Review: The impact of biomass burning and aqueous-phase processing on air quality: a multi-year source apportionment study in the Po Valley, Italy

Paglione et al.

General comments

The manuscript by Paglione et al. focuses on a positive matrix factorization (PMF) on organic aerosol (OA) mass spectra recorded over four years with an high resultion time-of-flight aerosol mass spectrometer (HR-AMS) at two different sites in Po Valley, Italy. The study aims to quantify the biomass burning organic aerosol via primary and secondary formation mechanisms in the polluted Po Valley region, known to be greatly impacted by high pollution levels. The largest new discovery in the paper was the quantification of the biomass burning organic aerosol (BBOA) formation and processing in the aqueous phase that is clearly motivated by a previous publication by Gilardoni et al. published in PNAS in 2016. As a result of the PMF analysis by Paglione et al., a factor with distinct BBOA mass spectral fingerprints together with a high degree of oxygenation that correlates with aerosol liquid water content was linked to aqueous BBOA formation. The contribution of this factor to the total OA recorded ranged all the way up to 100% during the cold seasons, which makes these results of high importance and atmospherically relevant. While some parts of the study are fairly nicely written and formulated, I suggest few major additions and changes to be done before a review round for detailed adjustments should take place.

PMF-analysis

First, as PMF plays a central role in the aqueous BBOA quantification, the description of the PMF analysis should not by any means be hidden in the supplementary material and it should be thorougly step by step explained. The PMF analysis process arises few concerns regarding a-values and the amount of repetitions performed (number of *iterations*) that seems not to be reported at all in the manuscript. I suggest you explicitly write down in the manuscript how many repetitions were conducted to make the readers aware of the statistical robustness of the solution. Currently, the vague description of the PMF analysis arises doubts of the solidness of the result.

For example, the justification of different a-values used in the multi-linear engine (ME-2) analysis is not clear. The high a-value used for HOA (a = 0.5) is exceptional, and I personally did not see why it was necessary. Previous studies suggest an a-value of approx. 10% for HOA. In contrary to this, the BBOA was constrained with an a-value of 5%. This is allows a rather low degree of variability for the BBOA mass spectrum in the PMF analysis despite the fact that BBOA is known to vary a lot depending on the burning material (even up to 30%). While the a-values chosen in the current study can in some cases be fully justified, the motivation still needs to be explicitly written down.

It is absolutely crucial that you carefully motivate the selections of the constraints (a-values) and the solutions (number of factors) in the manuscript main text. Please spend time on this to make sure your readers (and I) can follow your process. You can even create a flow chart to describe it, but try to avoid just transferring the table jungle from the SI to the main text, try to summarize the logic you had in decision making.

Here are two examples of publications where the PMF process is well documented:

Elser, Miriam, et al. "New insights into $PM_{2.5}$ chemical composition and sources in two major cities in China during extreme haze events using aerosol mass spectrometry." Atmospheric Chemistry and Physics 16.5 (2016): 3207-3225.

Daellenbach, Kaspar R., et al. "Long-term chemical analysis and organic aerosol source apportionment at nine sites in central Europe: source identification and uncertainty assessment." Atmospheric Chemistry and Physics 17.21 (2017): 13265-13282.

CO_2^+ release from the AMS vaporizer due to ammonium nitrate

Another important concern of mine is the CO_2^+ release from the AMS vaporizer coinciding with high ammonium nitrate loadings. This effect was introduced recently by Pieber et al. (2016) and investigated thoroughly with AMS-type instrumentation by Freney et al. (2019). My wonder is whether you quantified this effect with your instrumentation. How much CO_2^+ did you detect during your ionization efficiency calibrations? Did you modify your fragmentation table(s) and adjust the CO_2^+ introduced by ammonium nitrate?

When looking at the mass fractions of inorganic species during the cold season, I noticed that ammonium nitrate plays an important role. Correct me if I am wrong, but likely this hygroscopic PM constituent further promoted the water uptake

resulting in a correlation between aerosol liquid water and PM nitrate mass fraction. As higher nitrate mass fractions promote CO_2^+ release from the vaporizer, some CO_2^+ could be attributed to this artefact. Because the aqueous BBOA correlates with high aerosol liquid water content, some of the CO_2^+ detected during this time might be attributed to aqueous BBOA mass. This might lead to an overestimation of the aqueous BBOA concentration.

I suggest you quantify the importance of this artefact with your instrument. Importantly, if the artefact is significant, you should consider additional PMF runs with new fragmentation table setups.

References:

Pieber, Simone M., et al. "Inorganic salt interference on CO_2^+ in aerodyne AMS and ACSM organic aerosol composition studies." *Environmental Science & Technology* 50.19 (2016): 10494-10503.

Freney, Evelyn, et al. "The second ACTRIS inter-comparison (2016) for Aerosol Chemical Speciation Monitors (ACSM): Calibration protocols and instrument performance evaluations." *Aerosol Science and Technology* (2019): 1-13.