Atmos. Chem. Phys. Discuss., 5, S4170–S4174, 2005
www.atmos-chem-phys.org/acpd/5/S4170/
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Atmospheric
Chemistry
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Discussions

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

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Received and published: 28 November 2005

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 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 mecha-

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nisms 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). 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). In other instances the phrasing of references is not completely exact (see specific comments). References from the same author and from the same year are not always distinguished.

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.

- paragraph 3.2, page 9809: The authors refer to the isolation procedure of water-

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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.

- 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 substancesĚ” 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.

- 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 and 13C-NMR results.

- 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.

- 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.

- 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.

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

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”

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