Atmos. Chem. Phys. Discuss., 5, S3574–S3577, 2005
www.atmos-chem-phys.org/acpd/5/S3574/
European Geosciences Union

Atmospheric
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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: 3 November 2005

General Comment

The Authors report a comprehensive overview on atmospheric HULIS centred 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 characterisation 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

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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. 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.”

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.

Specific comments

1) The presence of HULIS in atmospheric samples can explain the low recovery of GC-MS 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.

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.

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.

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). 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;

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.

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.

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

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