

We thank the referees for their comments, which helped improving the quality of our manuscript. A point by point response (in blue) to the reviewers' comments (in black, italics) will follow. Changes in the text are indicated in in black.

Anonymous Referee #3

Comments on "Long-term chemical analysis and organic aerosol source apportionment at 9 sites in Central Europe: Source identification and uncertainty assessment" by Daellenbach et al. The manuscript presents new research which clearly fits within the scope of the journal. The text is well-written and fairly easy to follow. Some of figures, however, compile several information and are not as straightforward to interpret (e.g. Figure 8) – please make sure to modify them (color axis, split into subplots, etc.) to improve readability.

We removed the second axis (PBOA) in Figure 8 since the difference is only a scaling factor. We improved the readability of several figures.

The technique described here is a follow-up of the characterization of OA measurements based on filter collections followed by water extraction and analysis by HR-AMS, previously published, being the novelty a large statistics from 9 sampling sites and, most importantly, PMF analysis of the OA spectrum from filters. Although the former is unquestionably of scientific interest, it is the latter that will allow others to apply the technique and indeed reach its goals as described in the introduction. At its current stage, the manuscript doesn't fully achieve it.

Major comments:

* The description depth of the PMF applied to this very specific dataset doesn't seem to be proportional to its level of development in regard to the widely used techniques. Please detail it more carefully.

Based on the comments of reviewer 2 and 3 we have significantly adapted the parts related to the description of the PMF. We also highlighted more clearly the part of the model that is typically applied and the other parts that are developed within this work. For example, PMF is widely used, but the ME-2 implementation is not. Also, in the revised version of the manuscript, we do describe more clearly the steps we have adopted for the PMF solution selection.

"...

Source apportionment of the organic aerosol is performed using positive matrix factorization (PMF, Paatero, 1994). PMF is a statistical un-mixing model explaining the variability of the organic mass spectral data ($x_{i,j}$), as linear combinations of static factor profiles ($f_{j,k}$) and their time-dependent contributions ($g_{i,k}$), see Eq. 2 (where p is the number of factors). The index i represents a specific point in time, j an ion, and k a factor. The elements of the model residual matrix are termed $e_{i,j}$.

$$x_{i,j} = \sum_{k=1}^p g_{i,k} f_{k,j} + e_{i,j} \quad (2)$$

atrix, each filter sample was represented on average by 11 mass spectral repetitions to examine the influence of the AMS measurement repeatability on the PMF outputs. A preceding blank from nebulized ultrapure water was subtracted from each mass spectrum. The input errors $s_{i,j}$ required for the weighted least-squares minimization by the model consist of the blank variability ($\sigma_{i,j}$) and the uncertainty related to ion counting statistics and ion-to-ion signal variability at the detector ($\delta_{i,j}$; Allan et al., 2003; Ulbrich et al., 2009). We applied a minimum error according to Ulbrich et al. (2009), and a down-weighting factor of 3 to all fragments with an average signal to noise lower than 2 (Ulbrich et al., 2009). Input data and error matrices consisted of 202 organic ions. The organic fragments, $x'_{i,j}$, obtained from offline AMS analyses do not directly represent ambient concentrations. Therefore, the signal of each fragment was converted to such an ambient concentration ($x_{i,j}$ in $\mu\text{g m}^{-3}$), by multiplying the fraction of this signal with the estimated organic matter (OM) concentration. The latter was calculated as the product of the OC concentrations measured by the Sunset OC/EC analyzer and the OM/OC ratios from the offline AMS measurements $(\text{OM/OC})_{\text{oAMS}}$ (Eq. 3). Note that such scaling does not change the outcome of Eq. 2 since both data and error matrices are scaled in the same manner and the fingerprints ($f_{k,j}$) are not changed.

$$x_{i,j} = \frac{x'_{i,j}}{\sum_i x'_{i,j}} * \text{OC} * (\text{OM/OC})_{\text{oAMS}} \quad (3)$$

The Source Finder toolkit (SoFi v.4.9, Canonaco et al., 2013) for Igor Pro software package (Wavemetrics, Inc., Portland, OR, USA) was used to configure the PMF model and for post-analysis. The PMF algorithm was solved using the multilinear engine-2 (ME-2, Paatero, 1999). Normalization of the PMF solution during the iterative minimization process is disabled as implemented in SoFi (Canonaco et al., 2013). ME-2 enables an efficient exploration of the solution space by a priori constraining the $f_{k,j}$ elements within a certain range defined by the scalar a ($0 \leq a \leq 1$) from a starting value $f'_{k,j}$, such that the modelled $f_{k,j}$ in the solution satisfy Eq. 4:

$$f_{k,j} = f'_{k,j} + a * f'_{k,j} \quad (4)$$

$f'_{k,j}$ is the starting value used as a priori knowledge from previous studies and $f_{k,j}$ is the resulting value in the solution. In all PMF runs (unless mentioned otherwise), we used the high resolution mass spectra for HOA and COA (cooking OA) from Crippa et al. (2013b) as constraints, i.e. two rows of $f_{k,j}$ were set equal to the mass spectra of HOA and COA. Ions that were present in our datasets but not in the reference profiles for HOA and COA were inferred from published unit mass resolution (UMR) profiles (Ng et al., 2011 and Crippa et al., 2013c). For this purpose, the fraction of signal at a specific m/z in the UMR reference spectrum ($f_{\text{UMR},m/z}$) was compared to the fraction of signal of all ions at this m/z in the HR reference spectrum ($f_{\text{HR},m/z}$). The difference $f_{\text{UMR},m/z} - f_{\text{HR},m/z}$ was used as entries in $f'_{k,j}$ for such missing ions. For these ions, an a -value of unity was set. For the other factors, the factor

elements were fitted by ME-2. Alternatively, such missing ions can be also treated as ordinary factor elements, to be fitted by ME-2 with all other ordinary factor elements.

...”

** Section 4.2.2 seems quite weak, three methods to estimate PBOA are presented, but no clear conclusion is given other than it underestimates based on previous literature. From my perspective this section doesn't add too much to the manuscript and could easily be removed, however if the authors wish to keep it, please make sure to better constrain the methods into a valid scientific output.*

We believe that removing this section would be misleading and not sufficiently transparent and would hide the fact that SOOA might be overestimated due to the contribution of PBOA, which could not be separated by PMF. Our main objective is not quantifying PBOA, but rather its potential contribution to SOOA. Therefore, with the three approaches presented we attempt to estimate this PBOA contribution. These approaches suggest that PBOA would contribute between 0.3 and 1.0 give units, or 18-58% of SOOA during the warm season. In the revised version of the manuscript, we have clarified the aim of the section related to PBOA contribution estimation. This section reads as follows:

“... Unresolved sources in PMF are an inherent uncertainty of source apportionment analyses. As Bozzetti et al. (2016) show, PBOA can present considerable contributions to OA in PM10 (constituting a large part of coarse OA). In the present analysis, PBOA could not be separated by PMF (neither unconstrained nor using the mass spectral signature from Bozzetti et al., 2016). This inability might be caused by the low water-solubility and the absence of PM2.5 filters in the dataset. Since these coarse particles are only abundant in PM10 and not in PM2.5/PM1, the presence of both PM10 and PM2.5 samples, exhibiting a large gradient in PBOA, might allow an unambiguous separation of PBOA. The aim of this section is to estimate the influence of PBOA on the source apportionment results. A quantification of this fraction is, however, beyond the scope of this paper. In the following, we estimate the influence of PBOA in three alternative ways: ...

...”

Minor comments:

** Abstract. L.21: add the word “from” between μm and 9.*

As suggested by another reviewer, we added “at”.

** Abstract. L.24: remove “which is” and add a comma before related.*

The text has been corrected.

** P.2, L.31: Please remove “restricted to WSOA in”.*

The respective part has been removed.

** P.12, L.10: Remove the word “here”.*

The word “here” was removed.

* External gas-phase tracers (besides the use of NOx just to separate HOA, COA) could also add some information of the surrounding chemistry – for example, what is the ozone (over 24h, or just afternoon) in regard to SOOA and WOOA? And Ox?

For Zurich, we added a comparison of SOOA concentrations to ozone and Ox (O₃+NO₂):

“...

In Figure S7, we compare the SOOA concentrations to ozone and Ox (O₃+NO₂) for Zurich. The SOOA concentrations follow best the temperature ($R_{s,SOOA,temp}=0.65$, Fig. S7.a) but show also some correlation to ozone $R_{s,SOOA,O_3}=0.33$, Fig. S7.b) and Ox ($R_{s,SOOA,Ox}=0.38$, Fig. S7.c).

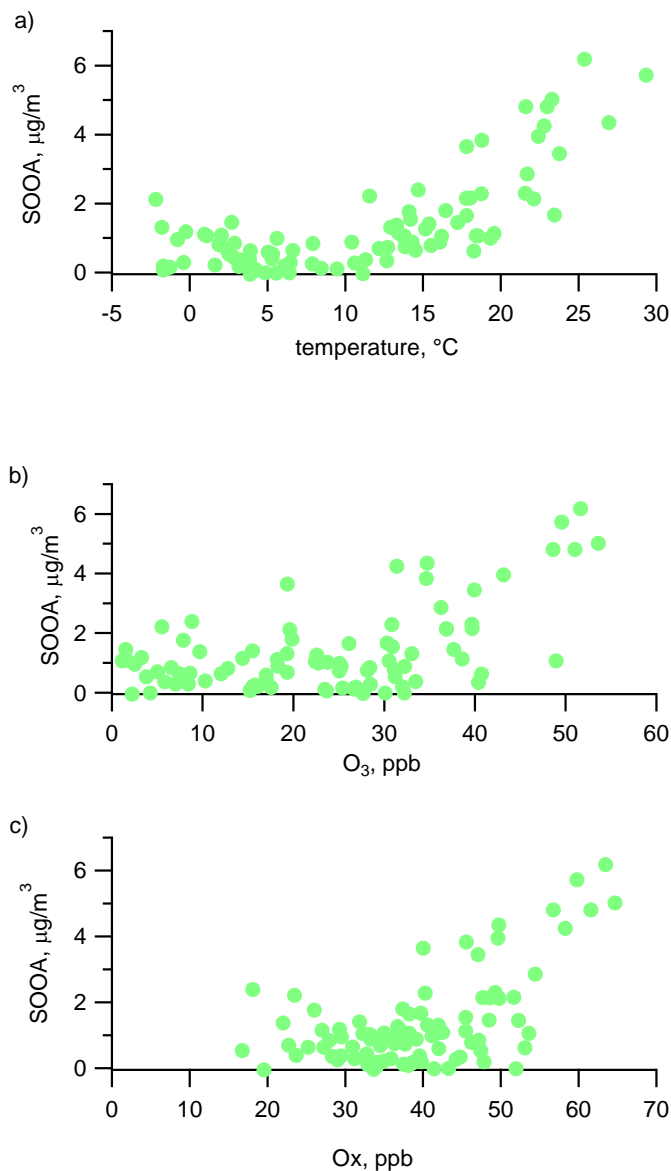


Figure S7: SOOA concentrations compared to temperature, ozone, and Ox (O₃+NO₂) for Zurich.

“...”

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