Atmos. Chem. Phys. Discuss., 5, S4815–S4825, 2005
www.atmos-chem-phys.org/acpd/5/S4815/
European Geosciences Union

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Atmospheric HULIS: how humic-like are they? A comprehensive and critical review" *by* E. R. Graber and Y. Rudich

E. R. Graber and Y. Rudich

Received and published: 2 January 2006

To the Editor, We appreciate very much the comments by the two reviewers; their input has helped to improve the presentation and clarity of the material in this paper. Essentially every comment has been addressed in the revised manuscript. In general, the following changes have been made: 1. The discussion of NMR results has now been divided into two subsections, one devoted to 1H-NMR and the other to 13C-NMR. This has greatly enhanced the presentation and clarity of these results. We have also included a new figure (revised manuscript, Figure 4A and B) showing 13C-NMR spectra for HULIS and fulvic acid. New material that was published since our review paper was originally submitted has also been incorporated (Tagliavini et al., 2005; Sannigrahi et al., 2005). [After the comments by Kiss] 2. We have expanded the discussion of the colloidal properties HULIS and humic substances, and included the new paper by Tabazadeh (2005). [After the comments of Facchini] 3. We have added a description of the collection of standard humic substances available at the International Humic Substances Society, and added text and rationale explaining why certain humic substances are better model compounds for HULIS than others. [After the comments of Facchini] 4. The discussion of FTIR spectral results for HULIS and humic substances has been expanded, including a new figure (revised manuscript, Figure 2B) showing an FTIR spectrum of a standard fulvic acid for comparison with the spectra for HULIS. [After the comments of Kiss] 5. We have included a summary of recent work by Dinar et al (2005) demonstrating that HULIS extacted from aerosol particles have much greater droplet activation efficiencies than fulvic acid. 6. In our conclusions section, we have specifically listed the features in which HULIS are similar to humic substances, and those features in which they differ. [After the comments of Facchini and Kiss]

Other minor changes have been made in response to comments by the two reviewers, and to reflect recent papers that have been published since we first submitted our review, to keep the review as up-to-date as possible. Detailed responses to the comments of the reviewers are found below, including an indication of where in the revised text the changes can be found.

Sincerely,

Ellen Graber and Yinon Rudich

Response to Comments by Kiss:

General comments In this comprehensive study the authors summarize the information presently available on humic-like substances. In addition to atmospheric HULIS aquatic and terrestrial humic substances are also examined from many aspects in order to make a thorough comparison. On the basis of this comparison the authors conclude that HULIS are not as humic-like as hitherto believed. By now it is evident

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU

that atmospheric HULIS are smaller compounds than aquatic or terrestrial humic substances and differences in other features (e.g. aromaticity, surface tension decreasing ability) can also be observed. These are most probably the consequences of the different formation mechanisms and the drastically higher reactivity of the atmosphere as compared to that of the hydrosphere or pedosphere. However, it should be noted that in some features aquatic and terrestrial humic substances differ in a greater extent from each other than from HULIS (e.g., FTIR spectra).

Response: While it is true that aquatic and terrestrial humic substances differ from each other in certain regards, it is not easy to comment at this stage that the extent of the difference is greater between them as compared to HULIS, because relatively few HULIS samples have been characterized, and those have been isolated in many different ways. Often, the entire WSOC fraction is characterized rather than a discrete HULIS fraction. In response to this comment and another one below, we have added an FTIR spectrum for an aquatic fulvic acid, and discussed its similarity to spectra presented thus far for HULIS (new Figure 2B and Section 4.3).

Comment: The HULIS name was given by Havers et al. because of the similarity to natural humic substances and to my best knowledge no other group of compounds with such high degree of similarity has been found. Consequently, in this respect I consider the HULIS name informative. Of course, it does not mean that HULIS can be replaced by natural humic substances in every aspect. Although this review is a valuable piece of work, some changes could further improve it: In some cases it is difficult to decide whether a conclusion is made by the present authors or the authors of the referred paper (e.g., page 9815, line 14-16; page 9823, line 18-19).

Response: This has been clarified in the revised text.

Comment: In other instances the phrasing of references is not completely exact (see specific comments).

Response: These have been corrected, as detailed below in response to specific comments.

Comment: References from the same author and from the same year are not always distinguished.

Response: This has been corrected.

Specific comments - paragraph 2, page 9805: On the basis of the 1H-NMR study by Havers et al. (1998)the authors concludes that atmospheric HULIS are richer in aliphatic and carbohydrate substructures than terrestrial and aquatic humic substances. However, from 1H-NMR information on the chemical environment of protons can be obtained but not on the carbon structure and this gives an alternative for the interpretation of 1H-NMR spectra. For example, the lack (or low intensity) of signal characteristic for aromatic protons means only that the abundance of aromatic hydrogen is low. However, this can be caused by either of two facts: 1. The abundance of aromatic structure is low (this is the interpretation above) 2. The abundance of aromatic structure is not low at all but most of the hydrogen atoms in the aromatic structure have been substituted by other atoms (e.g. side chains or functional groups) These alternatives should be kept in mind when interpreting NMR spectra.

Response: We greatly appreciate this comment by the reviewer. To clarify this point and the reviewed papers, the section presenting NMR results (Sec. 4.4) has been re-arranged, re-written to a certain extent, and expanded. We have now distinguished clearly between H-NMR and 13C-NMR results, and have introduced the latest paper by Tagliavini et al. (2005) presenting new H-NMR results for derivatized HULIS. The discussion is now more focused and informative.

Comment: - paragraph 3.2, page 9809: The authors refer to the isolation procedure of water soluble organic compounds on an Oasis HLB column by Varga et al. (2001). However, the results shown in this manuscript (i.e. 25% of WSOC in the effluent and 15% of WSOC retained irreversibly on the column) were obtained with silica based C18 column and not on Oasis HLB column. As it is discussed in Varga et al. (2001)

the irreversible adsorption on Oasis HLB column was negligible, while the recovery of WSOC (ca. 60%) was practically identical to that observed on C18 columns.

Response: The discussion of this paper has been made more precise.

Comment: - paragraph 4.3, page 9813: In the last sentence of this paragraph it is concluded that "In general, the IR spectra of atmospheric WSOC and HULIS have a rather more dominant contribution from polysaccharides than do humic substances." However, it is difficult to draw this conclusion from the IR results discussed in this paragraph. How can this statement be justified? The authors usually compare spectra obtained for HULIS with those obtained for aquatic or terrestrial humic substances. It would also be useful to do so with FTIR spectra, e.g. FTIR of Suwannee River fulvic acid or Nordic Lake fulvic acid from the IHSS homepage compared to FTIR of HULIS.

Response: This comment is well-taken. We have added an FTIR spectrum of SRFA to Fig. 2B (new), and revised the passage to reflect that the HULIS and FA spectra are very similar (Sec. 4.3).

Comment: - paragraph 4.4, page 9814: In this paragraph results from 1H-NMR are compared (contrasted) to 13C-NMR: Havers et al. (1998) found by 1H-NMR that most of the H atoms are present in polysaccharide and aliphatic structures and only a small portion of H atoms can be found in aromatic structures. However, it does not necessarily mean the lack of aromatic structures (see the comment above on paragraph 2)! On the other hand, Subbalakshmi et al. (2000) found by 13C-NMR that 45% of the carbon atoms can be found in aliphatic structures but a substantial aromatic component was also observed. The authors feel contrast between these results (no aromatic H by Havers et al. vs. significant aromatic carbon by Subbalakshmi et al.) and try to resolve it by suggesting that the NIST 1648 standard was oxidized during the time elapsed between collecting and analysis by Havers et al. How would the oxidation of organics explain the difference? This idea needs clear explanation or it should be omitted. Furthermore, I suggest highlighting the difference between the interpretation of 1H-NMR

Full Screen / Esc
Print Version
Interactive Discussion
Discussion Paper

and 13CNMRresults.

Response: These excellent suggestions follow on the earlier comment referring to NMR results, and have been fully addressed in the revised manuscript, section 4.4. Oxidation could affect aromaticity due to cleavage of aromatic bonds.

Comment: - paragraph 6, page 9821: In the experiments published by Kiss et al. (2003) solid phase extraction and subsequent LC-MS analysis were performed on the original aqueous extract (without ultrafiltration). Thus, average molecular weight estimates refer to the total HULIS fraction.

Response: This has been noted in the revised text.

Comment: - paragraph 6, page 9823: The authors compare average molecular weights obtained for HULIS with mass spectrometry and vapour pressure osmometry by Kiss et al. (2003) and claim that Kiss et al. explained the higher MW obtained with vapour pressure osmometry by HULIS aggregation in the solution. This is not completely exact, because Kiss et al. did not make such statement but referred to Rice and Weil (1994) who gave this explanation for similar results with soil fulvic acid. Nevertheless, the aggregation of HULIS compounds can be a reason indeed, but the possible negative bias of MS also leads to the same result as discussed by Kiss et al. and mentioned in this manuscript as well.

Response: This has been changed in the revised text.

Comment: - paragraph 9, page 9830: “HULIS-like compounds” is written in the title of the paragraph, which means: humic-like substances-like compounds. I suggest avoiding this structure.

Response: We have replaced the term “HULIS-like compounds” with HULIS.

Comment: - paragraph 9, page 9832: What did the authors mean by “chemical ionization (CE)-ESI-MS” when discussing the paper by Iinuma et al. (2004)?

Full Screen / Esc
Print Version
Interactive Discussion
Discussion Paper

Response: This has been corrected to capillary electrophoresis.

Technical comments - paragraph 5.1, page 9815: Tetramethylammoniumhydroxide was used in Py-GC-MS studies by Gelencsér et al. - paragraph 5.1, page 9816: “precipitated”, “sulfur” - paragraph 5.4, page 9818: “Suwannee” - paragraph 9, page 9831, line 27: “polymerization” - paragraph 10, page 9835: “bimodal”

Response: All technical comments have been corrected in the revised text.

Response to Comments by Facchini

General Comment The Authors report a comprehensive overview on atmospheric HULIS centered on the important question raised several times in the atmospheric chemistry community: “how humic-like are atmospheric HULIS”? a) In the abstract the central question is summarized and the Authors note that HULIS have a lower molecular weight and lower aromatic content as compared to terrestrial and aquatic humic substances. I believe that the Authors should stress both in the abstract and in the conclusions that the characterization of HULIS in atmospheric samples is mainly performed on aqueous extracts of aerosol (these are clearly a subset of HULIS), only few data are in fact based on alkaline extracts (no mass spectrometric measurements, for example) and more effort should be made also in the identification of HULIS in the fraction of aerosol non extractable in water.

Response: This was already discussed in the conclusions section of the original manuscript, but we have now emphasized the point even more so in the conclusions, and have added it to the abstract. We have also noted this throughout the text, where appropriate.

Comment: I do believe that the main conclusions on the difference in molecular weight and aromatic content could also be due to the limited number of observations of atmospheric samples (mainly on water extract) presently available. In particular, I suggest to remove in the abstract and in the last paragraph the sentence: “The essential differences as denoted throughout, point to the possibility that HULIS may not be nearly as humic-like as hitherto believed."

Response: In response to this comment, we have replaced this line in the conclusions section with a paragraph summarizing the similarities and differences between humic substances and HULIS seen until now (last two paragraphs of Sec. 11), and added the caveat that such differences and similarities may change as HULIS characterization improves. The original sentence was removed from the abstract.

Comment: b) Another important point which is lacking in the paper, which is partially connected to the solubility properties of HULIS and to the partitioning between the aqueous and insoluble phases of aerosol and cloud droplets, is a discussion on colloidal properties of HULIS and on the interaction with metals in solution. This latter aspect, which is very well known in the case of natural humic substances, should be included in the review (with the appropriate references) discussing the potential implication for atmospheric chemistry. The complexing properties of metals with humic substances have been studied by Gelencser et al. 2000 (by means of voltammetry). I suggest to add a paragraph to section 7 (on hygroscopic properties and surface tension) to discuss this aspect.

Response: The reviewer is correct that colloidal properties of HULIS could be very important for atmospheric properties of HULIS. It is unfortunate that to now, little data exist addressing this aspect of HULIS chemistry. The original manuscript had a section devoted to surface tension of HULIS solutions, and also included a discussion of metals complexing ability of HULIS, in the context of anodic stripping voltammetry. To address this comment, we have expanded the discussion of HULIS surface activity to include some of the essential parameters controlling the colloidal chemistry of humic substances (Sec. 7.3), and have added a discussion of the potential importance of such a colloidal character to atmospheric chemistry. This includes a short discussion from the new paper by Tabazadeh (2005). The passage concerning metals complexing ability of HULIS has been moved to this new expanded section entitled: Surface and

Colloid Properties (Section 7.3).

Specific comments 1) The presence of HULIS in atmospheric samples can explain the low recovery of GCMS analysis with respect to the total carbon measured: HULIS are polar multifunctional compounds that do not eluted through GC-MS columns; on the contrary, they can be eluted through LC columns and analyzed by spectroscopic methods in the same manner as natural humic substances.

Response: This is certainly true. Other reasons may also explain the low recovery of GC/MS analyses with respect to total carbon: polar or high boiling point compounds that cannot be volatilized in the injection port, inability to separate and identify the different compounds, the non-linear response of the MS detector to C in different compounds, etc.

Comment: 2) The functional group composition of HULIS is qualitatively the same of natural humic substances: oxygenated functional groups (mainly hydroxy- and carboxyl) on an aliphatic and aromatic back-bone. The recent paper by Tagliavini et al 2005 (in ACPD) shows indubitably that HULIS are polycarboxylic acids like other natural humic substances.

Response: Discussion of the new paper of Tagliavini has been added to the revised version (Sec. 4.4.1). To address the reviewer's concerns, we have now clearly stated where needed in the text that in terms of some features, such as polyacidity and polydispersivity, HULIS is similar to humic substances (e.g., last paragraph of paper). In terms of other characteristics, HULIS is not so-humic like, for example, in droplet activation efficiency. A new discussion on droplet activation by HULIS as compared to humic substances has been added (Sec. 7.2)

Comment: 3) The Authors note that atmospheric HULIS have a lower molecular weight compared to other natural humic substances on the basis of the mass spectrometric spectra and results of ultra filtration methods. This is not an original point since it was already discussed by Kiss et al. 2003.

Response: This is a review paper. The paper by Kiss is extensively discussed (Sec. 6).

Comment: 4) The Authors state that despite the various hypotheses reported in the literature, the origin of HULIS remains an issue. This point is misleading, because the reader may think that we have no conclusive data from experiments. Instead, several sources of HULIS have been detected in the atmosphere: e.g., Mayol-Bracero et al. 2002 showed that HULIS were clearly associated with biomass burning emissions. In general, in polluted environments, the concentration of HULIS is correlated to TC and therefore to anthropogenic emissions (e.g, Decesari et al., 2001).

Response: The original manuscript discussed quite extensively both field and experimental data related to hypotheses for HULIS formation in the atmosphere, including biomass burning as a source (Mayol-Bracero et al. 2002; Sec. 8). In the revised manuscript we have added the findings of Decesari et al. (2001) showing the relationship between urban pollution and HULIS content (Sec. 10).

Comment: What is not known is: a) the importance and the magnitude of possible natural sources of HULIS in the remote areas (apart the marine environment). b) the chemical mechanisms of HULIS formation. In this respect, as the Authors report, all the hypothesised chemical mechanisms cannot account for the full structure of HULIS. However, it would be also useful to discuss to which extent the different chemical pathways can account in terms of the structure of HULIS. For example: oxidation of soot by ozone (Decesari et al.2002) -> polycarboxylic aromatic acids; polymerization of aromatic acids and carbonyls in liquid phase by H_2O_2 (Gelencser et al., 2003) -> aromatic acids and phenols; polymerization of aliphatic carbonyls (Jang et al., 2003) -> polyhydroxy-aliphatic compounds and polyethers;

Response: We have added a discussion of the extent to which different chemical pathways can lead to different HULIS components, as suggested in the comment (Sec. 9, p. 33).

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU

Comment: 5) The Authors recommend a comparison between the different analytical methods for HULIS determination. It is suggested to add as a reference a paper by Limbeck et al. (2005), now in press in Analytical Chemistry. The paper shows interesting results in particular on the chromatographic fractions separated by ion exchange methods and by adsorption on hydrophobic cartridges. These fractions are partially overlapped, and this is the same chromatographic behaviour characteristic of other natural humic substances.

Response: We have now added to the manuscript a short description of the latest paper by Limbeck et al. in Anal. Chemistry. (Sec. 3.2, p. 7).

Comment: 6) The fact that HULIS are humic-like only to a certain extent is not surprising, given the different sources and the large variety of chemical formation and transformation processes which can produce HULIS in different environments. The previous studies on HULIS have referred to their similarities with natural humic substances because standards of these compounds are available and can profitably be used as surrogate for HULIS in laboratory studies. These laboratory studies were aimed at clarifying the effect of HULIS on physico-chemical properties of the aerosol. In this respect, it would certainly be helpful if the authors would try to clarify to what extent these standards can be used as models for HULIS. Different standards of humic substances (e.g., Aldrich HA, Nordic HA, Suwanee River FA, ect., some available as acids, others as salts of alkaline metals) have been used so far in the laboratory studies, often quite arbitrarily. Since natural humic substances include a very large variety of substances differing with respect to functional group composition, molecular weight and water solubility, the authors could at least indicate if and to what extent some humic standards could be used as a more appropriate surrogate for HULIS than others.

Response: We have added some discussion to this regard in the revised manuscript in two places: (Sec. 3.1, p. 5; Sec. 11, p. 39).

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 9801, 2005.