

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

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The authors thank Referee #3 for his/her precious comments and suggestions for further improving and clarifying the ACPD paper. We have considered all the recommendations, and made the appropriate alterations.

Organo-sulphates have recently come into the focus of organic aerosol research as potentially important components of water-soluble secondary organic aerosol. They were mainly identified as sulphate esters of abundant biogenic carbonyl compounds in both smog chamber and continental aerosol, and their rural concentration was very recently estimated to be 0.02–0.09 $\mu\text{g S/m}^3$. Very little is known about their concentrations in urban environments; it is expected to be rather low. Some further experiments are definitely needed to investigate their contribution to properties of HULIS, and specifically, their separation from HULIS by the isolation methods. Most sulphates are soluble

in water but the part with high molecular mass may not be. As far as the dissociation of the hydroxyl groups present in HULIS is concerned, it was neglected in the present conductivity measurements because of the acidic pH interval. We modified the text to clarify all these.

Our responses to the specific comments in the order of their appearance are as follows.

Response to Comment 1 The solid-phase extraction method applied was presented in detail in a separate paper which was cited. Now we added a new reference where the modifications leading to the one-step procedure actually utilized were described.

Response to Comment 2 We agree with the Referee that the OM/OC mass conversion factor for the dissolved HULIS can change with the HULIS concentration within the saturation concentration range (near the dissolution limit). It was found in an earlier study (ACP, 8, 2243-2254, 2008) that HULIS are completely water soluble up to a concentration of 1-1.5 g/l. Similarly, HULIS aggregates (micelle-like structures) are expected to occur above a concentration of 5-10 g/l (Atmos. Environ., 39, 5472-5480, 2005 or ACP, 8, 2243-2254, 2008). The ranges overlap somewhat with the upper end of the investigated interval. Nevertheless, the experimental data evaluated in the present work primarily correspond to smaller concentrations. It can be seen in Fig. 1, for instance, that the last three data were excluded from the data treatment because the activity coefficients of the corresponding solutions were smaller than unity. The OM/OC ratio for HULIS in this smaller concentration interval can be expressed by a constant. The incomplete and selective dissolution of the mixture (HULIS) as pointed out correctly by the Referee can represent an additional reason why the last three experimental data (for the partially saturated solutions) in Fig. 1 deviate from the linear line. A sentence was added to the Sec. 3.2 to include this effect as well.

Response to Comment 3 The molecular mass of HULIS was estimated in Sec. 3.3 by an interval. In the first extreme case, it was assumed that the molar ionic conductivity of the HULIS anion is negligible to the molar ionic conductivity of the H⁺ cation due

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to their very diverse masses and mobilities. In the other extreme case, the molar ionic conductivity of the HULIS anion was approximated by the molar ionic conductivity of common small anions (like fluoride anion), and this was added to the molar ionic conductivity of the H⁺ cation. The two mass values obtained in this way marked an interval of the possible molecular masses. The description was clarified in the new version.

Response to Comment 4 The upper index in the unit of the limiting molar conductivity was corrected in the text at three places.

Response to Comment 5 We presented rounded mean experimental data taking into account their estimated uncertainty. However, the data were stored and further evaluated in a numerical format that had 15 significant digits. The computational results were rounded off before they were given in the MS. This process caused the small and definitely seeming miscomputations.

Response to Comment 6 The average number of dissociable carboxyl groups was estimated by dividing the limiting molar conductivity ($LAMBDA_0$) of HULIS experimentally determined using Kohlrausch's empirical equation by the molar ionic conductivity of HULIS ($\lambda(HULIS) = \lambda(H^+) + \lambda(HULIS^-)$) represented by the molar ionic conductivity of the hydrogen cation (adopted from cited tables) and negligible or significant molar anionic conductivities. The upper case and lower case lambdas must have been modified in the referee's version of the paper. Naturally, the ratio of the limiting molar conductivity to the molar ionic conductivity, thus $LAMBDA_0/\lambda(HULIS)$ doesn't give the reciprocal of the dissociation degree, and the maximum number of dissociable carboxyl groups within HULIS doesn't depend on the HULIS concentration as correctly noted by the Referee. The text was extended to avoid any misunderstanding on his.

Response to Comment 7 It is extremely difficult to estimate the uncertainty of the molecular masses presented in Table 1 because they were calculated from the liter-

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ature data (functional group abundances) and the experimental conditions related to them were not exactly given. As an implication of this comment, we complemented Sec. 1 by a brief critically discussion of the reliability of the literature data adopted, and of their possible impact on the final results.

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

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