Atmos. Chem. Phys. Discuss., 13, C5970–C5972, 2013
www.atmos-chem-phys-discuss.net/13/C5970/2013/

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Identification of humic-like substances (HULIS) in oxygenated organic aerosols using NMR and AMS factor analyses and liquid chromatographic techniques" *by* M. Paglione et al.

Anonymous Referee #3

Received and published: 19 August 2013

This paper describes a comparison of aerosol measurements from filter-based techniques with those from an Aerosol Mass Spectrometer with a focus on organic functional groups. It is a complicated paper drawing comparisons of direct concentrations, concentrations separated by meteorological transport regime and by positive matrix factorization. However, the discussion is methodical and clear. I agree with the other reviewers that this is a worthy paper that needs minor revisions. As the first review has a long list of editorial corrections, here I only offer a few technical comments, mostly concerning methodologies and definitions.

1. While this work is unique, there has been at least one similar comparison that has been published and should be referenced: L. M. Russell, R. Bahadur, L.N. Hawkins, J. Allan, D. Baumgardner, P. K. Quinn, and T. S. Bates, Organic Aerosol Characterization by Complementary Measurements of Chemical Bonds and Molecular Fragments, Atmos. Environ., 43, 6100-6105, doi10.1016/j.atmosenv.2009.09.036, 2009.

2. Page 17200 – Lines 1-3 – Is the "term" OC truly based on the method of measurement or instead of "The term refers to..." do you mean "OC is measured as..." ?

3. You have not indicated why the organic aerosol is important.

4. Page 17202 – Lines 10-12 – It appears that the references Limbeck and Noziere should be switched.

5. Page 17202 – Lines 13 – "discovery" seems incorrect to me. LVOOA is a term invented to represent a particular mass spectrum commonly measured with the AMS. It was not a discovery.

6. Page 17202 – Line 18 – An important part of this overall comparison is the definition of WSOC. You define WSOC as the amount of unfilterable carbon after 1 hour in DI water and an ultrasonic bath, which leads me to a couple of questions: a) since organic molecules have a very large range of water solubilities, how do you know that you are deriving all the WSOC by your method?; b) in a different sense, can you be sure that all of the groups shown in Figure 3 (e.g. all the alkyls) are from water soluble molecules, or could some perhaps be simply included in the wash?; c) have you done any tests using a mix of model aerosols from which you can assess the ability of your methodology to produce mass closure between the sum of the OFGs and the WSOC?; d) although you have not indicated a motivation for WSOC, I assume that cloud condensation nucleus activity is one of the main motivations, and in that case how important is WSOC for CCN activity? Some discussion of these aspects of the WSOC is important.

7. Page 17207 – line 6 – Were there any significant particle losses associated with the Nafion dryers?

8. Page 17212 - line 14 – certainly it appears that there was a greater marine contribution to your aerosol during Period III, but given the level of OC, EC and NO3-, I think it is questionable that the aerosol was "mainly of natural origin".

9. Page 17212 - line 28 – references are not in the list.

10. Page 17216 – lines 24-25 – a reference to the SV-OOA pattern is needed.

11. Page 17217 – lines 13-14 – perhaps true, but sulphate is mostly secondary and so the air mass history and oxidants levels likely are a more direct cause.

12. Page 17219 – sulphate comparison – I agree that the flatness of the SO4= mass concentration is a factor, but the collection efficiency of the AMS could also be a factor here and not one that averaging will necessarily correct. Is the correlation different if you use the AMS sulphate without the CE correction?

13. Page 17220 – why is the NMR more sensitive than the AMS to C-H groups?

14. Page 17221 – lines 7-8 – could the fragmentation in the AMS create the appearance of more HOA than truly exists?

15. Page 17221 – lines 14-15 – MSA mass concentrations can be estimated from AMS measurements (e.g. Phinney et al., Deep-Sea Research II, 53, 2410-2433, 2006; Langley et al., Atmos. Chem. Phys., 10, 1287-1314, 2010; Zorn et al., Atmos. Chem. Phys., 8, 4711–4728, 2008.).

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 17197, 2013.