Atmos. Chem. Phys. Discuss., 9, C7217–C7226, 2009
www.atmos-chem-phys-discuss.net/9/C7217/2009/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Chirality and origin of atmospheric humic-like substances" *by* I. Salma et al.

Anonymous Referee #2

Received and published: 18 November 2009

General Comments

The authors apply a new technique to the characterization of humic-like substances (HULIS) in atmospheric aerosols. Circular dichroism measures the absorption of light and right-handed polarized light as a function of wavelength and yields information about the chirality of the analyte. Electronic circular dichroism (ECD) focuses on the UV portion of the spectrum, in which HULIS is known to be optically active. Vibrational circular dichroism (VCD) occurs in the infrared range, which is used to gain information about the optical activity of absorbing functional groups. The authors compare aerosols from a rural environment, an urban area, and those heavily impacted by biomass burning. HULIS is operationally-defined as the water-soluble, methanol elutable material isolated from a solid-phase extraction procedure. Total HULIS concentrations and HULIS mass-to-carbon ratios were reported.

There are several problems with the manuscript in its present form. Significant revisions and possibly additional experiments/measurements are needed before publication is recommended. The revised version must include presentation and discussion of the method detection limit, which has potential for significant bearing on the conclusions of this manuscript. The authors also need to discuss potential biases that may have stemmed from their operational definition of HULIS, especially with respect to calculated atmospheric concentrations, HULIS-C to WSOC ratios, and optical activity in the IR range. None of the HULIS extracts exhibit optical activity in the UV range of the spectrum by the ECD technique, while previous studies have illustrated that HULIS absorbs in the UV range. Hence, the reasonable conclusion is that the collected rural, urban, and biomass burning-impacted HULIS was not optically active. The optical activity observed by the VCD technique is associated with the carbonyl absorption band in the IR range and is very likely influenced by HULIS isolation artifacts. With a severe lack of data and no quantitative discussion of ECD and VCD results, the authors develop relatively broad conclusions on the origins of HULIS. These issues and others are discussed in detail in the following section.

Specific Comments

1. The development of new analytical methods (ECD and VCD) to the characterization of atmospheric HULIS requires determination of detection limit. This could be done using a surrogate (e.g. Suwannee River fulvic acids) or model compound. Detection limit should be reported in units of HULIS-C per volume. Additionally, the concentrations of HULIS-C in aerosol extracts used for ECD and VCD analysis should be documented in the manuscript, to demonstrate that samples analyzed exceeded this detection limit.

2. The sample results must also be discussed in light of the method detection limit. For example, optical activity was not measured in urban HULIS, yet it is not clear if this was due to the small amount of urban HULIS collected.

3. The authors place a large importance on biomass burning as a source of HULIS to the atmosphere and suggest that degradation of cellulosic material is the likely origin. Yet, they do not measure the major cellulose degradation product, levoglucosan, that can be used to trace biomass burning aerosol (Simoneit et al., 1999). Biomass burning has been shown to be an important contributor to ambient aerosol in urban and rural environments worldwide (Schauer and Cass, 2000; Zheng et al., 2006; Sheesley et al., 2007). The authors conclude the biomass burning-related HULIS is optically active whereas rural and urban HULIS is not, while it is highly probable the biomass burning impacted the rural and urban sites to some degree. Levoglucosan measurements would be extremely useful in determining if biomass burning aerosol was present at the urban and rural sites.

4. HULIS is a broad category of water-soluble high-molecular weight, polyacidic organic matter. In a given study, HULIS is operationally defined by the extraction, isolation, and analysis techniques utilized. For clear comparison to prior and future studies, it is strongly suggested that the authors clearly state their operational definition of HULIS.

5. The authors take at face value that the utilized solid-phase extraction procedure yields “pure HULIS” (page 19946, line 15 and 24; page 19949 line 13). However, studies of HULIS extraction by SPE have demonstrated that non-HULIS compounds are present in the HULIS-containing eluent. Low molecular weight carboxylic acids and oxy-substituted aromatic compounds that fall below the molecular weight range of HULIS have been isolated with HULIS. For example, Limbeck et al. (2005) show that lactic, oxalic, succinic, adipic, and phthalic are isolated in addition to humic acids. Emmenegger et al. (2007) show that C1-C6 monocarboxylic acids, succinic, adipic, hydroxybenzoic, lactic, and trifluoroacetic acids were not separated by SPE. Furthermore, Stone et al. (2009) characterized the SPE by the HLB column used in this study and showed that a wide variety of non-HULIS compounds were recovered in the HULIS fraction. These compounds included low-molecular weight acids, such as

n-hexanoic, n-octanoic, cis-pinonic, phenylacetic, methylphthalic, cyclopentanedicarboxylic, butanedioic, heptanedioic, octanedioic, tricarballylic, benzenetricarboxylic, and benzenetetracarboxylic acids, and known biomass burning compounds, including guaiacol, vanillin, acetovanillone, and syringaldehyde. These compounds, present in ambient atmospheric aerosol and biomass burning emissions (Saxena and Hildemann, 1996; Schauer et al., 2001; Decesari et al., 2006), are expected to interfere with the isolation of HULIS by SPE. Thus, the authors need to discuss the positive biases associated with their HULIS isolation method, particularly in the context of calculated ambient HULIS concentrations, OM/OC ratios, and HULIS-C/WSOC ratios. The possible impacts of these artifacts on optical activity are discussed later.

6. With respect to the calculated HULIS-C/WSOC ratios, the authors should discuss their findings in the context of the historic record measured in ice cores (Legrand et al., 2007). 7. A relatively long period of time elapsed between biomass burning sample collection (September 2002) and the publication of this paper in ACPD. How are the authors sure that the samples were not degraded or compromised?

8. On page 19946 at lines 18-19, the authors need to provide more information about sample extraction. Specifically, how were the samples extracted (e.g. by sonication, shaking, stirring, or other)? At what temperature? Were the “several aliquots” (line 23) combined prior to evaporation to dryness?

9. During the gravimetric HULIS analysis, if/how was ambient relative humidity controlled so that HULIS mass was not biased by hygroscopic uptake of water during weighing? 10. Page 19952, lines 2-4, how were the values of 72 and 70% obtained and why are they different from those presented in Table 1?

11. Page 19952, lines 5-8, how does the HULIS-C/WSOC ratio suggest that HULIS differs in urban/rural/forest burning environments, particularly in light of the potential biases discussed in comment 5? Moreover, how does this ratio provide any insight into HULIS formation processes?

12. Page 19949, lines 20-25, the authors infer that different ambient environments have a single “HULIS type” (line 21). However, ambient rural and urban atmospheres are known to contain particles from a wide mixture of source categories. Thus, making it most likely that HULIS in ambient environments derives from diverse mixtures of sources (e.g. for an urban environment, SOA from anthropogenic precursors, SOA from biogenic precursors, from aqueous processing of WSOC, from trash/waste burning, and from regional sources impacting an area, etc). The authors must discuss the possibility of HULIS in a given location being impacted by various sources.

13. Table 1 should report total OC and total aerosol mass for each environment.

14. Table 1 would be improved if the units for each line were included in the table. A reasonable place to add this would be in a column after the “Constituent” column.

15. Page 19950, lines 19-21, the authors suggest that biomass burning is an intense source of HULIS relative to rural and urban environments based on absolute concentrations of HULIS. The authors should also compare and contrast the relative contribution of HULIS-C to total OC and HULIS-C to total PM2.5 in the different environments.

16. Page 19950, lines 23-25, in comparing the night-to-daylight differences in HULIS C, a more meaningful comparison would be made if the authors compared the HULIS-C to total OC and HULIS-C to WSOC ratios. This would control for the larger concentrations of pollutants at night and provide insight to the chemical differences in HULIS between nighttime and daytime.

17. Page 19950, lines 13-16, in comparing the results of this study to the SMOCC study, the authors should make a direct comparison of the measured PA fraction (Decesari et al., 2006) and HULIS estimated this study. The chemical information obtained by Decesari et al., is surely available to these authors if the samples were. The direct comparison would eliminate the “difference of the occurrence of the maximum burning activity over the period represented by the selected samples…” and would warrant a thorough discussion of the “possible differences in the separation protocols applied.”

18. Figure 1- Please set the x-axis in Panel A to 190nm-280nm.

19. Figure 1- It is not clear if the differences in absorbance in Figure 1, panel B are related to differing absorbance of samples or reflect the concentrations of the samples analyzed. A more meaningful and quantitative comparison would be possible if the y-axis were normalized to the mass of HULIS-C in solution (e.g. y-axis units would become Absorbance/[HULIS-C]).

20. By definition, HULIS absorbs in the UV range (Graber and Rudich, 2006). The lack of observed chirality (in clear excess of the measurement uncertainty) in the UV range in any of the samples indicates that none of the isolated HULIS is chiral. This is a fundamental problem with the conclusions drawn from this dataset.

21. The one sample active to ECD (rural site) is written off by the following statement: “it cannot be excluded that the spectra for rural HULIS reveal chirality” (page 19953, line 9). No discussion is provided of what this result might mean if the authors accept the optical activity of the rural HULIS as real.

22. Figure 3- It is not clear if the differences in absorbance in Figure 3 are related to differing absorbance of samples or reflect the concentrations of the samples analyzed. A quantitative comparison would be possible if the y-axis were normalized to the mass of HULIS-C in solution (e.g. y-axis units would become Absorbance/[HULIS-C]).

23. Since HULIS absorbs in the visible region of the electromagnetic spectrum and exhibits a yellowish color in aqueous solution, why was this region of the spectrum not investigated by CD techniques?

24. Page 19954, lines 12-13, the authors state that based on IR spectra, “lignins contribute remarkably to the HULIS formation in biomass burning.” However, in light of comment 5 and the potential for low-molecular weight lignin precursors with aromatic rings and carbonyl bonds (e.g. vanillin, syringaldehyde, or acetovanillone), this result may be an artifact and not attributable to HULIS.

25. The VCD data suggests that the carbonyl bond, which is attributed to lignin (page 19954, line 11), in the biomass burning environment is in close proximity to a chiral center. Meanwhile, the authors state on page 19943, line 4 that lignin is not optically active. This is another fundamental problem with the conclusions drawn from this paper.

26. The VCD activity of the biomass burning sample is taken at face value, not discussed in the context of possible biases or artifacts. This one measurement serves as the basis for major conclusion of the manuscript that biomass burning HULIS is optically active.

27. With respect to the VCD data for the biomass burning sample, Is the rotation of light (right or left) in the same direction as that of cellulose or other biopolymers that may be contributing to the observed HULIS?

28. With respect to the title of the manuscript, “Chirality and origin of atmospheric humic-like substances,” it is suggested that the word “origin” be removed, since no novel insights into the formation of HULIS is provided in this manuscript.

Technical Corrections

a) Run-on sentences detract from the manuscript’s readability (e.g. p. 19940, lines 1-5; p. 19944, lines 21-25 and 25-29)

b) Page 19945 and elsewhere, liter should be abbreviated with capital L per SI.

c) Page 19941, line 4, “since HULIS makes up a major…”

d) Page 19943, lines 1-3, requires revision.

e) Page 19944, lines 6-10, “including secondary HULIS as a major component” needs clarification and reference.

f) Page 19944, lines 15-16, “since their expected precursors are not chiral…”

g) Page 19944, line 20, “environment, but”

h) Page 19944, line 21, The phrase “Secondary HULIS generated in the gas phase usually condense onto existing particles…” is contradictory to the current knowledge of HULIS. By definition, HULIS is refractory (i.e. will not be present in the gas phase) (Graber and Rudich, 2006). This statement is problematic because it is not clear if HULIS is generated in the gas phase and because if it were formed in the gas phase it would most certainly condense.

i) Page 19944, line 24, “biomass burning can, however, provide…”

j) Page 19945, line 10, “quartz fibre filters were pre-baked”

k) Page 19945, line 15, “from 3 to 10 June”

l) Page 19945, line 22, “collected at a pasture site…”

m) Page 19945, lines 25-26, “were taken from 18 to 22 September”

n) Page 19946, line 3, “were collected with a high-volume…”

o) Page 19946, line 5, “filters were pre-baked…”

p) Page 19946, line 24, “was measured by gravimetry. Weighing was repeated…”

q) Page 19951, lines 20-26, please be consistent in naming of figures. It would be easiest if the authors used Figure 1a and Figure 1b consistently and throughout the text. At present, there are references to Figure 1a and Figure 1b as well as Figure 1 Panel a and Figure 1 Panel b. I suggest removing the “Panel” notation altogether. This comment also applies to page 19952, lines 17-20.

r) Page 19951, lines 27-28, Additional details are needed in the following sentence: “The dissolved concentrations were approximately 0.4, 0.4; 0.4g L-1, respectively.” It is not clear what concentrations are being referred to (perhaps HULIS-C?). Also, it is not clear what “respectively” refers to. If this refers to the samples listed in the legend in the panel, they should be repeated here in the text for clarity.

s) Page 19953, line 25, “The similarity between the rural and urban HULIS is greater than…”

t) Page 19954, line 5, “biomass burning HULIS, likely due to…”

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 19939, 2009.