

Dear Referee #3,

Thank you for your comments on our manuscript. Please find below your comments in blue and the authors' responses in black.

This paper presents an analysis of ACSM data from the Po Valley, Italy, using ME-2 factorisation. While this is becoming an increasingly common form of measurement and analysis, this paper remains relevant because it is the first such analysis of one of the most polluted rural sites in Europe and may have implications for regional pollution in this area. The results aren't particularly surprising and the technical developments are incremental at best, however the results and quality assurance data are presented in a very comprehensive manner and the results analysed in the context of air quality control policy, so it makes an overall contribution to the science in these regards. Overall, this paper is well-written and I would recommend publication after the authors consider the following minor comments.

General comments:

The paper currently lacks a comparison with other AMS factorisations done at this site, specifically Decesari et al. (2014, doi:10.5194/acp-14-12109-2014) and Dall'Osto et al. (2015, doi:10.1021/acs.est.5b02922). This strikes me as a major omission.

The studies of Decesari et al. (2014) and Dall'Osto et al. (2015) are reported in the revised version of the manuscript accordingly. However, please note that both studies were conducted at a different south-eastern site of the Po Valley (San Pietro Capofiume, ca. 300km distant) and for short-time windows representing single seasons, hence limiting comparisons with our study. The following paragraphs have been added or modified:

I.73-76 (paragraph added in agreement with referee#2 suggestions as well):

"In addition, studies based on aerosol mass spectrometer measurements have been conducted in the Po valley, with the aim of characterizing specific phenomena (e.g. fog events, cooking aerosols) or seasons (Dall'Osto et al., 2015; Decesari et al., 2014; Gilardoni et al., 2014; Saarikoski et al., 2012)".

I.283-286: "Note that COA could not be evidenced, likely due to the type of site studied (regional background) and the lower sensitivity, time- and mass-to-charge-resolution of the ACSM compared to classical AMS instruments (further discussed in Sect. S2; see also Dall'Osto et al., 2015 on this subject)."

I. 406-409: "A distinct peak is however observed around noon, probably caused by enhanced photochemical production of secondary organic compounds, and increased BLH favouring downward mixing of advected pollution, especially during summer (Fig. 4; Decesari et al., 2014)."

I. 416-420: "This observation could be due to i) local production of sulfate with increased photochemical production around noon at the study site and/or ii) diurnal changes of the atmospheric stratification in the Po Valley as described by Saarikoski et al. (2012) and Decesari et al. (2014), enhancing aged particle contribution during the middle of the day and the afternoon."

Supplementary Material, I.66-67:

"Further discussion on the presence (or absence) of cooking factors at rural sites of the Po Valley can be found in Dall'Osto et al. (2015)."

I am struggling to see what the mass spectral marker analysis in section 4.2 contributes to the conclusions of the paper. The analysis exhibits behaviours broadly similar with the results from the factorisation and while speculative conclusions are offered for the behaviours, these are largely inconclusive. The section could do with being shorter and more focused on the analyses that result in new scientific insight.

We wanted to present a mass spectral marker analysis in this study since it is the first time mass spectra measurements of organic aerosols are reported in the upper Po Valley. The main information presented in this section - which differs from the factorisation analysis - are:

- i) acid species dominate the OA composition with respect to non-acid oxygenates;

- ii) most acid and non-acid oxygenates have been formed before reaching the study site, i.e. have been imported from other regions;
- iii) a first estimation of the oxygen-to-carbon (O/C), OM-to-OC (OM/OC), hydrogen-to-carbon (H/C) ratios and the carbon oxidation state (OSc) is made.

We nevertheless agree with the referee that this section do not contribute significantly to the main conclusions of the paper, and its results are consequently only briefly mentioned in the abstract or the conclusion sections. Following the referee suggestions, this section 4.2 has been shortened as follows:

Former I.459-460, removed: “favoured by low temperatures as previously found for semi-volatile OOA”;

Former I.462-463, removed: “, although the amplitude of their daily cycles is less pronounced than that of acid species (~1 and 3%, respectively)”;

Former I.466-469, figures removed: “(~2%)”, “(~1%)” and “medians of 13-16% and 7-8% depending on the time of the day, respectively”;

Former I. 481-490, paragraph moved in the supplementary material as a Section S3, and replaced by:

“Uncertainties associated with these estimates - in particular based on ACSM measurements - are discussed in Sect. S3. Comparisons with studies using (HR-ToF-) AMS instruments will not be reported and only variations within this dataset will be discussed (see Sect. S3).”

#### Specific comments:

Line 328: Given that  $m/z=60$  results from a primary emissions from biomass burning, it is possible that its presence in OOA is more likely due to factor mixing than SOA production. Such an issue is very possible, given the variations within BBOA and the mass spectral resemblance of primary HULIS to LV-OOA (e.g. <http://www.atmos-chemphys.net/15/2429/2015/>).

Heringa et al. (2011) and Cubison et al. (2011) report that  $m/z=60$  can be found in secondary biomass burning OA. Similarly, HULIS can be associated with secondary BBOA generation, as e.g. mentioned by Graber et al. (2006):

“Different suggested mechanisms for HULIS generation during biomass burning include: (i) soil-derived humic matter lofted into the air as a result of combustion; (ii) HULIS generation via chemical transformations during combustion and thermal breakdown of plant lignins and cellulose; and (iii) recombination and condensation reactions between volatile, low molecular weight combustion products (Mayol-Bracero et al., 2002).”

We also agree with the referee that the mass spectral resemblance of primary HULIS to LV-OOA might explain the previous observation. The following sentence has been added in the text accordingly:

I. 328-330: “Note that the mass spectral resemblance of primary humic-like substances to LV-OOA might also partly explain this observation (e.g. Young et al., 2015), i.e. that a small fraction of primary OA is found in this factor.”

Line 349: While a good correlation between the BBOA factor with 60 and 73 is worth reporting, this only indicates that the factor follows these markers; to take this as a sign of accuracy, one must assume that these markers are accurate reflections of actual BBOA, which may or may not be the case.

We indeed assume that 60 and 73 are accurate markers of biomass burning here, referring to Lee et al. (2010) and references therein (l. 312).

Line 362: None of these tests do not exclude the possibility that there is a degree of rotational freedom between factors. Such freedoms can change magnitudes of signals without significantly changing their time series. It’s also possible that exchanges between factors can be via a third factor (e.g. OOA).

We agree that a degree of rotational freedom between factors cannot be excluded in PMF analyses. This specific reason has been mentioned in the manuscript as follows:

“Although uncertainties associated with the accurate apportionment of HOA and BBOA cannot be excluded (e.g. due to rotational ambiguity), (...)”.

We however believe that the a-value sensitivity test (third test mentioned) partly assesses the degree of rotational freedom influencing the separation of factors. In fact, decreasing the a-value (i.e. the factor profile constraint) leads to higher rotational freedom. Figure S4 shows that a-values variations have little influence on factor contributions, which means that the reported results appear to be rather robust.

Line 397: Other reasons for a seasonal high of sulphate are plausible, such as changes in source regions due to seasonal changes in the prevailing wind direction, or changes in the amount of rainout.

We agree that both reasons mentioned by the referee are plausible. The sentence line 397 has been tempered as follows:

“Expected seasonal variations of the chemical composition of NR-PM<sub>1</sub> are observed, with (...) higher sulfate contributions during summer, which can e.g. be associated with enhanced photochemical production (Seinfeld and Pandis, 2006) and lower amount of rainout (Fig. S5) (...).”

Line 407: The statement that the midday peak is due to in situ photochemistry is at odds with the discussion towards the end of the paragraph, where this is rightfully treated with scepticism. This could be tested by comparing SO<sub>4</sub> with SO<sub>2</sub> and looking for a diurnal pattern in the fraction of oxidised sulphur as SO<sub>4</sub>. However, I would expect it more likely that the peak is due to the increased PBL height during the day favouring downward mixing of advected pollution. As pointed out, the timescale of formation of SO<sub>4</sub> is too long to expect a pattern like this to result from chemistry.

This sentence has been revised accordingly as follows:

“A distinct peak is however observed around noon, probably caused by enhanced photochemical production of secondary organic compounds, and increased BLH favouring downward mixing of advected pollution, especially during summer (Fig. 4; Decesari et al., 2014).”

Technical comments:

While conventional, the definitions of the seasons used should be given in the main text rather than just a figure caption.

The following sentence has been added in the main text (l. 144) accordingly:

“Seasons are defined as spring (MAM), summer (JJA), autumn (SON) and winter (DJF).”

Line 178: Please specify the ‘classical program’ used for PMF.

The ‘classical programs’ used for PMF have been specified as follows:

“Contrary to classical programs used to resolve PMF (e.g. PMF2, PMF3), ME-2 allows any element of the F and G matrices to be constrained with a certain degree of freedom.”

SI line 20: Please use scientific rather than engineering notation.

Scientific rather than engineering notation has been used accordingly.

SI line 102: Correct “Error! Reference source not found.”

Corrected:

“Correlations with independent measurements are further discussed in Sect. 3.2 of the manuscript.”

Figure S5: Do the curved lines on these plots represent actual data or a nonlinear interpolation between points? If it is the latter, the algorithm should be specified and justified.

The curved lines represented a nonlinear interpolation between points in the previous version of the manuscript. Curved lines are removed in the updated figure.

## References

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