

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.

M. Paglione et al.

m.paglione@isac.cnr.it

Received and published: 23 October 2013

The authors would like to thank Anonymous Referee #3 for his/her comments.

The Referee's comments followed by our replies are listed below.

All specific grammatical and stylistic corrections suggested by the Referee were taken into account in revising the manuscript.

Comment 2. Page 17200 – Lines 1-3 – Is the “term” OC truly based on the method of
C8379

measurement or instead of “The term refers to. . .” do you mean “OC is measured as. . .”?

&

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

Reply. We rephrased the first part of introduction highlighting the importance of OC:

"Atmospheric aerosol particles directly impact air quality, visibility and atmospheric transparency, through scattering and absorption of light (i.e., direct climate forcing effect) and by modulating the formation and properties of clouds (i.e., indirect climate forcing effect) which in turns contribute to control the climate system at both regional and global scales (Ghan, 2007; IPCC, 2007; Ravishankara, 2005). Organic Aerosol (OA) constitutes a major fraction (10–90%) of the submicron (PM1) particulate mass globally (Kanakidou et al., 2005; Zhang et al., 2007) whereas the rest of the mass consists of soot, inorganic salts, metals and elements. Whereas the elemental and inorganic fraction of the aerosol mass has been quite well featured, the composition of the organic fraction is still poorly characterized due to analytical challenges arising from the fact that atmospheric OA is a complex mixture of thousands of organic compounds with a great variety of different properties, such as oxidation state, volatility and hygroscopicity, and extremely diverse sources and atmospheric reactions."

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

Reply. Authors thank the Reviewer for the right observation: it was an oversight, thanks.

Comment 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.

Reply. “Discovery” will be substituted with “identification”

Comment 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.

Reply. Clearly, WSOC recovers the compounds dissolved from filter samples under laboratory conditions, which do not necessarily correspond to the organic compounds in aqueous solutions under atmospheric conditions. Typically, a large excess of water is used in laboratory, therefore the operationally-defined WSOC can be considered as an upper boundary for atmospheric WSOC. In the present study, we were mainly interested in comparing the chemical classes emerging from off-line analysis to the AMS factors characterized by their specific O/C ratios. The actual solubility range covered by the operationally defined WSOC is uncertain. Psichoudaki and Pandis (ES&T 2013, 47, 9791–9798) have investigated this issue and concluded that the solubility range of WSOC is more impacted by the actual mutual miscibility of the organic components than by operational parameters in the sampling and extraction methodology. In their study, two extreme cases were examined in order to bound the range of interactions of the various organic aerosol components with each other. In the first they assumed that the organic species form an ideal solution in the particle and in the second that the extraction of a single compound is independent of the presence of the other organics. In the second case, even poorly soluble compounds such as hydrocarbons and

C8381

PAHs are recovered into WSOC. During our experiment, it is plausible that hydrocarbons were present in the aerosol phase in a mixture correspondent to the AMS factor named HOA. Since hydrocarbons have generally a very good mutual solubility with a near-ideal behavior (De Hemptinne, Aqueous solubility of hydrocarbon mixtures. Rev. Inst. Fr. Pet. 1998, 53, 409–419), we conclude that their dissolution in laboratory actually obeyed to the first or the two cases presented by Psichoudaki and Pandis and that consequently HOA were not recovered into WSOC (following the “ideal model” in Fig. 2 of Psichoudaki and Pandis 2013). This confirms our assignment of HOA to WINOC rather than to WSOC in the carbon budget presented in Fig. 8 of our paper.

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

Reply. While it is likely that small particles may have been lost in the sampling line set up, the good correlation between AMS measured concentrations of inorganic compounds and MARGA observed concentrations (Mensah et al., 2012) is taken as indication, that for PM1 composition no significant loss processes occurred in the sampling system used.

Comment 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”.

Reply. “mainly” was substituted with “likely”

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

Reply. We will add them, thank you.

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

Reply. We will add the following citations to this aspect of the manuscript: -Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Ulbrich, I. M., Ng, S. N., Worsnop, D.

C8382

R., and Sun, Y.: Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review, *Anal. Bioanal. Chem.*, 401, 3045–3067, doi: 10.1007/s00216-011-5355-y, 2011 -Zhang, Q., Alfarra, M. R., Worsnop, D. R., Allan, J. D., Coe, H., Canagaratna, M. R., and Jimenez, J. L.: Deconvolution and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry, *Environ. Sci. Technol.*, 39, 4938–4952, 2005 -Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prévôt, A. S. H.: Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra, *Atmos. Chem. Phys.*, 7, 1503–1522, doi: 10.5194/acp-7-1503-2007, 2007

Supplemental Material in: Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaatto-Vaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimojo, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, *Science*, 326, 1525–1529, doi:10.1126/science.1180353, 2009

Comment 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.

Reply. To more clearly reflect this aspect we changed the corresponding sentence to now read: "LV-OOA is generally associated with the particulate sulfate fraction due to their common secondary sources and comparable low volatility."

C8383

Comment 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?

Reply. We agree with the Reviewer, that the AMS collection efficiency correction is a critical issue in the data analysis and interpretation. The collection efficiency applied to this data set follows the collection efficiency procedure developed for the EUCAARI campaign. This procedure takes the impact of nitrate on the collection efficiency and its dominance over the European continent into account (Nemitz, E., et al. (in preparation). "European submicron aerosol chemical composition derived from a campaign-based Aerosol Mass Spectrometer network." ACP). Independent comparisons these AMS results to other instruments such as MARGA show a high correlation indicating the appropriateness of the applied collection efficiency correction (Mensah et al. 2012).

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

Reply. The word "sensitive" was inappropriately used here. We actually meant that HNMR has a higher specificity for aromatic and C-H groups than AMS. Indeed, HNMR spectroscopy in D₂O provides a direct speciation of hydrogen atoms bound to carbon atoms, while it provides only an indirect information on C-O groups.

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

Reply. The authors agree to the Reviewer that the evaporation and ionization scheme of the AMS causes increased fragmentation compared to e.g. NIST mass spectra. However, the authors are not aware of any indication for an artificially increased appearance of HOA due to the fragmentation within the AMS. The authors rather believe that the lack of such a factor in the NMR analysis is due to the expected non-water solubility of aliphatic compounds, which fragments dominate the mass spectrum of the

C8384

HOA factor.

Comment 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.).

Reply. We thanks the Reviewer for this comment. Applying the fragmentation pattern given by Langley et al. 2010 to the high resolution measurement of CH₃SO₂⁺ and taking into account the observed relative abundance of CH₃SO₂⁺/CH₄SO₃⁺ of 4.5, we now quantify MSA as $\sim 7.52 \cdot [\text{CH}_3\text{SO}_2^+]$. Figure 6 was changed accordingly. Please note that the MSA concentration derived from AMS analysis is still significantly (10 times on average) lower than the concentration assigned to the NMR factor correlating with MSA.

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

C8385