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Atmospheric Chemistry and Physics Discussions

Interactive comment on "How many carboxyl groups does an average molecule of humic-like substances contain?" *by* I. Salma and G. G. Láng

Anonymous Referee #3

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General comments:

Humic like substances (HULIS) are of important constituents of tropospheric aerosols, thus the knowledge of their chemical and physical properties are of utmost importance to assess their role in atmospheric processes. The authors study the molecular weight, dissociation constant and number of carboxylic groups of an average HULIS molecule using the results of conductivity measurements. Conductometry is not a specific method for carboxylic acids, thus the contribution of other compounds to the conductivity should be also considered. The authors consider the carboxylic group as the only acidic group in the isolated fraction of the water soluble organic carbon. The organosulphates might also contribute to the acidity/conductivity of the investigated samples affecting the results. The article is generally well written and worthy of publi-

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cation after clarification of some points.

Specific comments:

Page 10009: The extraction procedure and the modified one step procedure is not explained, please add more details or a reference to the extraction/isolation procedure.

The mass concentration of the HULIS solution was calculated from the TC data using a mass/carbon conversion factor. This conversion factor might change with the concentration, since as the solution is diluted more and more hydrophobic compounds might dissolve, which contain less amount of polar groups. On the other hand since the samples were filtered using a 0.22 m pore size filter, the filtered samples might contain aggregates, thus overestimating the mass concentration of dissolved HULIS, which are relevant for the conductometric measurements.

Page 10011: The value given for lambdaHULIS- needs to be better clarified. Which kind of structures were took into account and what is the uncertainty of this estimation?

Page 10012: The unit of limiting molar conductivities is not correct.

Page 10013: There are some small miscomputations in the article. (E.g. on page 10013; M=A * lambda0; 76 g S-1 dm-2*325 S cm2 mol-1/100=247g mol-1)

Page 10014: The last paragraph on page 10014 is not clear. The authors use the following equation: Average number of dissociable carboxyl groups= L0/L ,where L is the limiting molar conductivity, of HULIS experimentally determined for molecular masses of 248 and 305. L is the molar ionic conductivity of HULIS. This equation is basically gives the reciprocal of the dissociation degree. Since the dissociation degree depends on the concentration, its reciprocal also depends on the concentration. This would mean that the number of dissociable carboxyl group of an average HULIS molecule is a function of the concentration. How would the modelled pH value change if an average HULIS molecule would have contained 1.1-1.4 carboxylic group? It is also possible that other compounds (e.g. organosulphates) contribute to the higher

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pH value of the samples. How much is the uncertainty of the results if this other component class is also considered?

Table 1 contains only rough estimates on the average molecular weight. Please indicate the error of this estimation.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 10005, 2008.