

Reply to Anonymous Referee #1

We thank Referee #1 for the constructive criticisms and her/his meticulous review. We also apologize for the imperfect proof-reading in some parts of the text.

Referees' comment: General comments. While the breadth of analytical techniques employed is certainly impressive, the synthesis of the separate analyses to create a coherent narrative is less so. In its current form the manuscript is simply too long, and the disparate conclusions drawn from the separate analytical techniques need to be interpreted with more care. The reader is referred to the wrong figure in several places, and naming conventions for particle types are confusingly interchanged throughout the discussion. Crucially, conclusions drawn regarding aerosol mixing state using the reported data are highly speculative at times as discussed below. A stronger emphasis should be placed either on the impact of meteorology upon regional air quality in this remote environment (the mixing down of the residual layer aerosol is interesting), or on source apportionment of organic aerosol at this site (the described comparison of NMR and AMS OA PMF certainly has potential), or upon the complementary nature of the aerosol mass spectrometers used and how this helps to determine aerosol mixing state more effectively (as implied by the title). In attempting to address all three of these points none are managed effectively. There are certainly data of significant value here, however, and streamlining the article significantly would make it far more accessible. Assessing detailed aerosol composition and mixing state comprehensively using these complementary tools is a worthwhile undertaking.

Reply: These general comments are dense of criticisms. Some are substantial (e.g., incomplete data analysis and speculative conclusions) and we address them in the discussion below. Other are merely stylistic: the excessive length of the text, the need of refocusing the paper on one of the three major discussion points. For these last aspects, we would like to clarify to Referee #1 our objectives and our own concept of the paper:

- a) The present manuscript was meant to provide a summary of an intensive field campaign, reporting the measurement strategy, the core instrumentation and the major scientific findings. The current manuscript size is on the order of 13,000 words. Other intensive field studies published in ACP and cited in this paper have 17,000 words (Dall'Osto et al., Atmos. Chem. Phys., 13, 8991-9019, 2013) and 25,000 (Harrison et al., Atmos. Chem. Phys., 12, 3065-3114, 2012). Also the number of figures (15) is reasonable for this kind of campaign summary papers (e.g., McMeeking et al., ACP 2010, 13,000 words and 11 figures, or Adhikary et al. ACP 2010 with 13,000 words and 20 figures). Therefore, the length of the paper is appropriate for the scope of this study. However, we accept the Referee's suggestions to cut the text in Sections 3.1, 3.2 and 3.3.
- b) In this paper we privileged comprehensiveness to the detailed analysis of datasets from the individual mass spectrometers. We wanted to show the potential of a suite of complementary state-of-the-art measurement techniques in respect to addressing diverse key issues related to the aerosol atmospheric life cycle. If we failed in adequately referencing some of the measurement aspects (like for PMF-AMS), these will be implemented in the supplementary material without affecting the length of the main manuscript. However, as the literature is already plentiful of "AMS studies" in several places in the world, we felt that more integrated approaches would be desirable and more innovative. For this reason, we want to keep all the major themes of discussion in the paper, and we believe that a good organization of the sections is sufficient to make the paper accessible to a selective reader. For instance, the current split of the discussion section into the two sections 4.1 (mixing state) and 4.2 (organic source apportionment) already provides a good frame for guiding the reader through the specific discussion themes.

Finally, Referee #1 complains that the reader is referred to the wrong figure in several places, and naming conventions for particle types are confusingly interchanged throughout the discussion. We found that three times the text referred to the wrong figures. Sometimes the identification of the panels within a figure was done using labels (a, b, c) in the text instead of "top, middle, bottom". We apologize if this was distracting, and we will remove these small inconsistencies in the new version of the paper. A change in naming convention was introduced for the ATOFMS clusters, but this was clearly explained when the clusters were

defined and described (pages 9294 to 9296). A first “standard” nomenclature was immediately replaced by labels which already take into account an interpretation of the nature of these factors in this study, and which we believe facilitates a reader who is not familiar with ATOFMS in understanding the chemistry and sources of each particle type.

Referees’ comment: Specific comments: The abstract is overly long and contains some content better suited to an introduction. Streamlining the manuscript would make the content more accessible. In the main manuscript, the laborious description of air mass types is unnecessarily long, involves too many subcategories and therefore cannot be followed when referred to later with respect to aerosol composition. Furthermore, can these features really be described as representative of all other “heavily populated areas. . . of Eurasia and North America” that exhibit “complex orography”? Meteorology in the Po Valley is not necessarily transferrable to other sites/continents.

Reply: Accepted. The abstract will be shortened. In respect to the representativeness of the experiment, the key meteorological features to be considered are clearly listed in the text: a) a dry summer which is characteristic of subtropical climates, hence prolonged clear sky conditions and high photochemistry, b) a complex orography which is responsible for the set-up of mesoscale circulations driven by the thermal gradients between the mountains and the low lands, which can be superimposed to the land/sea breezes. Such impact of summertime mesoscale circulation on aerosol concentration fields has already been highlighted in regions such as California (e.g., ACP, 12, 7647-7687, 2012), Spain (Dall’Osto et al., 13, 8991-9019, 2013), Nepal (Prabha et al., JGR, doi:10.1029/2011JD016754, 2012).

Referees’ comment: Descriptions of gas-phase precursors are also too long and detract from the focus on aerosol composition. It should be reduced down to a brief discussion of the main points- knowledge of gas phase nitric acid and SO₂ mixing ratios and hydroxyl radical concentrations, and how these are related to changes in aerosol chemical composition. The organic gas phase data from the TAG instrument should also be reduced in length with brief reference to aerosol composition where appropriate. Using alkanes to support traffic emissions and benzoic acid to support SOA formation is suitable, but the length should be reduced.

Reply: We will compact sections 3.1, 3.2 and 3.3 keeping only the information really useful for the understanding of the main atmospheric processes at issue (e.g., the PBL meteorology). We will shorten section 3.8 (TAG) but we will keep the discussion of the PMF factors, which is schematic and already easy to follow.

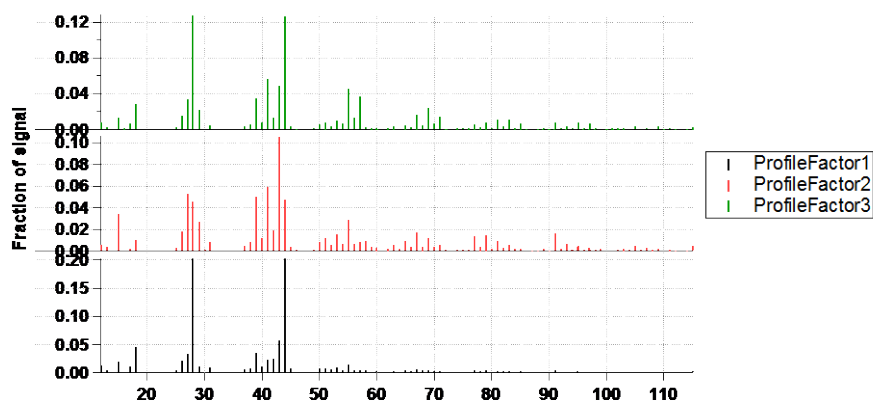
Referees’ comment: With respect to amines, why is only TMA observed in the ATOFMS data when DEA and TEA are also observed in the NMR OA results? Is there a sensitivity issue? Amine mixing state is mentioned in the abstract but is not described further in the manuscript.

Reply: The ATOFMS was only able to see TMA during this fields study (mainly peak at m/z 59). DEA and TEA are usually seen by the ATOFMS at m/z 86 (Angelino et al. ES&T 2001) but in this study such mass fragment was seen only sporadically with no clear time trend. The reason why ATOFMS could not detect all the alkylamines observed by NMR spectroscopy cannot be easily explained, but there may be a sensitivity issue of ATOFMS with some chemical forms of the individual alkylamines, e.g., with counter ions not considered in the study of Angelino et al. 2001.

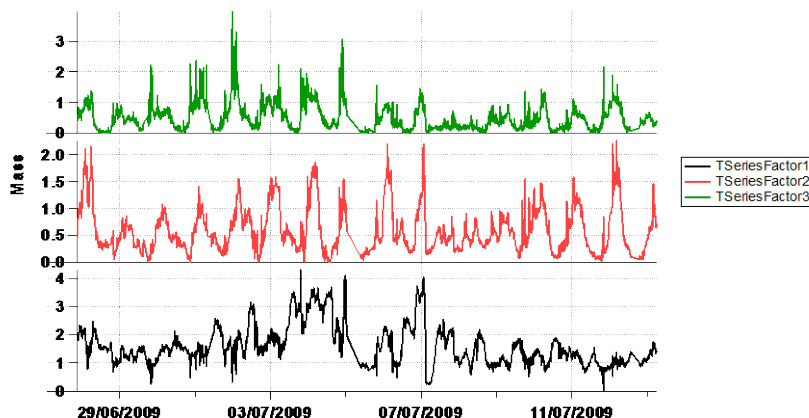
Referees’ comment: The separation of LVOOA into two factors is also not convincing, and is validated/constrained through a separate instrument that broadly measures aerosol mixing state, not organic aerosol composition. The mass spectra of both factors are almost identical (Fig S7), and the zoomed region of the MS that is referred to in the text is not included. Also, in the main text the splitting of the LVOOA factor is supported through reference to Fig. 10C which does not actually show this data. The middle panel does show benzoic acid vs the LV-OOA-MO factor but LV-OOA-LO is not included for comparison.

Reply: Even if the differences in the spectral profiles are not evident in Figure S7, LV-OOA-MO is in fact more oxidized than the LV-OOA-LO, as witnessed by the different O/C ratios, 0.78 vs. 0.70. The two factors differ substantially especially in their time trends, with one more clearly reflecting the contribution from regional-scale sources (see Section 4.2). The occurrence of two types of OOA with a similar volatility behaviour is not new in the literature of PMF-AMS studies. For instance, similar observations were done in California during the CARES experiment, where two types of OOAs associated with two kinds of background aerosols were observed (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 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):

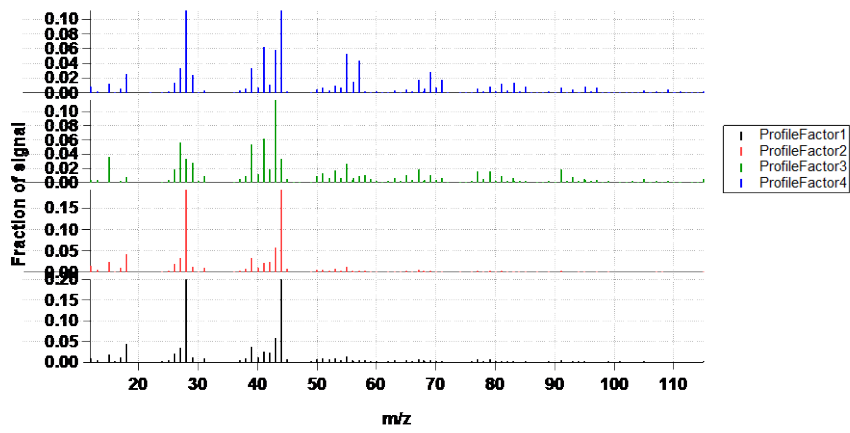


(a)

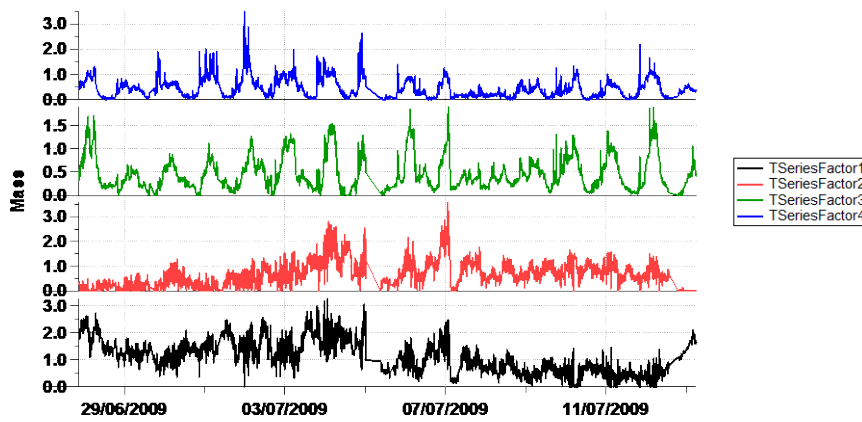


(b)

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

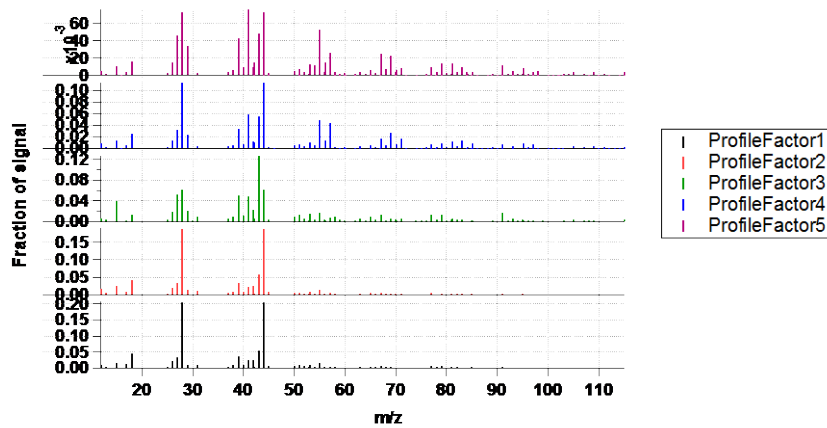


(a)

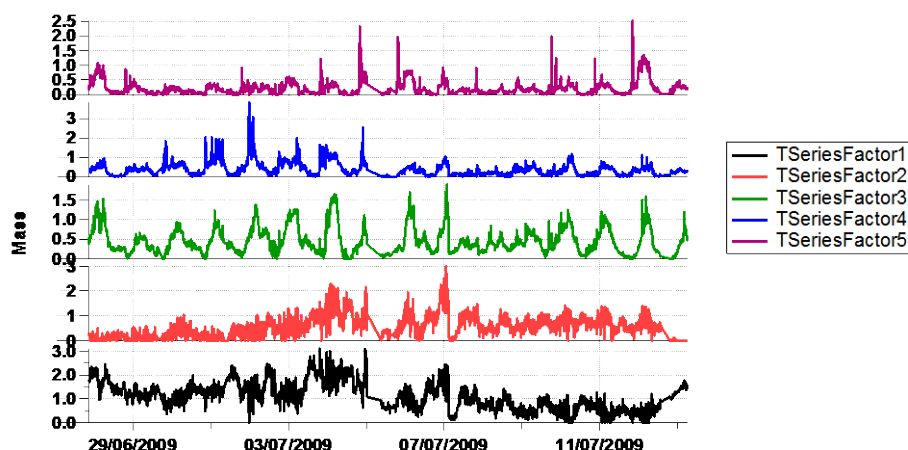


(b)

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 |

Referees' comment: The SP-AMS data are uncalibrated and it is stated that the temporal trends for OA, inorganics and BC are representative of changes in mass concentration. The temporality may be relevant for the individual species, however, in the absence of calibrated RIE values for BC relative to the other species, how can a pie chart such as that shown in Fig. 5 (bottom) be reliable or meaningful? This has implications for the interpretation of BC mixing state too. Why was the SP-AMS not operated alternately in SP laser on/off modes to assess BC associated material vs externally mixed material? Instead the separate HR-ToF-AMS instrument is used for comparison. Thus, knowledge of accurate collection efficiencies and relative ionization efficiencies are important here. Was the thermal vaporizer removed from the SP-AMS completely?

Reply: The SP-AMS was operated with the vaporiser removed, so on/off method was not possible. While an IE calibration was lacking, RIE values can be assumed based on Onasch et al. (2012), so the relative abundances are still meaningful. While this carries with it an uncertainty due to the lack of an in situ calibration, experience has taught us that the RIE values will not vary by too large an amount, so the pie chart in figure 5 is still informative.

Referees' comment: A collection efficiency of 0.5 was applied for the HR-ToF-AMS, and this is stated to be in line with Middlebrook et al (2012), when in fact that study describes that the

collection efficiency can be calculated more accurately by considering aerosol composition than using a fixed value of 0.5.

Reply: The Middlebrook parameterisation, when applied to this dataset, results in a constant CE of 0.5 due to the aerosol never being dominated by ammonium nitrate or acidic sulphate.

Referees' comment: In section 3.5/3.6 why are chemical processes observed in London used to explain aerosol processing at this site? Are the sources expected to be similar? Condensation of nitrate at high relative humidity and low temperature is not specific to London.

Reply: The ATOFMS has consistently shown in four different field studies (Port Talbot, UK; London, UK; Barcelona, Spain; Bologna, Italy) that two types of nitrate can be seen. This was first reported in the study carried out in London (Dall'Osto 2009) and for this reason the study is cited.

Referees' comment: Why was a MAC value of 10 m² g⁻¹ chosen for the PSAP absorption conversion to mass concentration?

Reply: As explained in Section 2.6, this comes from a review work of MAC values for Europe (Zanatta et al., in preparation; presented at the 2013 ACCENT-Plus meeting in Urbino, Italy).

Referees' comment: The description of single particle types is also overly long and could be reduced to simply support the mixing state conclusions regarding BC drawn from the SP-AMS measurements. Why are 8 particle types shown when 12 are identified?

Reply: Four of the particle types (4 out of 12) were characterized by time trends consisting mainly in a series of spikes, pointing to some very local source (possibly small fires or traffic around the station). Since we could not relate such effects to any of the other chemical classes or tracers, we omitted these four ATOFMS factors from the discussion. In respect to the 8 main particle types, we disagree with the Referee: as most readers are not familiar with the ATOFMS clusters, we prefer to provide a description, as well as an interpretation, of their mass spectra.

Referees' comment: Furthermore, the names of these classes change around during the manuscript and do not always match the figures, and therefore this section becomes very difficult to interpret.

Reply: A change in naming convention was introduced for the ATOFMS clusters, but this was clearly explained when the clusters were defined and described (pages 9294 to 9296). We will correct the small inconsistencies in the labels used in the figures respect to the text (e.g., "NIT-Local" instead of "NIT-Loc.").

Referees' comment: There are also unsupported claims regarding mixing state. For the EC type, how can an EC core be effectively vaporized while coating material is not? And in the absence of signal for any secondary material how can a regional source be applied here? An isobaric interference for OA and potassium is referred to but not assessed.

Reply: The ATOFMS is particularly sensitive to elemental carbon (EC) due to the laser used for the LDI process in the ATOFMS. It is likely the EC-type particles (or "EC-Reg" using the nomenclature introduced for our study) are actually soot aerosols internally mixed with other secondary species, which are simply not seen by the ATOFMS. It is worth noting that several matrix effects can alter the sensitivity of ATOFMS towards EC or towards the chemical compounds present in the "coating" of the particles. For instance, the occurrence of secondary species like nitrate or sulphate could limit the electron availability, leading to a suppression of the negatively charged EC fragments (Reinard, M.S., Johnston, M.V., Journal of the American Society for Mass Spectrometry 19, 389-399, 2008). Reduced formation of negatively charged ions in real-time laser desorption/ionization mass spectrometry can be caused also by the presence of particulate water (Neubauer et al., 1998). Therefore, negative ions are more difficult to create than the positive ones. The above effects can be responsible

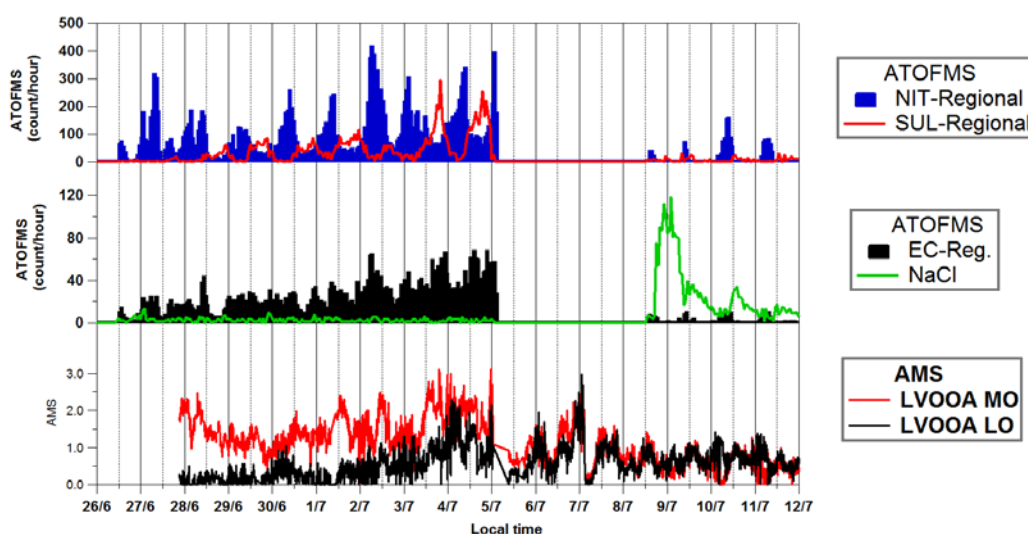
for the lack of negative mass spectra for certain particle types observed by the ATOFMS. It should be noted that such matrix effects are greater for aged particles, enriched in secondary material and in particulate water. For these reasons, the EC-type (or “EC-Reg”) particles seen in this study are not interpreted as fresh EC aerosols (which would have shown also a negative mass spectrum) but rather as soot aerosols actually mixed with compounds of unknown composition (possibly organic, with a lower content of inorganic ionic species). This model can explain why the ATOFMS EC-Reg particles are observed in the accumulation mode with a mean diameter of 700 nm, similarly to the soot particles containing elemental carbon and clearly mixed with secondary inorganic or organic compounds, like EC-NIT (or “NIT-Reg”).

Referees’ comment: How does the local source of K particles in London inform their apportionment as local here? Where is ECSUL in the graph? Names change around here and cannot be followed. The ATOFMS data should be connected to the SP-AMS findings more explicitly.

Reply: The source attribution of ATOFMS “NIT-Local” was suggested as “local” because of its temporal trends and its size distributions. Briefly, NIT-Local appeared to be produced in areas affected by urban pollution sources during night-time, whereas NIT-Regional was associated mainly with air masses transported at the regional scale because greater concentrations were found in periods of stagnant conditions. Nitrate in locally produced aerosol was present mainly in particles smaller than 300 nm, whilst the regional nitrate presented a coarser mode, peaking at 700 nm. The phenomenology of the ATOFMS nitrate particles observed in this study fits well that previously seen in London (Dall’Osto et al., 2009).

Referees’ comment: Correlation coefficients are used selectively throughout the manuscript. Why provide this value for LVOOA-MO relative to existing LVOOA datasets but not provide it for LVOOA-LO, for example? Are these very different? The fact that the factors need to be recombined to match the NMR HULIS factors also suggests that they should not be split in the first place. And what is OOA regional? Why is temporality of the SPAMS factors not included in the supplement?

Reply: We will complete the description of the HR-ToF-AMS factors, including more information, like the specific O/C ratios, aiming to clarify the actual differences between factors. We assigned to LV-OOA-MO a more “regional” character because it shows higher concentrations during the first week of the study, under stagnant conditions, and similarly to the ATOFMS clusters NIT-Reg and EC-Reg (see figure below):



The mass spectra of LV-OOA-MO and of LV-OOA-LO are both consistent with published spectra for LV-OOA type aerosols. These two factors are certainly very different from the factors with a low O/C ratio (such as HOA and COA) and they both must be attributed to organic mixtures characterized by a high content of carboxylic acids. They could represent two stages of OA ageing. The similar but not coincident results provided by the NMR analysis of HULIS are in line with the interpretation of the nature of LV-OOAs described as oxidized organic compound mixtures whose variability in this study can be reduced to two stages of an ageing process. The split between the less aged and the more aged component is performed differently by NMR with respect to AMS, because the two techniques are sensitive to different chemical structures and functional groups, which may exhibit distinct rates of formation/destruction in the atmosphere. AMS is in fact more sensitive to the oxygenated functional groups containing C=O double bonds, while proton NMR spectroscopy is more sensitive to the C-H groups (in the water-soluble fraction).

Referees' comment: In section 3.7.2 HOA is described as internally mixed with BC. All non-refractory species detected using the SP-AMS in SP mode must be associated with BC to be detected in the first place. The fact that fewer SP-AMS OA factors are resolved than HR-ToF-AMS factors may also be due to the presence of externally mixed OA containing no BC. This would be consistent with the cooking particle type and the rest of the discussion. The end of this section regarding RIE and detection efficiency issues is highly speculative and misleading, with no supporting evidence.

Reply: While there is no specific evidence to support variations in RIE, there is similarly no evidence to discount it. This is a highly important caveat because conclusions about the mixing state of the factors can be made if variations in RIE can be explicitly discounted or accounted for. The text has been reworded as follows: "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: The start of Section 3.8 belongs in the Method section.

Reply: True, we will move it to Section 2.5

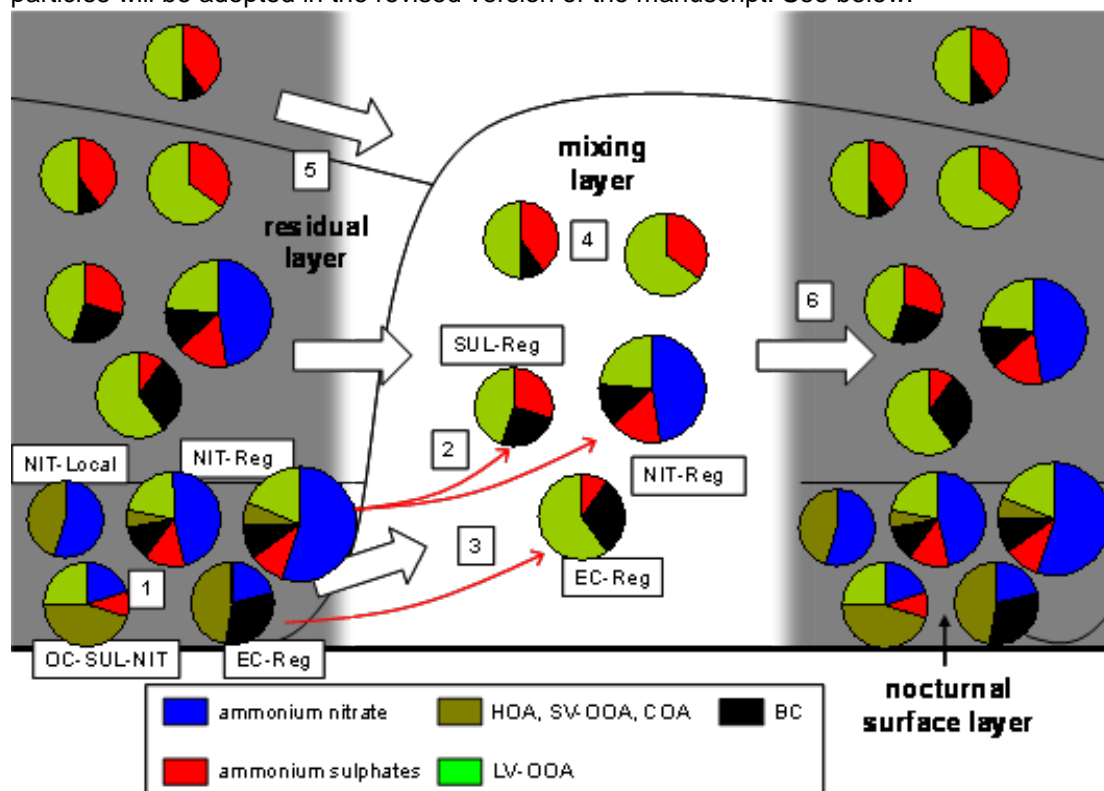
Referees' comment: Section 4.1 is very speculative, as is Fig. 13. This is unfortunate because this may be the most interesting aspect of the manuscript. There needs to be a clear distinction drawn between what the aerosol mass spectrometers can and cannot confirm regarding this schematic. Conclusions drawn based on speculation are expressed as fact in several places. It is stated that particles exist that contain an EC-sulphate core that is not detected by the ATOFMS when these particles are coated with ammonium nitrate. While partial ablation of a particle is certainly possible, why would ammonium nitrate and sulphate not be mixed, especially under humid conditions, and detected simultaneously in the coating?

Reply: The ATOFMS cannot directly provide quantitative information on the concentrations of aerosol chemical compounds (Gross et al., 2000; Dall'Osto et al., 2006). During this experiment we observed diurnal cycles in the ATOFMS aerosol populations with a clear anticorrelation between the sulphate-containing and the nitrate-containing soot particles (NIT-Reg and SUL-Reg, respectively). Since the latter are bigger than the former, we interpreted such diurnal cycles as resulting from the night-time condensation of ammonium nitrate on the

sulphate-containing soot particles seen in daytime. We agree with the Referee that at night-time nitrate and sulphate must be equally available in the coating of deliquesced aerosols. The very small mass fragments attributable to sulphate in the NIT-Reg (EC-NIT) negative mass spectra can be tentatively explained by a) the much greater mass fraction of nitrate with respect to sulphate in these particles, and to b) matrix effects for the presence of particulate water under the high relative humidities typically found at night during the experiment.

Referees' comment: The core-shell-shell arrangement depicted for these particles in the bottom-left of Fig. 13 is misleading as there is no evidence to support that this structure exists.

Reply: Accepted. A new representation leaving undefined the actual internal structure of the particles will be adopted in the revised version of the manuscript. See below:



Referees' comment: Furthermore, it is stated that “the ATOFMS is probably insensitive to changes in coatings of particles very rich in BC”, but there is no evidence for this. In fact, the reverse has been demonstrated; partial ablation is more likely to highlight changes in coating composition than to result in vaporization of the refractory core only. See depth profiling work by Zelenyuk (2008) and thermodenuder single particle work by Pratt (2009).

Reply: The statement “the ATOFMS is probably insensitive to changes in coatings of particles very rich in BC” is not true in general but can hold under certain circumstances, like a) when changes in coating composition are determined by compounds with a high ionization potential (such as most organic compounds), and b) when BC is not present in the particles as a true core but rather as inclusions at the edge of the particles (K. Adachi, S. H. Chung, P. R. Buseck, J. Geophys. Res. 15, D15206, 2010). The actual internal structure of soot particles mixed with secondary species is in fact still debated. This will be clarified in the text.

Referees' comment: Why would the SPAMS sensitivity for coated BC decrease to the extent where these particles are not observed? If anything, coated BC is focused more effectively during transmission through the sizing region and therefore should be detected with greater efficiency than fresh fractal BC, which may diverge from the particle beam (Onasch 2012).

Reply: We agree with the Referee and we will omit the sentences “Since the secondary aerosols formed during daytime (i.e., photochemically) are not volatile, they tend to accumulate over time, and their mass ratio with respect to the primary components (such as BC) tends to increase (step “4”). As a consequence, a fraction of these particles are not seen or seen with slight sensitivity by both SP-AMS and ATOFMS”.

The most likely explanation for the SP-AMS measurements not recovering the totally of the non-refractory mass observed by the HR-Tof-AMS is the occurrence of particles missing a BC inclusion (i.e., with organic matter, sulphate and nitrates completely externally mixed with BC). Theoretically, the production of aerosols not containing soot can be explained by new-particle formation, which takes place very frequently in the Po Valley. Recently, also primary combustion particles were shown to be partly externally mixed with BC (Li et al., *Atmos. Chem. Phys. Discuss.*, 14, 15323–15361, 2014; Liu et al., *Atmos. Chem. Phys. Discuss.*, 14, 16291–16349, 2014). Reddington et al. (*Atmos. Chem. Phys.*, 13, 4917-4939, 2013.), also showed that particles not containing a BC core are more frequently observed than predicted by CTMs. We will implement the discussion in the text, by explicitly introducing the apparent external mixing of BC in the background aerosol in the Po Valley.

Referees’ comment: Furthermore, if both instruments really were subject to these significant effects, could any solid conclusions be drawn regarding BC mixing state here at all?

Reply: The assessment of the mixing state of the aerosol chemical compounds, and particularly of BC, is of primary importance for understanding several important atmospheric processes (Bond et al., 2013). Unfortunately, the experimental determination of the BC mixing state can be very challenging, because all the available measurement techniques show several limitations. The SP-AMS and ATOFMS spectroscopic methods used in this study are no exceptions, but they are preferable to alternative methods (such as HTDMA) for the accumulation mode size range. The Referee already pointed out specific caveats with the methodology used in this study. In spite of these sources of error, we believe we can draw the following qualitative but solid conclusions:

- There is evidence for a substantial amount of non-refractory particulate mass externally mixed with BC. This is based on the comparison between the HR-Tof-AMS, PSAP and SP-AMS measurements summarized in pie charts of Figure 5. In particular, the nitrate and sulphate concentrations determined by the HR-Tof-AMS are three to four times greater than the PSAP BC concentrations, while ratios of 0.4 are found in the SP-AMS. To remove the inconsistencies between the HR-Tof-AMS+PSAP and the SP-AMS in the ratios between non-refractory inorganic ions and BC, one should apply a MAC value in the PSAP unrealistically low (lower than 3 m²/g). Therefore, the depletion of non-refractory compounds in the SP-AMS with respect to the HR-Tof-AMS is real, according to our observations.
- The ATOFMS shows a substantial amount of particles with organic compounds or inorganic ions externally mixed with BC, especially during the second week of the campaign (Figure 14). The fraction of the particles carrying non-refractory compounds which is actually mixed with BC was 70% during the first period characterized by stagnant conditions and recirculation of pollutants, while it dropped to 30% - 50% during the second, cleaner period. Since we cannot exclude that the ATOFMS did not measure the totality of the particles unmixed with BC, the above ratios must be considered as upper limits.
- The non-refractory compounds unmixed with BC and observed by the ATOFMS in the clusters NIT-Local, K-CN-Amines and OC-NIT-SUL show diurnal trends with nocturnal maxima and broadly correlated with the PMF-AMS factors HOA and COA. This result is in line with recent studies showing that combustion emissions can emit substantial amounts of organic particles not containing BC (Li et al., *Atmos. Chem. Phys. Discuss.*, 14, 15323–15361, 2014; Liu et al., *Atmos. Chem. Phys. Discuss.*, 14, 16291–16349, 2014).
- The ATOFMS EC-type aerosol shows a time trend which is evidently impacted by the recirculation of pollutants at the regional scale. Such particles, showing a mode at 700 nm, must be attributed to aged soot, even if ATOFMS was unable to characterize the nature of the coating. Based on correlation analysis (Table 2), we can speculate that the coating of such aged soot aerosols is prevalently accounted for by organic compounds determined by the AMS as LV-OOAs, and, to a lesser extent, by

ammonium sulphate. The reason why sulphate mass fragments were not seen in the spectrum of the EC-Reg cluster could not be fully clarified, even if matrix effects such as from the presence of particulate water can be blamed.

We will reword the conclusion section by highlighting the above findings and clarifying what are the observations for which we can furnish only tentative (speculative) explanations.

Referees' comment: The final sentence is highly speculative: "The behaviour of these metrics for aerosol mixing state becomes more confused in the afternoon/evening, possibly because of the insensitivity of ATOFMS to some types of organic coatings on the large EC particles". Again, ablating the EC core should result in detection of the coating material. Selectivity of the desorption/ionization laser for BC-containing particles is more likely to manifest as an overprediction in the fraction of BC-containing particles present in the total population, rather than as a reduction in sensitivity for coating materials.

Reply: Accepted. We will omit the sentence "The behaviour of these metrics for aerosol mixing state becomes more confused in the afternoon/evening, possibly because of the insensitivity of ATOFMS to some types of organic coatings on the large EC particles" as well as the metric used for reporting the BC mixing state from the SP-AMS in Figure 14. We acknowledge that the coincidence of the diurnal trends of the metrics used for SP-AMS and those for ATOFMS in Figure 14 may be fortuitous and the discussion too speculative. We will retain the mixing state metrics from the ATOFMS in Figure 14 to show the differences between the two campaign periods characterized by different meteorological conditions.

Referees' comment: Discussion of chloride displacement with nitrate for single sea salt particles should refer to Gard et al 1998.

Reply: True, we will correct the reference.

Referees' comment: The authors pose questions to the reader at times during the manuscript, which should be avoided.

Reply: We found one question mark in the full manuscript (Page 9310, line 8), which obviously was not a question directed to the reader. We will remove this interrogative phrase.

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.

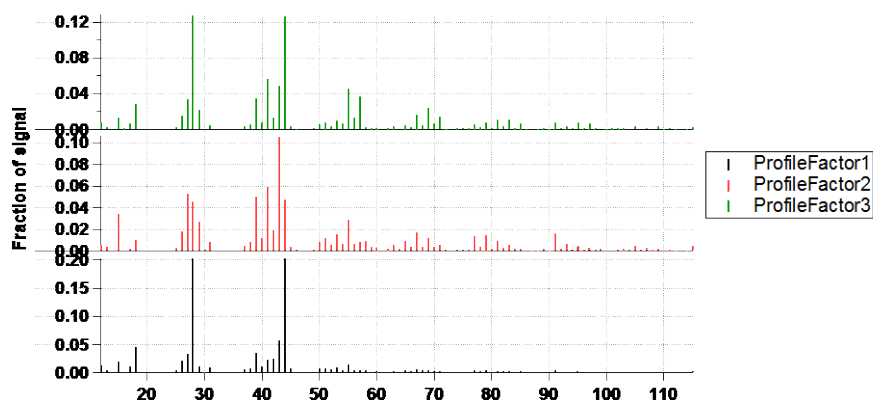
We acknowledge that the individual datasets would have needed a deeper analysis, especially for the PMF-AMS factors, for which a vast literature database is available for comparison. We will improve the characterization of the AMS factors in the main text as well as in the supplementary material, by 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.

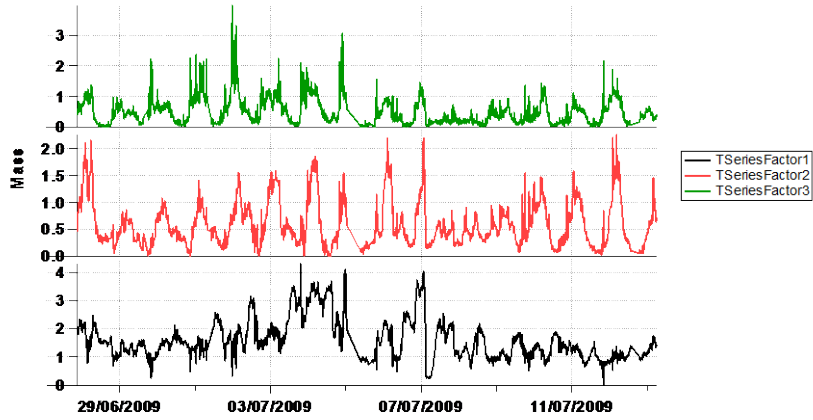
Reply: Analogous results (two OOA types, one more oxidized than the other, with similar spectra, similar diurnal cycles, different time trends) were obtained in previous experiments (Setyan et al., Atmos. Chem. Phys., 12, 8131-8156, 2012).

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):

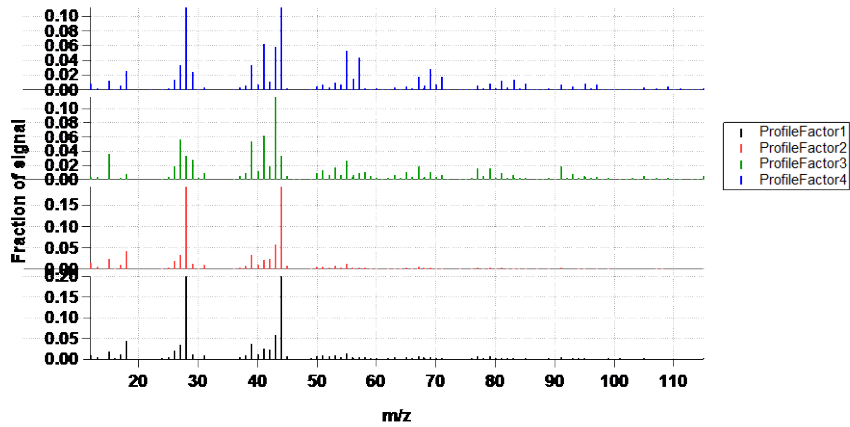


(a)

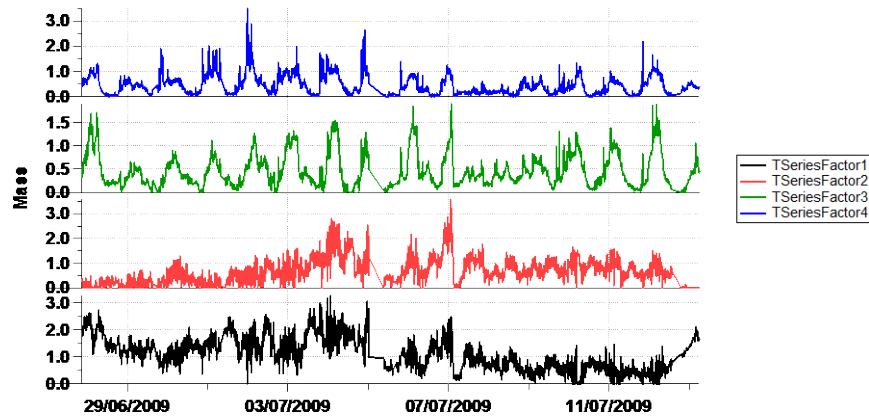


(b)

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

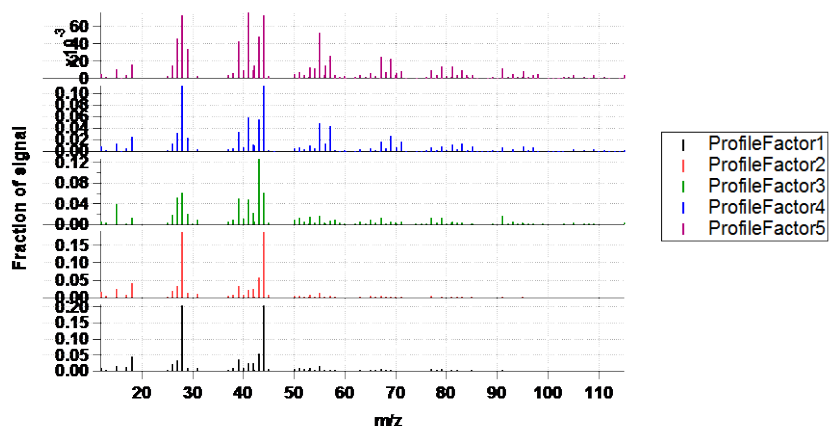


(a)

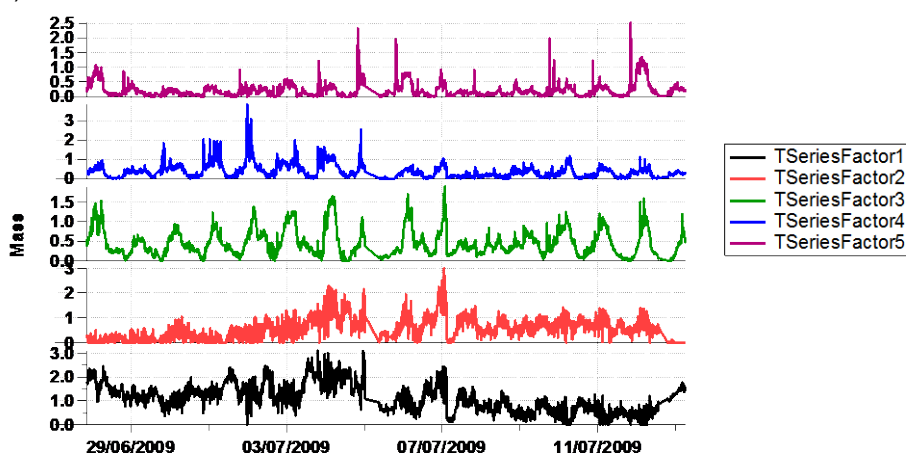


(b)

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



(a)

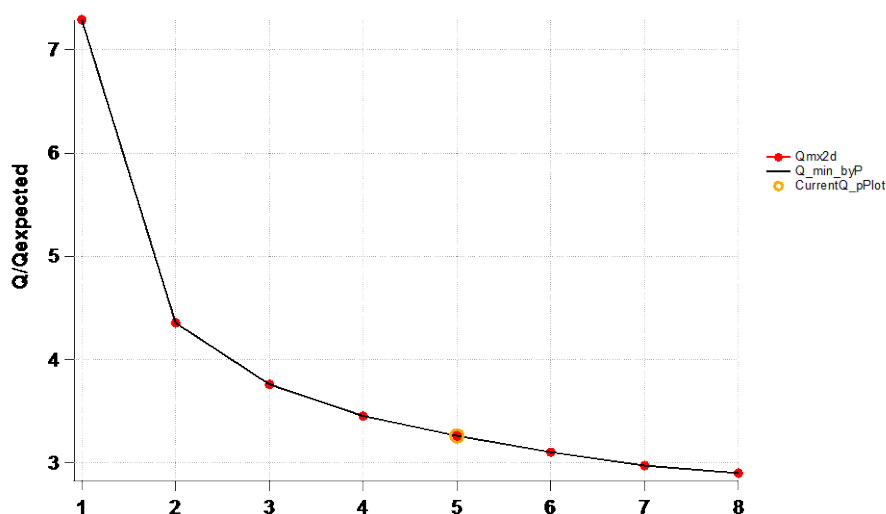


(b)

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.