

# ***Interactive comment on “Variations in the chemical composition of the submicron aerosol and in the sources of the organic fraction at a regional background site of the Po Valley (Italy)”***

**by M. Bressi et al.**

**Anonymous Referee #3**

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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

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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.

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.

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-chem-phys.net/15/2429/2015/>).

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.

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).

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

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in the amount of rainout.

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.

Technical comments:

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

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

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

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

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.

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