the spectral absorption characteristics were made. On p 7347 there is mention that the mesaurements were made on only one night-time sample - was this part of the combined sample or was it an individual sample? If so, do you expect this sample to be representative of all others, and why? On p 7349 absorption measurements are stated to have been made on “daytime and nighttime samples” - how many? Why were two different solvents used? Is there an expected effect of solvent on the optical properties?

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Reply: Before the measurements using the HULIS from the SMOCC campaign, we performed test measurements with standard humic acid solution and with HULIS isolated from fresh biomass burning aerosol. In the latter case, oak wood was burnt and the smoke was introduced in a container from which the aerosol was collected on quartz filters. The HULIS were isolated with the same procedure used later for the SMOCC samples. The HULIS so obtained did not (re)dissolve in water, therefore acetonitrile was used to ensure complete dissolution. Since sufficient HULIS mass was necessary for the measurement in this study, we did not test the dissolution properties of the SMOCC HULIS, but used the solvent that had proven to be appropriate. The acetonitrile solution was used only for particle generations, and no spectrophotometric measurements were done on it. The absorption spectra of 2 HULIS-samples (B2 and E2) (dissolved in water) were measured with the spectrophotometer. This is now stated in section 2.2.

Since there might be a solvent effect on the structure of the freshly formed HULIS (oak fire samples) their optical properties might be different in different solutions. It should be noted that the absorption spectra of humic compounds also depend on the pH, mainly because of structural change of the molecules (humic acid precipitates below pH=2).

Comment by reviewer: General: In most of the text, the term HULIS is used for what is actually an aerosol generated with a nebulizer. As mass absorption and scattering coefficients of an aerosol depend on the size distribution, these results strictly apply only to a HULIS aerosol with this specific size distribution. The larger mass scattering coefficient measured for the night-time sample could be due to a different size distribution (the mass absorption coefficient is not so dependent on size distribution as the mass scattering coefficient), but size distributions are not given (please supply them in the revised MS).

Reply: As mentioned above we have now include size spectra (Figure 2), which show that the size distribution of the nighttime sample is slightly shifted towards larger sizes

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(from 53.5 to 57.4nm). Since the difference in observed particle density and real part of the refractive index accounts for only a 10% increase, the observed 25% increase in mass scattering coefficient for the nighttime sample is mainly due to the difference in particle size, i.e. it is not a difference in the material properties of HULIS.

However, since according to Mie theory both the aerosol mass absorption and scattering coefficient (at ˜550nm) is smaller for 55 nm than for 200 nm particles (realistic size for Amazonian biomass burning aerosol), we wrote in the manuscript, that our values obtained for the generated HULIS aerosol can be considered as a lower limit for HULIS present in ambient fine aerosol.

Comment by reviewer: Section 3.1: Why do you expect a diel variation of optical properties of HULIS?

Reply: See above (comments to section 2.1)

Comment by reviewer: p 7348, last par.: were the calculations by Horvath (1993) and Bohren and Huffman (1983) made for the same refractive index you obtained for the HULIS aerosol? If not,they might not apply, as the mass absorption coefficient depends strongly on refractive index. In this case, I would advise to run a Mie calculation for the proper refractive index.

Reply: As already indicated above we have run Mie calculations for the proper index of refraction to confirm that the mass absorption coefficient determined for 55 nm HULIS particles can be considered a lower limit for realistic ambient particle sizes of about 200 nm). The manuscript has been corrected in accordance with the results.

Comment by reviewer: p 7350, lines 17-20: sentence is incomplete.

Reply: The sentence has been modified.

Comment by reviewer: Section 3.2 please specify that the mass absorption and mass scattering coefficients were obtained for the HULIS aerosol produced in the lab and not to HULIS as such.

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Reply: Done.

Comment by reviewer: Figure 1 and 2: please use larger fonts (or enlarge whole figure) - they are difficult to read on a printout.

Reply: Done.

Comment by reviewer: Figure 3: please include instrument in figure caption

Reply: Done.

Reference

Hoffer, A., Gelencsér, A., Blazsó, M., Guyon, P., Artaxo, P., Andreae, M. O.: Chemical transformations in organic aerosol from biomass burning, Atmos. Chem. Phys. Discuss., Vol. 5, 8027-8054, 2005.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 7341, 2005.