**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Characterization of high molecular weight compounds in urban atmospheric particles" *by* V. Samburova et al.

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General comments

This manuscript deals with the molecular weight estimation of humic-like substances (HULIS) extracted from urban aerosol. Since HULIS account for a significant fraction of the water-soluble organic content of atmospheric aerosol, their characterization is important to understand the formation, interactions and the role of these compounds. The authors used size exclusion chromatography with UV-VIS detection and laser desorption mass spectrometry to obtain information on the molecular weight of HULIS and UV-VIS spectroscopy to quantify these substances. A number of questions arose while reading the manuscript. Answering these questions (where possible) would increase

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the quality of the paper. The uncertainty of the MW and concentration values should be estimated and clearly declared when assumptions are used.

Specific comments (including technical ones as well)

Introduction

The names of authors are mispelled on page 439: Line 4: Fuzzy should be Fuzzi Line 14: Kryváscy should be Krivácsy) Line 16: Zapoli should be Zappoli

Experimental:

Page 440 line 14: The authors refer to Krivácsy et al., 2000 as an example for the extraction of HULIS from atmospheric particles with basic solvent such as aqueous sodium hydroxide. However, Krivácsy et al. analyzed fog samples and did not use basic solvent for extraction.

Results

Page 442 line 25: Here the authors write about "peaks in the high molecular weight range". It is important to emphasize that in aqueous SEC a number of secondary inter-actions may occur that hinder the molecular weight determination from retention times. In this study alkaline mobile phase was applied to reduce hydrophobic interactions. Furthermore, 0.3 M NaCl was used to suppress electrostatic interactions between the negatively charged stationary phase and the negative analyte ions. Nevertheless, there is no guarantee that the secondary interactions have been eliminated as discussed also by the authors on page 443. The two types of standards (PMA and PEG) gave significantly different calibration lines evidencing that there were unwanted secondary interactions under the conditions applied. PMA was selected to give MW estimates due to its acidic character. On the other hand, even with PMA unrealistic MW values (40 or even less) were obtained for compounds eluting after 7.6 min. So, the authors concluded that the late eluting compounds were closer to PEG in polarity. I feel this approach a little bit arbitrary: different standards are selected for different parts of the

chromatogram in order to obtain "realistic results". In my opinion it should be the other way around: appropriate standards should be selected that fit the chemical nature, size range, shape, etc. of the analyte and then MW estimates could be obtained. However, as long as these features of the analyte are unknown MW estimation by SEC is very uncertain. In this case only qualitative results can be obtained, e.g. similarity to standards, more exclusion (size or ionic?) for Aldrich humic acid (AHA) than for the aqueous or alkaline aerosol extract, etc.

Page 443 line 4: Which dicarboxylic acids were examined?

Page 444 and 445: Possible MW limit is concluded from mass spectra on page 444 but unwanted processes (fragmentation, multiple charging, cluster formation, etc.) are not discussed, only partially mentioned on page 445. This makes the conclusions on the MW uncertain. It would be useful to summarize briefly the experience with LDI-MS on aquatic and/or terrestrial humic substances to give a hint on the uncertainty of the MW estimates. The LDI-MS parameters are listed on page 441. Are they the result of some optimization for the current application or were they found in other relevant application in the literature?

Page 445 and 446: The authors used AHA for the spectroscopic quantification of HULIS. The prerequisite for such a quantification is the equality (or at least similarity) of specific absorption coefficients at the wavelength used. The authors state on page 446 that: "The extinction coefficient of the humic acid standard and HULIS (depending largely on the types and concentrations of chromophores) might be different for the same retention time window, which would introduce an error for the quantitative estimates. However, so far no better-defined alternatives to humic acid are available and the quantitative comparison with the total organic carbon (see below) indicates that the current estimates are reasonable." I think it is a better approach to isolate some HULIS from the urban samples (e.g. Varga et al., Talanta 2001) and then to determine the specific absorption coefficient. This value can be used then for further samples. (Although, in case of 3 samples the isolation is not a time-consuming work and gives

more reliable results then the spectroscopic estimates.) This way the error introduced by the difference in absorbance of HULIS and AHA can be eliminated. Without such a justification the estimated concentration values possess a significant uncertainty and this should be declared in relevant parts of the paper (also in the abstract and the conclusions).

References

The names of several authors are misspelled, e.g. Andraccio - Andracchio Etgerton - Etgrton Zappoly -Zappoli

Also, a spell-check and a grammar-check throughout the text would eliminate some errors.

Figures

Figure 1 What wavelength was used to create the chromatograms?

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 437, 2005.