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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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This work described fundamental research covering many aspects of atmospheric HULIS properties. Some part of the work (e.g. MW determination) uses questionable methods thus the results are less valuable, whereas the determination of dissociation degree and solubility is novel and more interesting. However, direct atmospheric relevance of most of the results is much weaker than that implied by the authors, since pure HULIS particles do not exist as such and the presence of inorganic ions tremendously affects all the properties they studied. Nevertheless the results are still valuable in terms of characterization of pure HULIS and comparison of some osmotic properties with those of humic matter from other environmental compartments.

Specific comments:

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Page 1987 Line 14 and 24 It seems that the solubility measurements were performed actually twice, since the conductivity measurements were also followed by TOC determinations. Were the solubilities calculated from the latter also included in the results?

The manuscript reports mean mass concentrations for the major types of carbonaceous compounds and their operationally defined sub-fractions (WSOC, WinSOC). Since the two samples were collected for one week each (Page 1985, Line 25), what is the meaning of the "mean"?

Page 1991, Line 12: Why did not the authors dilute SRFA solutions to the level at which they experience no overloading?

Page 1991, Line 28 It was an interesting finding that the molar absorptivity of HULIS did not show a plateau in the low concentration range, indicating that some association behavior may be operative.

Page 1992 The use of molar absorptivity for molecular weight (MW) estimation, developed specifically for humic and fulvic compounds, should be strongly discouraged. The reason is that atmospheric HULIS were shown to be so much departed from terrestrial and aquatic humic matter, in terms of their average MW and formation mechanism. It is questionable, for example, which value of molar absorptivity was chosen from a monotonically decreasing curve for HULIS (page 1991, Line 28)? Thus, any application of this simple approach would have required careful validation against independent methods, which was actually not reported in the paper. It is not convincing at all that relevant optical properties are almost identical (Page 1992 Line 20), this most likely refers only to the shape of the UV-VIS spectrum but not to the existence of any relation to apparent MW as proven for terrestrial and aquatic humic matter. Therefore it is not surprising that the method yielded significantly higher average MW values than those determined with three independent methods (Page 1992, Line 8). It was a kind of circular argument that the authors found average MWs markedly outside the range the validity of the correlation was originally proven (Page 1993, Line 20). This is actually

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manifested in Table 1 (Page 2006) which shows that all parameters markedly depends on the degree of dilution the HULIS solution is analyzed (while it does not depend on SRFA within the range of uncertainty). Even if MW might interpreted by some associations (though MW actually decreases with increasing concentrations, which is just the opposite that would have been expected), the variations of aromaticity is more difficult to interpret

Page 1994 Line 8 It is not specified which method is used for the estimation of the aromatic carbon abundance.

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