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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.

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The authors would like to thank Anonymous Referee #2 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 Pg 17215 line 16-17: The authors mention that Factor 2 looks like HULIS or

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humid acid, but that the conditions were dry during the secondary processes leading to the formation of factor 2 organics. I feel like there is more to say here, perhaps another thought? It wasn't clear why it was interesting that the conditions were dry. Perhaps the authors are suggesting that the secondary processes were gas phase and not aqueous?

Reply. This is actually our belief, but the implications of this finding were left to the reader, because the assessment of the relative contributions of "traditional" vs. "aqueous" processes to SOA and HULIS formation during this experiment is not the primary topic of this paper.

Comment Pg 17216 line 17: When using PMF on AMS data, there is some precedent for downscaling the importance of m/z 44 (Ulbrich et al., 2009, Section 2.3.1) by increasing the error associated with m/z 44, m/z 18, m/z 17, and m/z 16. This help with the author's observation that factor spectra are predominately controlled by a few m/z peaks.

Reply. The authors thank the Reviewer for raising the issue of the importance of correct data treatment. We evaluated the impact of down weighting on the PMF result by comparing the results of three different degrees of down weighting. The errors at the m/z's 16, 17, 18, and 44 were taken as given by the analysis software, multiplied by a factor of 2 (standard), and multiplied by a factor of 4, respectively. Neither the resulting mass spectra nor their temporal contributions show any significant change. We therefore conclude, that not only the pure existence but also the distinct pattern of the highly oxygenated factor 4 from AMS data is real and not due to an overestimated importance of m/z 44.

Comment Pg 17220 line 8: the authors sometimes use R for Pearson's correlation and sometimes R2. It would be more helpful to keep one metric for consistency.

Reply. We will convert all correlations in the manuscript in R-values, because it can be useful to track possible negative correlations between chemical compounds or factors.

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Comment Pg 17221 lines 11-23: While it's true that the two techniques are uniquely sensitive to certain functional groups, it's worth noting the the time resolution of the two measurements likely also plays a role in the outcome of the factor analysis, and in the sources they are able to recognize and separate.

Reply. It is certainly true that the different time resolution plays in general an important role in factor analysis outcomes, as clearly acknowledged later in the same section (Pg 17221, line 28).

Comment Pg 17223 point (c) in the last paragraph: this point is really hard to follow. Please reword this. I am not sure even what the main conclusion is for this point, but it sounds important.

Reply. The identification of F1-AMS (LV-OOA) with possible WSOC components analyzed by NMR spectroscopy was not based on correlation analysis (Table 5a), but followed as a corollary from the assignments of the remaining factors. More specifically: 1.F4-AMS (FA-OOA) was assigned to F2-NMR based on their good correlation in time trends, 2.F3-AMS (HOA) was assumed, i.e. to take part to WINOC, 3.It was found that WINOC showed an excess of carbon with respect to HOA, therefore we assumed that the least oxidized fraction of OOA (mainly from SV-OOA) contributed to WINOC, 4.It is possible that some semivolatile organics (SV-OOA) were lost during the off-line chemical analysis, 5.The carbon budget (Fig. 8) at the light of the above considerations indicates that F1-AMS (LV-OOA) must take into account some of the WSOC not already included in F2-NMR, and therefore compounds traced by F1-NMR and F3-NMR must contribute to F1-AMS (LV-OOA). We will rephrase this paragraph in the new version of the manuscript.

Comment Figure 7: are the linear regression fits done as a least-squares in the y variable or a total least squares? The fit may change in total least squares, which would be the correct regression if the authors believe both metrics have approximately equal uncertainty.

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Reply. We had initially used here the ordinary least squares (OLS) regression because is the most common method used to define a line of best fit for a set of bivariate data plotted on X-Y axes. Many investigators instead use the total least squares (TLS), also called reduced major axis (RMA), to define the line of best fit when the variables on both axes are measured with error, since OLS assumes that X is measured without error (Smith et al., American Journal of Physical Anthropology, 140:476–486, 2009). Many other investigators, however, continue to use OLS in all the circumstances depending also on the interpretation of results and so there is no consensus about the best universal method of fitting. Following the suggestion of the Referee #2 we re-calculated the regression line equations with a total least squares method. We reported here (in additional Fig.1 below) these new equations and graphs. However, since our X data (HPLC_PA) are considered as a reference method to estimate the HULIS sensu stricto we believe that the use of OLS was appropriate (Smith et al., 2009). Moreover, as you can see from the graphs, the TLS results show quite different slopes, less consistency with the measured average mass ratios between the variables compared to those showed in the OLS results: average mass ratios HPLC_PA/F2-NMR and HPLC_PA/F4-AMS (reported at Pg 17222, lines 11-12 of the text) of 30% and 27% correspond well (even if not perfectly) with the OLS slopes of 3.79 and 2.51 with respect to TLS slopes of 7.06 and 4.95 of HPLC_PA/F2-NMR and HPLC_PA/F4-AMS respectively. In any case our main purpose here was to highlight the parallel time trends and so the correlation coefficients between the measurements, and the correlation coefficients (R and R²) are defined independently of the line fitting criterion and do not differ for ordinary least regression (OLS) and total least squares (TLS) (Smith et al., 2009). For this reasons (1-the substantial importance in the discussion of the R-values, not dependent of fitting criterion, 2-the supposed pertinence in OLS application, and 3-the better consistency with average mass ratios), in order to avoid giving misleading information to the readers, we prefer to eliminate the two lower panels in the Fig. 7 and leave there just the upper panel (time trends) commenting in the text only the correlation coefficients R.

Additional reference: Smith et al., American Journal of Physical Anthropology, 140:476–486, 2009

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

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13, C8373–C8378, 2013

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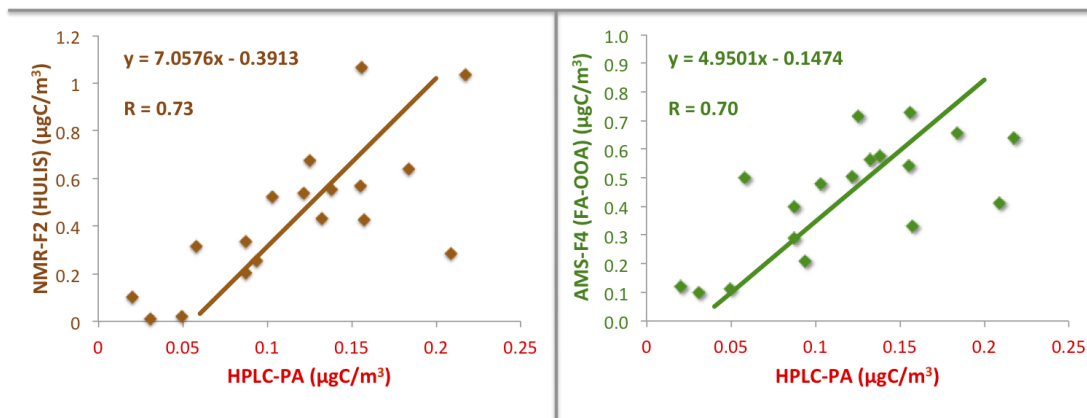


Fig. 1.

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