

## ***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 #2**

Received and published: 21 July 2008

This manuscript is concerned with the carboxylic acid functionality of atmospheric humic-like substances (HULIS), which make up a large proportion of atmospheric water soluble organic carbon. Understanding the acidic qualities of HULIS is important for understanding the impact of HULIS in many atmospheric functions. While the title of this manuscript, "How many carboxyl groups does an average molecule of humic-like substances contain?", purports to consider the topic on a wide basis, in essence, the scope of the manuscript is very limited.

1. This manuscript may be more suitable as a note or letter to the editor than a full-scale publication. All of the data used in this work has been previously published, and the current work represents an additional mathematical manipulation of the data. As such, I believe they can substantially shorten the experimental section, making sure to

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



clearly state that the data they use has been previously published (Salma et al. 2008).

2. The literature data they quote in Table 1 for carboxyl group abundances refers to average values reported in those sources, instead of individual sample results. In the case of Samburova's data (Samburova et al. 2007), there is also titration data, where summer aerosol had 9.3% carboxyl groups (p. 4709), not the average 5.4% used here. This makes a huge difference in MW estimates, and thus to the thesis of the manuscript. Indeed, I feel that the authors were overly selective in their treatment of available literature data, and did not do a sufficiently broad assessment. This is particularly important, considering the title of the manuscript, which requires a much more thorough approach.

3. The authors should describe how they calculated the average molecular mass from the data of Tagliavini et al (2006). In that work, that the number of carboxylic groups was estimated from the number of carboxylic H atoms compared with H atoms of other groups. It is not straightforward to estimate molecular mass from this kind of data. Besides the difference in source of HULIS (urban aerosol vs. biomass burning aerosol), another source of difference between the data of Samburova and Tagliavini may be the isolation method.

4. It seems that the most obvious conclusion from the analysis in Table 1 is that there may be some problem with the low estimates of COOH abundances obtained from the H-NMR work of Samburova et al. After all, a HULIS molecule of 834 Da bearing a single carboxyl group would not have many of the characteristics that HULIS have been shown to possess. Perhaps the problem arises in the conversion of H-NMR hydrogen abundances to carbon, seeing as the conversion factor for the different functional groups is not straightforward, as discussed in Fuzzi et al., (2001) and Tagliavini et al (2006).

5. This being the case, the calculations of MW from the electrochemical conductivity data which are based on the single carboxylic group per molecule would not have

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

much meaning. A compound with MW in the range of 248 to 305 Da with a single COOH group would be similar to, for example, stearic acid (MW 284), which is certainly not water soluble. And how can the authors reconcile the difference between their estimated MW with that of what they estimate for Samburova's data (Table 1), on which their calculation is based?

6. In short, I quite agree that the number of carboxylic acid groups in a HULIS molecule is an important question, but I don't think this manuscript does a fair job in answering it.

---

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

