

Reply to Anonymous Referee #2

We thank the Referee for her/his positive comments and useful suggestions. We provide below a point-by-point reply to her/his comments.

Referees' comment: The deployments of multiple spectrometric techniques are impressive, yet they also limit the deep analyses of each dataset that was analyzed individually and briefly in this study. Although most results and conclusions are supported each other, some are speculative. Actually, I was expecting more new findings from the multiple techniques in this study, which I was a bit disappointed.

Reply: This paper presents a focus on aerosol compound mixing state and on organic composition at a continental rural site. For both discussion points, we based our analysis on the comparison between the HR-ToF-AMS dataset with those provided by parallel spectroscopic techniques. Clearly, the results of the HR-ToF-AMS itself, including the PMF-AMS findings, offer little novelty with respect to the existing AMS literature, as all organic factors found in this study have already been identified in previous experiments. On the other hand, this makes our observations more representative of the general dynamics governing the organic aerosol evolution over continental areas: Thanks to the comparison between the HR-ToF-AMS, SP-AMS, NMR, ATOFMS and TAG results, new information about the chemical nature of many "standard" AMS factors (HOA, COA, SV-OOA, LV-OOA) was eventually achieved in this study.

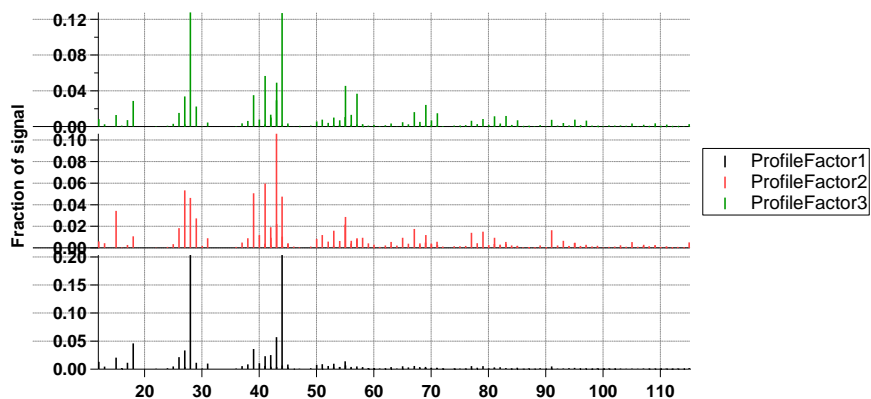
We acknowledge that the individual datasets would have needed a deeper analysis, especially for the PMF-AMS factors, for which a vast literature database is available for comparison. We will improve the characterization of the AMS factors in the main text as well as in the supplementary material, by providing some key diagnostics (e.g., the O/C and H/C ratios, etc.).

Referees' comment: The separation of LV-OOA-MO and LV-OOA-LO is speculative. In particular, the authors didn't present any PMF diagnostic plots in supplementary. The mass spectra of LV-OOA-MO and LV-OOA-LO are very similar, but I am surprised that their diurnal profiles (Fig. 7) are also very similar although their time series (Fig. 9) are quite different.

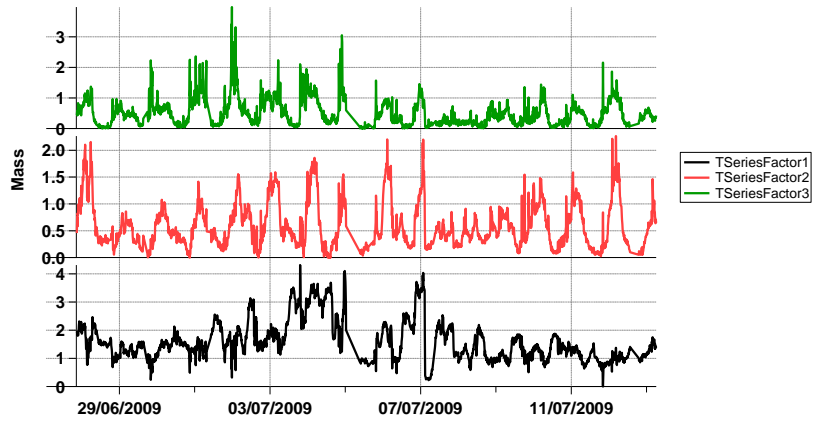
Reply: Analogous results (two OOA types, one more oxidized than the other, with similar spectra, similar diurnal cycles, different time trends) were obtained in previous experiments (Setyan et al., Atmos. Chem. Phys., 12, 8131-8156, 2012).

The main reason for considering two separate factors for the LV-OOA in this study is that such divide occurs early in the PMF analysis when the number of factors is progressively increased. By adopting a four-factor solution, when the COA is still undifferentiated, PMF already distinguishes between LV-OOA-MO and LV-OOA-LO. Increasing factor number from four to five does not perturb the contributions and the spectral profiles of the two LV-OOA types (see figures below)

3-factor solution for the HR dataset, mass spectra (a) and time series (b):

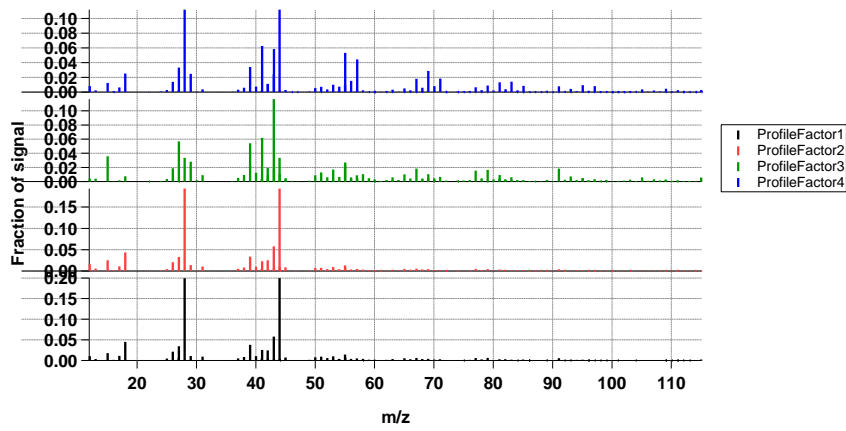


(a)

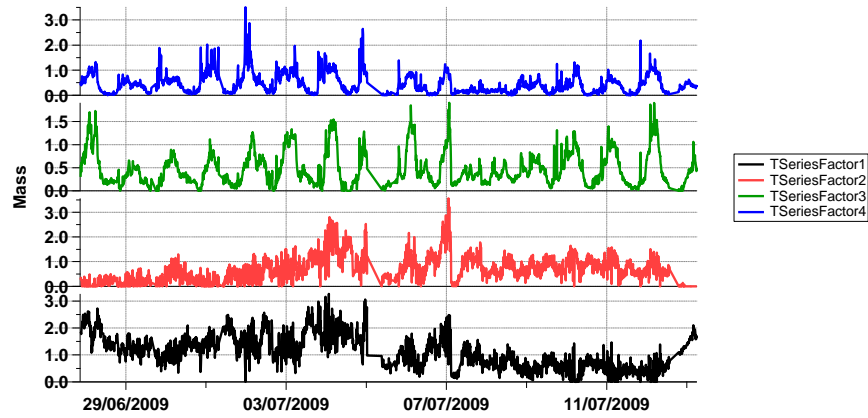


(b)

4-factor solution for the HR dataset, mass spectra (a) and time series (b):

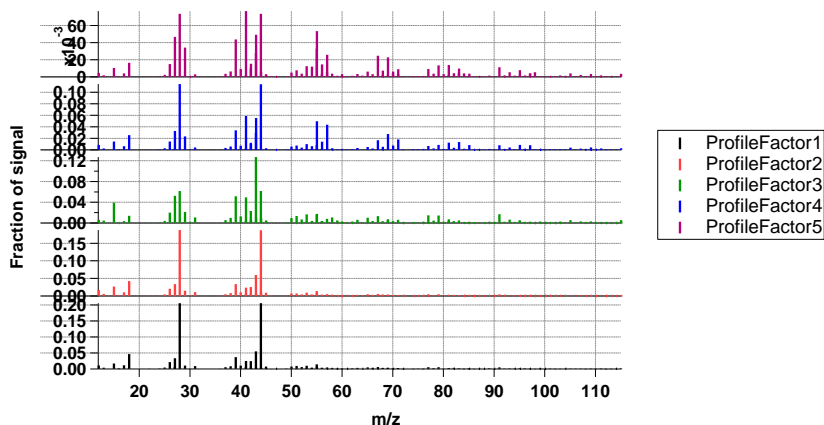


(a)

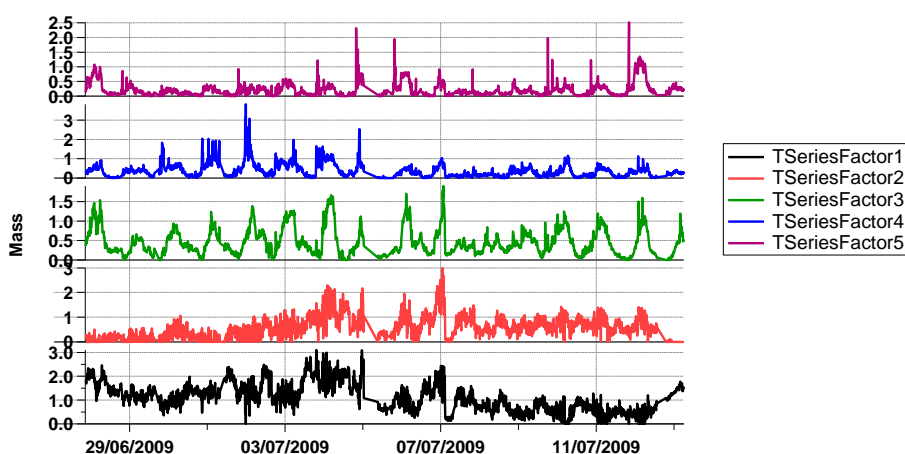


(b)

5-factor solution for the HR dataset, mass spectra (a) and time series (b):



(a)

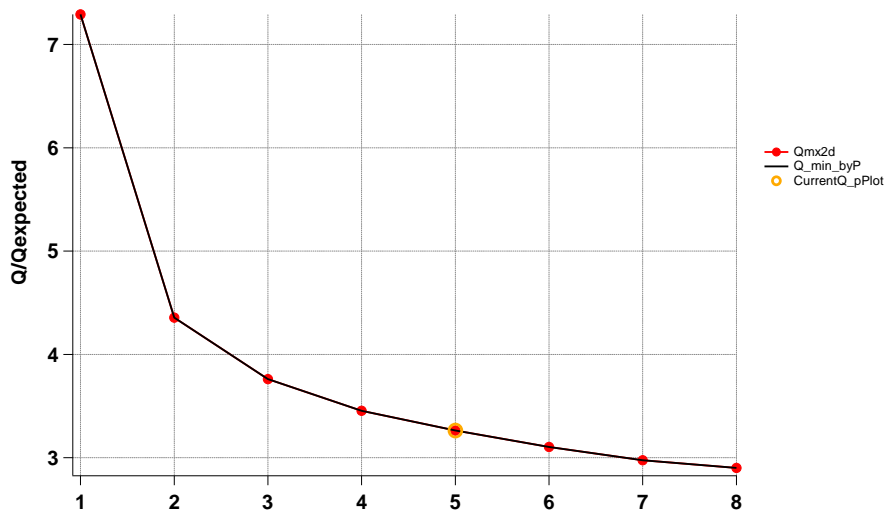


(b)

A summary of the PMF-AMS results with varying the number of factors is given in the following table:

Number of Factors	Factors	Note
2	HOA/OOA	General HOA and OOA factors, mixed together
3	HOA/OOA/SV-OOA	Large residuals at key m/z's and time periods.
4	HOA/SV-OOA/LV-OOA-LO/LV-OOA-MO	LV-OOA-LO/LV-OOA-MO are split, showing with different time trends.
5	HOA/SV-OOA/LV-OOA-LO/LV-OOA-MO/COA	A new factor COA is found. Distinctive diurnal cycles for the factors, and mass spectra that compare well with database MS. Better correlation with concomitant measurements than with the four factor solution (increase average R^2). Factors LV-OOA-LO and LV-OOA-MO are very conservative ($R^2 > 0.98$) relative to the four factor solution. The new factor COA comes mainly from SV-OOA and partially from HOA. The new COA factor is supported by several external measurements (NMR, ATOFMS).
>5	Splitting	HOA and the single LV-OOAs begin to split

Finally, the inspection of the change of Q/Q_{exp} with the number of factors does not show any net transition in the explained variability:



The above graphs will be included in the Supplementary material of the revised manuscript.

Referees' comment: PMF analysis of SP-AMS dataset identified $C_xH_yN^+$ ions, why HR-ToF-AMS didn't have (Fig. S7)? The nitrogen-containing fragment at m/z 73 that was attributed to amines was suspicious, and also we cannot see nitrogen peak at m/z 58. Amines generally present fragments at m/z 30, 58, 72 and 86.

Reply: We inspected the m/z 73 peak and actually found that is not an amine peak but a $C_3H_7NO^+$ fragment, probably originating from an organic nitrate. We will correct the text. Given that the AMS response to organic nitrates is still not clear (also because of the evident difficulties to handle dangerous standards in the lab), some differences in the instrumental response between the SP-AMS and the HR-Tof can be expected.

Referees' comment: The authors concluded that the fewer PMF factors from SP-AMS was due to the shorter record period, why the authors choose the same period of HR-ToF-AMS data as SP-AMS to do another PMF analysis, and then have a direct comparison between two AMSs.

Reply: There are several explanations for the limited agreement between the PMF results from the HR-ToF-AMS and those from the SP-AMS, including some instrumental artefacts. Following the Referee #1's suggestions, we decided to treat these aspects in more detail. We will then add the following paragraph to the main text:

"For this reason, beside the good correlation between the HOAs extracted from the two datasets ($r^2 = 0.45$), attributing the SP-AMS factors to the HR-ToF-AMS factors is challenging. A lack of a HR-ToF-AMS factor being present in the SP-AMS factors could indicate that it is externally mixed with BC, which would seem reasonable in the case of the cooking factors. Similarly, organic matter measured by SP-AMS seems to have a lower LV-OOA contribution compared to the HR-ToF-AMS (In fact, the HR-ToF LV-OOA-MO correlates better with the SP-AMS OOA-Day ($r^2 = 0.65$) than with the SP-AMS LV-OOA), which may indicate that a substantial fraction of the LV-OOA is externally mixed with BC, although this may be due to technical differences between the vaporisation methods. It may be that the decarboxylation process responsible for the characteristic OOA mass spectrum during normal AMS vaporisation does not occur in the same manner in the SP-AMS. Furthermore, it is also possible that the vapours may be detected in the SP-AMS at different effective relative ionisation efficiencies (RIEs), which may affect the relative concentrations. More characterisation work will be required to explicitly evaluate this."

Referees' comment: In addition, the authors can simply calculate the elemental ratios (e.g., O/C ratio) of each PMF factor to judge the oxidation degree of each OA factor.

Reply: True. We provide below a table with the specific O/C ratios for the PMF-AMS factors from the HR-ToF-AMS:

Factor	O/C
HOA	0.05

COA	0.24
SV-OOA	0.37
LV-OOA-LO	0.70
LV-OOA-MO	0.78

Referees' comment: Some abbreviations were not used consistently throughout the manuscript, e.g., HRToF-AMS (HR-TOF-AMS), LV-OOA-MO (LVOOA-MO), etc. Some figures (e.g., Fig. 7, Fig. 10) missed labels (a), (b), and (c), which are hard to follow in the text. There are many places that need careful proofread. For example, page 9299, line 7, should be [C₂H₃O]⁺; line 9, should be (LV Low Volatility); line 19, Fig. 10c was not correctly referred; line 25, $r^2 = 0.9$, two references, which LV-OOA was compared?

Reply: We will correct all abbreviations and clarify all small inconsistencies in the text.