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Discussions

Interactive comment on "ACTRIS ACSM intercomparison – Part 2: Intercomparison of ME-2 organic source apportionment results from 15 individual, co-located aerosol mass spectrometers" *by* R. Fröhlich et al.

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Author reply to: Anonymous Referee #3

Referee comments are written in **green** Author replys are written in **black**

Changes in the text of the article and the supplement are shown in the attached pdf documents (see pdf documents in supplementary to this comment). There, additions are shown in **blue**, deletions in **red**.

The manuscript provided a comprehensive inter-comparison of 15 co-located aerosol mass spectrometers, 1 HR-ToF-AMS, 1 ToF-ACSM, and 13 ACSMs (ACTRIS ACSM network). It is found that while the mass spectra and time series of various species are comparable to each other, there is a fairly large variation in the f44 values across all instruments. PMF/ME-2 analysis is performed on all datasets and the results are discussed. Using these results, it is suggested that while the range of f44 values in the organics data lead to variable f44 values in the factor profiles, the mass contribution of each factor does not seem to be affected to a large extent. This is undoubtedly an important piece of work and would be of great interest to the scientific community, particularly the ACSM users. I think this work is extensive and the analyses are thorough.

However, there are two main major comments regarding the manuscript that should be addressed prior the publication of the manuscript in AMT. Firstly, more information needs to be provided in the SI to justify the choice of PMF/ME- 2 solutions. There is no mention of varying FPEAK values or seed values, thus it is not clear whether the authors have evaluated how these parameters might affect the solutions (and if FPEAK values other than zero are used). Diagnostics plots of Q/Qexp, residuals, effects of FEAPKs/seeds (if applicable), etc should be provided. It is important such information be included in the SI of the manuscript so that readers can evaluate whether the selected PMF solutions can be justified. In my opinion, an extensive section in the SI needs to be devoted to such kind of information.

We agree with the referee that more information about the diagnostics has to be provided and added an extensive section dealing with the PMF analysis to the Supplementary Information (P20 onwards, 17 pages, 10 figures). See also replies to Anonymous Referee #1.

FPEAK rotations were not used, instead the a value approach described in the manuscript was applied to investigate the solution space around the global Q minimum which provides better control over rotations than the more random FPEAK.

There are also multiple incidents where the anchor profile for ME-2 input is chosen by performing PMF analysis up a large number of factors to “extract” out that profile. The authors need to provide justification on how such a decision is made. For instance, in the PMF analysis of the HR-ToF-AMS data, it is stated that when the analysis is extended to eight factors, the HOA and COA then become unmixed and are used as anchor profiles. Please document and explain clearly what criteria are applied in making such choices. More specific comments can be found below.

Details and justifications can be found in the newly added Sect. 3 of the Supplementary Information and more information about procedures were added to the main text (P1578 L 25).

Secondly, given such a rare and invaluable opportunity for inter-comparison of multiple co-located ACSMs, I think one of the very important contributions of the manuscript would be to provide recommendation for ACSMs users to evaluate how the variable f44 values in their data would affect source apportionment results. This is extensively discussed in the manuscript of course, but only from the point of view of comparing the performance of the individual ACSMs (among themselves, and with respect to HR-ToFAMS).

In Sect. 3.5.4 “ACSM specific recommendations” we provide recommendations for ACSM SA in addition to recommendations given by Crippa et al. (2014) and Ulbricht et al. (2009). There we also specify consequences of the differences of f44 for ME-2 source apportionment procedures (P1587 L18 20). Additionally we find that the f44 differences do not have a large effect on the source apportionment results (the contributions) since all instruments show comparable results. However the profiles do look different. We state that in the conclusions (P1589 L 4).

The results shown in Fig. 7 are promising in that the mass fractions appear to be fairly comparable across all instruments (except for the COA factor).

Yes, one of the main messages of this publication is that source apportionment results

are not affected to a large extent by the differences in f44 as long as no too tight constraints are applied to the f44.

However, all these results are the outcomes of multiple constraints that have been imposed during the analysis and availability of prior information about the aerosol composition at the site (e.g., absence/presence of COA, various source profiles, etc).

The application of constraints does not force the solutions to show similar contributions, the constraints are applied to assist the model in the separation of COA in the ACSM datasets which is not possible in an unconstrained PMF most likely due to large covariance of BBOA and COA-like aerosols (P1580 L 19).

Basically the ME-2 algorithm looks for linear combinations of profiles and time series with minimum (weighted) residuals in a multidimensional solutions space. Not in every case the global minimum, i.e. the mathematically best solution found by the model also represents the case which best explains the reality, i.e. the physically most realistic solution. There are several ways to explore the solution space “around” this global minimum looking for local minima which may capture the reality better. One way e.g. is FPEAK suggested by the referee which is frequently used in the PMF-2 solver. By forcing rotations into the factor matrices the Q values are increase, i.e. the model looks for good solutions outside the global minimum. However, the FPEAK does not allow much control over the chosen rotations which is why another more recent approach was applied in this study: the a value which is only available in the ME-2 solver. Here specific limits on some dimensions of the solution space are given, one can also call this a more directed rotation of the factor matrices. These limits are now more directed compared to FPEAK, since to some extent knowledge of previous studies is included in the rotation. More information can be found in the respective publications (e.g. Canonaco et al. 2013, Paatero 1999 or in the “Guidance Document for PMF Applications with the Multilinear Engine” from the American EPA).

However (similar to Crippa et al. (2014)) we do recommend to use as little constraints as possible and suggest ways how to extract profiles directly from the data set at hand in favour of externally measured profiles, but if solutions verifiably improve (to be proven e.g. by external data or other means) there is no reason to mistrust the applied constraints.

And in any case the presence of prior information (internally or externally) can only improve the solution of a source apportionment and it is strongly advised to use this information.

It is not clear how other individual ACSM datasets should be analyzed in the absence of all these additional information, which is likely the case for most future studies.

Every PMF source apportionment study relies on the availability of additional information since sources must be verified by some means. Also the selection of good solutions (e.g. number of separated factors) needs verification (one of the reasons why it was a really important request by the referee to show more diagnostics for the PMF analysis in the Supplementary Information).

With such a large intercomparison effort, could the authors provide some suggestions for scenarios where only one ACSM is available?

As detailed in the replies to Anonymous Referees #1 and #2 this study is not best suited to give such recommendations because, for such a study, a large number of datasets from various locations/seasons would be more suitable. We could only give specific recommendations for this one PMF analysis which may not be applicable to other datasets. Crippa et al (2014) analysed 25 AMS datasets with the ME-2 solver and gives a guideline / recommendations how one should approach ME-2 when only one instrument is available. These recommendations can also be applied to ACSM datasets. The European ACTRIS network created a large database of long-term ACSM data providing the opportunity for a similar publication with ACSM data in the near future.

From this study we can add some (technical) ACSM specific recommendations to the ones from Crippa et al (2014) (Sect. 3.5.4). And we additionally recommend choosing anchor profiles found in the dataset at hand over database profiles since there may be instrument specific differences in the profiles (e.g. f44).

For instance, by performing PMF analysis on each of the ACSM datasets alone, it seems that the authors can only resolve HOA, BBOA, and OOA factors. The authors specially look for the COA factor in the ACSM dataset (by constraining the source profile) based on the results from HR-ToF-AMS data. In the absence of HR-ToF-AMS, would the unconstrained ACSM PMF solution (i.e., HOA, OOA, BBOA) be "good enough", though, justified from Fig. 6, such unconstrained solutions result in a fairly large variation in the mass fractions?

No, in our opinion the three factor solution would not be satisfying due to the points stated in P1578 L 14: "The three factor solutions showed larger instrument-to-instrument variability and less correlation to external measurements for most ACSMs (especially of the HOA factor) than the four factor ME-2 solutions presented hereafter". For the 2-week dataset of the intercomparison an unconstrained PMF does not give good SA results. The additional constraints of ME-2 are necessary. However, the cited statement also implies that an inclusion of an additional COA-like factor improved the picture which will be seen as a strong argument for the operator (There are others also without the HR-AMS data, see reply to Anonymous Referee #2).

For clarification the following sentence was added to P1578 L17: "Amongst others, the stated points present a strong argument against the three factor unconstrained PMF and for an introduction of a COA profile also if the additional information of the HR-AMS PMF was not available in the first place."

Or, would the authors suggest that one should always constrain the HOA factor in the analysis of ACSM data?

No, constraints should only be applied if factors cannot be unmixed / separated without constraints. This is also included in the recommendations of Crippa et al. (2014). However, there it is also recommended to always check the differences between constrained/unconstrained HOA. Also in the presented case HOA is only constrained if the correlations with external data showed improvement compared to the constrained HOA time series. Additionally, if the HOA factor in an unconstrained case showed better correlation with external data than in the constrained case this HOA profile was saved and used as anchor in the constrained 4 factor PMF.

A new paragraph explaining the criteria for the extraction and procedures was added after P1578 L25.

The authors seem to suggest that the HOA anchor profile does not have a strong influence on source apportionment results. With this, if no prior studies at the same site have been conducted, should a “typical HOA profile” be used as the anchor profile for future ACSM PMF/ME-2analysis?

The results of the different HOA profiles show large similarities for most instruments, but as the referee correctly states below there are outliers showing larger differences. Therefore we cannot state that the selection of HOA does not have an influence in the recommendations section.

On the other hand it was shown by Ng et al. (2011) DOI: 10.1021/es102951k that HOA profiles show large similarities in different studies and therefore the choice of the HOA anchor is thought to be less crucial than the choice of e.g. a BBOA factor showing larger variations at different sites.

We recommend in Sect. 3.5.4 that in any case it is preferable to find an HOA directly from the dataset it is later used in (e.g. by extracting it from higher factor solutions if possible), if this is not possible it is advised to use several different anchor profiles and compare the results. We added this point to the recommendations.

These are just some suggestions/thoughts, but I would encourage the authors to think

deeply how they could best use these valuable datasets to provide more concrete recommendations on analyzing individual ACSM datasets with variable f44 values, in the absence of additional mass spectrometers (i.e., where there is no HR-ToF-AMS or other ACSMs to compare the “answers” to). Given that this manuscript is submitted to AMT, I think that it is important and critical that more of such recommendations be included in the manuscript.

We feel that the recommendations given in Sect. 3.5.4 (also dealing with f44) are the most important outcomes we can add to the recommendations of Ulbricht et al. (2009) and Crippa et al. (2014) from this study.

Specific comments

1. Page 1570, lines 23-28. Does this drift affect both the “filtered/background” and “ambient” data? How is the correction determined? How do the authors assure that the drift in the “filtered” data can be applied to the “ambient” data (since the background data need to be subtracted from the ambient data during analysis to get the difference spectra)? Please clarify.

The description of the drift was clarified in the text and Fig. S1 was added to the supplement to support the explanation (see also reply to Anonymous Referee #1). We identify this drift as a drift in the IE/AB ratio. Calibrations before and after the campaign show a large difference in this ratio. All ions in the chamber, no matter if they come from the chamber background or from ambient aerosols, are assumed to be affected similarly by the change in ionisation efficiency. This is why in our opinion we can use the decay of the background ion signal (e.g. from tungsten) also to correct the ambient “difference” signal. If there was no ambient signal at a specific m/z then the difference signal should not exhibit a drift (which was confirmed) since one would then subtract just the ion signal of the chamber background from the ion signal of the chamber background (i.e. the same) which both show the same decrease. We use the signals where we see highest background concentrations and at the same time no or only small ambient concentrations to exclude potential contamination by real trends, but in general any ion which appears in the background could be used.

2. Page 1571, line 7. How is eqt 6 used to downweight the weak signals? According to Ulbrich et al, the weak and bad variables are downweighted by fixed values (for instance, the weak variables are downweighted by a factor of 2), which does not involve eqt 6. Please clarify.

It does involve equation 6 in the way that by downweighting a variable one increases the uncertainty σij of this variable, i.e. the contribution of this variable to the summed Q which drives the PMF model is reduced. This way the variables weight on the model algorithm is decreased.

3. Page 1572, line 2. What is "corrected" ToF-ACSM time series? (what are they corrected for?)

We removed "corrected" since it may be confusing at this place. What we meant is that the shown ToF-ACSM time series is the one that was corrected for the drift described before.

4. Page 1573. Do the authors have comments/speculations on why the ToF-ACSM has the highest f44?

There are theories but at this point they still need to be investigated in detail. A discussion of this would be out of the bounds of this paper but may be the topic of another publication.

5. Page 1575. Section 3.3, HR-ToF-AMS source apportionment. a. It is important that more information to be provided in the SI regarding the details of the PMF analysis. Are FPEAK / seed values varied? How do the residuals for different factor solutions look like? Please include all the relevant diagnostics plots in the SI, including (not limited to) Q/Qexp, residuals, mass fractions, FPEAKs, etc. I think the authors likely have checked all these, but it is important to show them in the SI so readers can evaluate the solutions

themselves and ensure that the authors' choice of the solution (i.e., 4-facotr solution) can be justified.

We agree. See reply above and reply to Anonymous Referee #1.

b. Page 1575, line 16. Is the unusually high f44 in HOA only, COA only, or both? Why is a high f44 regarded as a sign of mixing of HOA and COA?

This is a good remark. In Fig. S19 the mean profiles of ten 4 factor unconstrained PMF runs can be found. There are signs of factor mixing (similar time series of two factors) but no high f44 in HOA. The manuscript was changed accordingly. Covariance of factors is a more reliable sign of factor mixing. We thank the referee for spotting this mistake.

c. Page 1575, line 16-17. The authors wrote "an extension of the analysis up to eight factors leads to an unmixing of the two factors". The HOA and COA factor profiles are fairly similar (the most outstanding difference is that COA has high f55), how do the authors decide that with eight factors, the HOA and COA are not mixed anymore? What are the criteria for "unmixing"? Please be very specific about this and explain this in details.

This should now be explained sufficiently in the Supplementary Information. Important indicators for unmixing are diurnal cycles of the COA. However, although HOA and COA may seem to have similar profiles the mixing was rather between COA and BBOA which have similar time trends than between HOA and COA. Also in the HR COA and HOA spectra are less similar than in UMR. E.g. there is a large difference in the two fragments $C_3H_3O^+$ and $C_4H_7^+$ at m/z = 55.

d. Hoes do the BBOA and OOA MS and time series obtained from the unconstrained PMF compared to that from the PMF/ME-2 analysis? Please discuss this. Specifically, how different are the f44 values in the BBOA and OOA factors (if any) with the unconstrained vs PMF/ME-2 analysis?

BBOA and OOA are not constrained, also in the final result. Only COA and HOA anchor profiles are used, the rest of the factors are completely free. It is difficult to present a comparison of f44 since especially the factors correlating with BBOA tracers in the unconstrained case are varying a lot depending on seed and also the OOA shows some variation. And of course f44 depends on all other variables. It can be read from the added R2 coefficients now shown for all solutions in the supplement that they are only slightly smaller in the unconstrained case than in the constrained case for OOA and BBOA (at least for one of the mixed BBOAs), i.e. time series are similar.

e. Page 1577, line 4. Has the flat OOA diurnal trend been observed in previous field studies conducted in the area? The correlation of OOA and sulfate (nitrate) does not appear to be particularly strong. Why? Are the diurnal trend of sulfate and nitrate also flat?

Yes, Crippa et al. (2013): doi:10.5194/acp-13-961-2013 found also a relatively flat sulphate diurnal during winter 2010. The diurnals trends (and concentrations) of both nitrate and sulphate in this study (S968) look very similar to the ones during our intercomparison campaign: see Figure at the end of this comment.

f. Page 1577, line 18. The authors noted that the high f44 in BBOA could be indicative of aging. Later in the paragraph the authors mentioned winter wood combustion. Do the authors think that this is the main source of BBOA? If so, I would think this could be local and might not be subjected to too much aging?

Yes, we think that by far the largest source is residential heating. As Anonymous Referee #1 mentioned BBOA profiles can also already vary at the source (this information was added to the manuscript with references) so it is not necessarily implying ageing. But still ageing in our opinion is possible since the station lies far inland in a very populated area and residential wood combustion is also used in other places in France and can be transported there. It is likely that it is an average/mixture of local and regional BBOA sources. Crippa et al. (2013): doi:10.5194/acp-13-961-2013 found a more re-

gionally influenced BBOA in winter 2010 at the same location.

6. More details need to be provided regarding the choice of the COA and HOA anchor spectra for ME-2 analysis.

A recommendation to test several anchor spectra if available and compare the results (e.g. to external data) was added.

a. Page 1578, line 20. Why is a "verified anchor spectrum from a previous study at the nearby measurement site" used for COA? Why not use the COA spectrum obtained from the HR-ToF-AMS PMF analysis of this study? Shouldn't this be more relevant than the spectrum obtained from the previous study?

Yes, this would indeed have been a very good alternative. But on the one hand the used reference actually is from the same site just three years earlier and on the other hand the COA from the HR analysis is very similar to the applied COA (cf. Fig. S6).

b. Page 1578, line 24. What do the authors mean by "extracted from a previous PMF solution with a higher number of factors. . ...". I suppose just like section 3.3, the authors run PMF analysis (completely unconstrained? Or with COA constrained? Please clarify) up to a "higher" number of factors, and then at some point decide that the HOA factor is "extractable"? How do the authors decide on when (which solution) the HOA factor is "good enough" to be extracted and used as input MS for ME-2 analysis? Please provide more details and clearly explain how this is done.

A new paragraph explaining the criteria for the extraction and procedures was added after P1578 L25.

c. Page 1579, line 5. The authors wrote "the influence of an alternative anchor proved to be only marginal". The authors should clearly specify what influence they are referring to. If it's the mass fraction of factors, I do not agree that the influence is "only marginal", given that they can be up to ~30% for some factors.

This was correctly spotted. In most cases results are similar but there are outliers (e.g.

#7, #12, TOF). The statement was adjusted accordingly.

7. Page 1586, line 1. ACSM #7 also seems to show a large deviation?

Revised.

Technical comments

1. Page 1574, line 28. “Is is noted. . ..” should be “It is noted. . .”.

Revised.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/8/C1059/2015/amtd-8-C1059-2015-supplement.zip

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 1559, 2015.

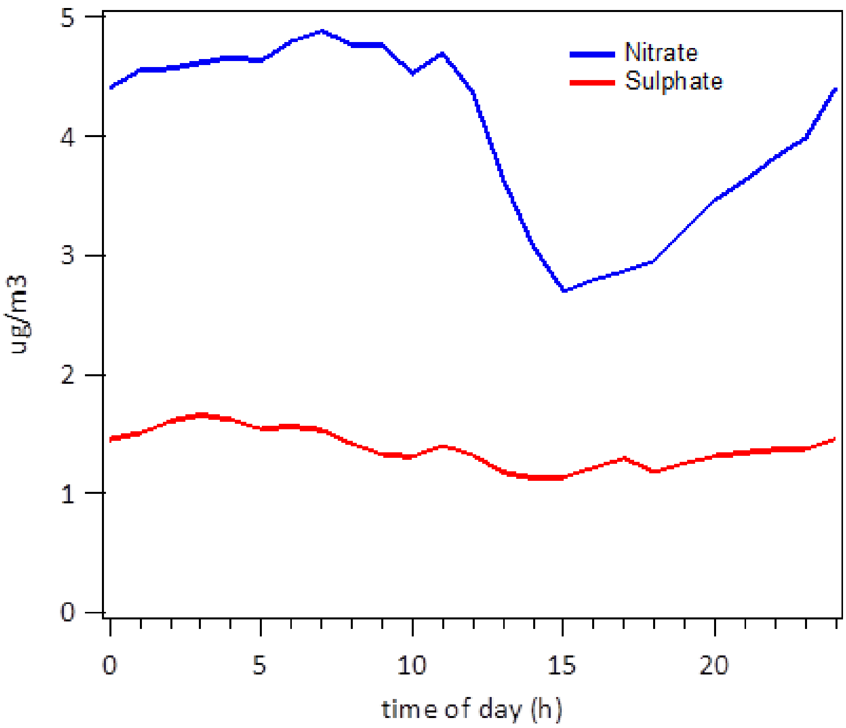

Fig. 1.