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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

I. Salma and G. G. Láng

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The authors thank Referee #2 for his/her precious comments and suggestions for further improving and clarifying the ACPD paper. We have considered all recommendations, and made several alterations. Our specific responses to the comments are as follows.

Response to Comment 1 We shortened the experimental section, stated now explicitly that the measured data were already published (and cited the corresponding paper) according to the Referee’s request. We just note that the presented evaluation of the experimental data - for instance - led to new and valuable conclusions on the acidic dissociation constant of HULIS, made it possible to determine the average molecular mass of HULIS in perfect agreement with the earlier results with a method that is rather different in principles from the previously utilized approaches, and it al-

lowed to estimate the number of carboxyl group within HULIS. Some data (e.g., pH values) were presented earlier in figures, and they were not used in that stage of the evaluation and interpretation.

Response to Comment 2 Little information is available on the carboxyl group abundance in HULIS. NMR can be considered to be the most elaborated method at presence for this purpose. We cited both major papers we were aware of and quoted the relevant data without selection. The value shown in Table 1 from Tagliavini et al. (ACP, 6, 1003-1019, 2006) is based on a single sample, while the data from Samburova et al. (Atmos. Environ., 41, 4703-4710, 2007) were obtained by averaging nine individual values for the summer and winter samples. Carboxyl group abundance data were also obtained in Samburova et al. by pH titration, and the mean value by the titration for the summer samples was indeed somewhat larger than that determined by H-NMR (9.3% with respect to 5.7%) mainly due to two individual outlier data. The difference was attributed by the authors of that paper to the fact that “hydrolysable groups such as esters might affect the acid quantification by titration, if they are present in complex compound mixtures”, and they also concluded that “quantification of carboxylic groups cannot be deduced directly from the titration”. This is why we preferred to compare the data derived by NMR to the corresponding data by NMR. We modified the text now to clarify these, and indicated now the spread in the H-NMR data sets by adding standard deviations to the mean abundances in Table 1. The issues of the differences in the literature data, and of some non-uniform features inherent to HULIS are also dealt with in Responses 4 and 5.

Response to Comments 3 The mass percentage of the carboxyl group for the PA chemical fraction was roughly estimated from the mol% of the carboxyl carbon and carbon percentage of several main functional groups in the PA fraction that were all reported in Tables 6 and 9 of the cited paper (ACP, 6, 1003-1019, 2006) assuming - in accordance with text of the paper - 1 carbon atom in 9 to be present in carboxyl group. In this way, we obtained a mass percentage of 28.8%. After we had submitted the MS, we

ACPD

8, S6022–S6025, 2008

received a more precise value of 25.5 m/m% on request from a lead author of the cited paper (S. Decesari), and we adopted and utilized now the later data in the ACP MS, and modified the text in Sec. 1 and Table 1 accordingly. We agree with the Referee that the different isolation methods in use for HULIS can cause substantial and systematic uncertainties. We stated this in our several previous papers on HULIS (e.g., J. Geophys. Res., 111, D23205, 2006 or Atmos. Environ., 41, 4106-4118, 2007). We thought it was redundant in the present shorter paper. Nevertheless, we added a brief sentence to Sec. 3.1 now in order to include this possibility as well.

Response to Comment 4 The comment directed our attention to the necessity of discussing the reliability and uncertainty of the adopted abundance data and, in particular, their impact on the estimated molecular mass. As a result, we extended Sec. 1 by a brief critical discussion of the literature data utilized including the uncertainty related to the conversion of the H-NMR hydrogen abundances to carbon amount, and cited an excellent reference of Fuzzi et al., Geophys. Res. Lett., 28, 4079-4082, 2001. We reformulated this part of the discussion paper to emphasize the limitations of the approach.

Response to Comment 5 HULIS are inherently composite materials for which uniform behaviour and properties cannot always be expected. Spontaneous change in the aggregation and conformational states can take place under even slightly changing solution or other conditions, which can cause significant differences. In this view, the molecular mass estimated to be between 250 and 310 Da is not unconformable to the value of 830 Da derived from the data of Samburova et al. (Atmos. Environ., 41, 4703-4710, 2007), especially when the estimate is compared to the other data of 2500 and 3300 Da obtained by assuming three or four carboxyl groups in HULIS, respectively. Moreover, the agreement between the modelled and measured pH data was rather good.

Main general purposes of the paper are to outline the importance of the carboxyl group within HULIS, and to document that some conclusions that are derived from the exist-

ACPD

8, S6022–S6025, 2008

Interactive Comment

ing data sets are not always consistent with our general knowledge on HULIS. Further investigations are definitely required and are very desirable in this topic. The conclusions and ideas formulated in the present MS can very well contribute to the progress.

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