Atmos. Chem. Phys. Discuss., 8, S1351–S1354, 2008
www.atmos-chem-phys-discuss.net/8/S1351/2008/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Properties of atmospheric humic-like substances – water system" *by* I. Salma et al.

I. Salma et al.

Received and published: 7 April 2008

The authors would like to thank the Referee, Yinon Rudich of Weizmann Institute of Science, Israel for his precious and competent comments and suggestions for further improving and clarifying the manuscript. We have considered all the recommendations, and made the appropriate alterations. Our specific responses to the detailed comments are as follows.

Response to Comments 1-3, 5, 13 and 15 The suggestions were mostly adopted. We just note that the discussion paper already contained a large number of (more than 60) references, and that a comprehensive collection of related publications can be only subject of review type papers.

Response to Comment 4 We agree with the Referee that some properties of HULIS do

depend on seasons. The first and second aerosol sampling campaigns dealt with in the paper were performed at the same site in May and July, respectively for one week each. During these time periods, however, the average micrometeorological conditions were rather similar, and the chemical air quality parameters for both periods were also close to each other. The later agreement was demonstrated in section 2.1 by two important chemical species, namely by the ranges and medians of the daily mean PM10 aerosol mass and by the mean and maximum concentrations of ozone. It is thought, therefore, that the formation processes of HULIS were similar for both sampling periods, and that the possible deviations in the properties of these HULIS samples were within the experimental uncertainties. A brief sentence was added to the text to clarify this.

Response to Comments 6, 8-9 The collection of organic aerosol species by quartz fiber filters is subject to sampling artefacts. On the one side, the collection process alters the gas-particle equilibrium of a number of condensable constituents of the aerosol (as semi-volatile organics) which leads to negative (evaporative) bias, and on the other side, adsorption of some gaseous compounds (mainly volatile organics) by the collection substrate can occur, resulting in positive (adsorptive) bias (Jacobson et al., 2000). It is generally assumed that the positive sampling artefacts prevail in collections with quartz fiber filters in cities (Turpin et al., 2000; Viidanoja et al., 2002; Salma et al., 2004). The sampling artefacts for organic aerosol constituents including HULIS were investigated by tandem filter subtraction method (Fitz, 1990; Kirchstetter et al., 2001) in a previous study in Budapest (Salma et al., 2007). The aerosol samples were collected on sets of two (front and back) quartz fiber filters of the same lot number in series. The back-to-front concentration ratio for HULIS was 17% (practically equal to that for organic carbon), thus significant. Direct adsorption of HULIS being a polymer-type material in considerable amounts on the (back) filters is rather unlikely due to their low volatility. The presence of HULIS on the back filters was explained by their formation during the sampling process via adsorption of volatile (aromatic) gaseous precursors on the filter surface and their heterogeneous reactions with oxidants (e.g., O3, OH, NO3), which was followed by polymerisation or oligomerisation similarly to the

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formation paths in the atmosphere. A reference to the paper discussing the sampling artefacts for HULIS in urban-type aerosol samples and its conclusions in more detail and a brief indication of the issue was added to the text at the required places in order to specify the statements.

Response to Comment 7 The uncertainty of the aromatic carbon content in HULIS calculated as the standard deviation of several measured data was estimated to be 10-12%. The text was completed accordingly.

Response to Comment 10 Contributions to the absorbance at a wavelength of 280 nm from the other compounds present in the aqueous samples were neglected because it is the electron transition in structural subunits of humic substances that dominate the effect (Traina, 1990). The corresponding sentence was modified to make it clear now.

Response to Comment 11 The complementation was adopted by modifying the sentence.

Response to Comment 12 A short sentence was added in order to include the possible effects of the constituents of HULIS with very large molecular mass.

Response to Comment 14 We agree with the Referee that the van't Hoff factor for HULIS is directly related to the solution pH. This is the reason why the pH values for the experimental data were also indicated in Figs. 3 and 4. The pH depends on the acid dissociation constant of carboxyl groups present in the HULIS molecules. The issue is dealt with in detail in another manuscript that is practically finished and is to be submitted to the ACPD very shortly. A brief sentence was added to indicate all this.

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 1981, 2008.