

Interactive comment on “Molecular insights on aging and aqueous phase processing from ambient biomass burning emissions-influenced Po Valley fog and aerosol” by Matthew Brege et al.

Anonymous Referee #1

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GENERAL COMMENTS

This paper describes high resolution mass spectrometry (HRMS) and NMR analysis of water soluble organic compounds (WSOC) in four samples selected to represent fresh and aged aerosol particles as well as fresh and aged fog droplets. Results of this work generally support the importance of aqueous processing of organic aerosols. The data set is definitively interesting and worth publishing. The paper can be improved by addressing several issues described below. In addition, for the amount of new information presented in this paper it is too long. I would recommend shortening it and making it more focused on new findings.

C1

My main criticism of this paper is its reliance on just one sample of each type (fresh aerosol, aged aerosol, fresh fog, and aged fog) to draw far reaching conclusions about chemical processes that are responsible for aging of WSOC. Furthermore, samples come from completely different dates making it quite difficult to faithfully compare them. This is much less satisfying and convincing than the approach taken by the authors in Gilardoni et al. (2016) that looked at the fog dissipation events. The authors rely on aerosol mass spectrometry (AMS) analysis, specifically on the f44-f60 correlation plots, to classify the samples. To prove to the readers that this classification works as expected the authors should compare at least two HRMS data sets from different filters that are supposed to be identical based on the f44-f60 AMS classification. Why not take a couple of samples (as opposed to a single sample) corresponding to closely spaced points in Figure 1 and compare their HRMS data? I am willing to bet that the authors would find very different molecular composition for these supposedly similar samples. If this is the case, the comparison of the HRMS data between different conditions becomes more difficult and potentially not even possible.

SPECIFIC COMMENTS

Abstract: To avoid confusing the readers I recommend removing the prefix “high resolution” in front of ToF-AMS in the abstract and in the text. I understand that this how this instrument was called when it was designed but it is a stretch to call it a high resolution instrument especially in a paper that relies on FT-ICR as the main method. Using simple “ToF-AMS” should be sufficient.

P1L21: particles containing organosulfates might activate more easily accounting for the higher fraction of organosulfates in fog droplets compared to aerosol particles.

P1L25: it would be useful to also add ranges for O:C and H:C for the “fresh” samples so that one can compare

P5L26: it should also be pointed out that valence of 3 is used for N, so the extra double bond in the nitrooxy compounds is not counted

C2

P5L29: the authors should warn the readers that OS developed by Kroll et al. (2011) only works for CHO compounds, and that it also fails for peroxides. This formula cannot be used for CHOS and CHON compounds. The authors should check their text so that they do not over interpret results from this formula

P12L20: the fact that these compounds show in a single daylight sample does not constitute proof that these compounds are related to photochemical properties. This is one example of several statements made by the authors for which they do not have sufficient data. To claim something like this, they would need to demonstrate presence of these compounds in many daylight samples (not one!) and absence in many nighttime samples.

P13L15: another example where a conclusion is made (about sulfite radical involvement) without having needed data to prove it

Figure 5: What message is conveyed by this figure that cannot be more easily conveyed with average O:C values? I do not see how it helps interpret the data. Two versions of this figure exist, one in the text and one in the SI section. I would just keep it in the SI section or remove altogether.

Figure 7: it would help explain how the spectra were normalized before the subtraction. The result of the subtraction obviously would depend on the choices made in the normalization.

Table 3 and Table S1: it would be useful to specify peak abundance (such as very high, high, medium, minor or something similar). Also I would point out in the caption that the "identities" specified in one of the columns are for reference only – the fact that formulas match does not mean that this where these compounds came from.

S2: it states it there that the assignments were cut off above m/z 500 but assigned peaks in figure S3 go beyond 600

S2: please explain the "rule of 13" – this must be some sort of a mass spectrometry

C3

jargon

EDITORIAL COMMENTS

P1L34: remove "evolving"

P2L7: "and more" -> "and other compounds"

P2L14: this sentence needs a revision (incompatible list items)

P6L26: "rich of" -> "containing"

P10L30: two sets of references need to be joined in one

P10L31: "act" -> "acted"

Figure 4: the choice of colors makes it hard to differentiate between them

Table 2: "mass" -> "molecular weight (g/mol)"

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C4