Interactive comment on "Investigating types and sources of organic aerosol in Rocky Mountain National Park using aerosol mass spectrometry" by M. I. Schurman et al.
Anonymous Referee #1

Author Response: Please see in-line responses denoted by "AR:"

This manuscript reports the characterization of submicron aerosols with an Aerodyne HR-ToF-AMS at a remote site in the Rocky Mountain National Park (RMNP) in summer 2010. By applying PMF to the organic aerosol mass spectral data, the authors identified three OA factors, including a low volatility OOA that correlates with sulfate, a semivolatile OOA that correlates with nitrate, and a local BBOA that shows enhanced signal at m/z 60 and 73 in the factor mass spectrum and appeared to be related to campfire burning. The sources of the particles at RMNP are discussed based on particle composition, size modes, and meteorological measurements. The authors also mentioned that the results of this study appear to be representative of typical summer-time condition at this location according to historical measurement data in this region.
This work provides important, new information about aerosol chemistry and sources at a background site in the Front Range area. The work is carefully conducted and the manuscript well written. The scope of the work also fits well to ACP. I thus recommend publication on ACP after the authors respond to the following comments.

A main portion of this manuscript deals with organic factors determined from PMF analysis of the AMS organic matrix and the usage of this information to interpret aerosol sources. However, some aspects of the PMF results are questionable. For example, the Q/Qexpected values (Fig. S1) are much lower than 1, suggesting an overestimation of the errors.

AR: Thank you for your rigorous reading! Yes, this error overestimation is explored in the supplement (pp. 2/line 28 – pp. 3/line 17), following error propagation from signal-error determination in the data acquisition through downweighting during PMF analysis; we have expanded this discussion somewhat based on your comments.

The SV-OOA and BBOA factors are very similar, in terms of both mass spectra and time series. A large fraction of the m/z 60 and 73 signals goes to the SV-OOA factor. All of these suggest factor mixing. Recombining factors from the solution of a larger number of factors seems promising, but more information should be given. It is important to show the mass spectra and time series of the 6 factors and offer details on how the recombination was performed. How do the BBOA* calculate from recombining the 6-factor solution compare to BBOA from the 3 factor solution?

AR: Thank you for your feedback; some of this information was shown in the supplement, and this section has now been expanded. Additions include: mass spectra (MS) and time series (TS) for 6-factor solution (Figure S3), with correlation coefficient (r) values between the factors' TS and MS; an explanation of how the six factors were recombined into three; coefficients of determination (r^2) between recombinant *BBOA, *SV-, and *LV-OOA and inorganic species (Table S1) and between recombinant factors' mass spectra (Table S2); and more extensive comparison of the original and recombinant BBOA factors.

Detailed comments:

The abstract and the summary both make references to historical measurement, it will helpful to give some details.
AR: Citations, data types and sources, and relevant statistics for comparison with historical data are described in Table 1; the caption has been revised to include more methodological details for the historical measurements.

Page 19878, Line 1, replace Zhang et al. 2005 with Zhang et al., 2011.
AR: Done; thanks for your feedback.

Page 19879, line 9 -10, it says "a DMPS study-average submicron size distribution shows that the AMS aerodynamic lens transmits _ 98.7% of submicron mass". What is 98.7% corresponding to? How was this determined? Note that the AMS lens transmission is size dependent.
AR: Yes, we took into consideration the size dependence of AMS lens transmission. We multiplied the volume distribution from the DMPS (analogous to mass assuming constant particle density, but in any case the units cancel) by the aerodynamic lens transmission function, and divided that by the DMPS volume distribution (Liu et al., 2007); this assumes that our instrument's lens transmission function is the same as that of Liu et al.'s instrument.

Page 19880, give information about how CPF is performed.
AR: Page 19880, Lines 8-10 give the method of calculation and the threshold used for filtering (thresholds were applied using a mask wave in IGOR, but could be accomplished similarly in any number of programming languages). We included this information in text instead of equation format to save some space.

Page 19880, line 22, saying that the sulfate "timeline less featured" is vague. Please be specific.
AR: Thank you; it now reads, "Sulfate concentrations are lower and less variable…"

Page 19909, Figure 5, it will be interesting to add the ratios of other elements too, e.g., C/H, C/N.
AR: Thank you, this has been done.

Page 19883, line 22 -25, the logic is not clear – why is the fact that S(VI) species result from S(IV) oxidation the reason that particles containing sulfate have been subject to advanced oxidation?
AR: This has been reworded; we mean merely that, while it is certainly possible for S(VI) to partition to a less-oxidized particle, contemporaneous transport (and attendant oxidation) of S-species and organics will tend to yield highly oxidized organics in concert with S(VI), as has been observed in numerous ambient datasets.

Page 19884, line 3-4, if thermal partitioning is the reason for LV-OOA increase at night, why nitrate does not show the behavior? In fact, all OA factors increase at night, suggesting a BB influence that "contaminates" the OOA factors.
AR: The increase at night is observed in sulfate, ammonium, and nitrate diurnal profiles as well. This was alluded to in Page 19881, line 15, but has now been rewritten to be explicit.

Page 19885, line 26, what does "arbitrary" mean?
AR: Under the dictionary definition, "arbitrary" is not precisely the right word, as it implies a distinction made without logic or reason, and SV- and LV-OOA do have explicit definitions in the AMS community (namely, which of m/z 43 or m/z 44 contains more signal, respectively). The point we are trying to make is not that the definitions of SV- and LV-OOA are technically arbitrary, or that semi- and low-volatility material don't behave differently/have different sources, but that ambient aerosol oxidation varies continuously such that a particle subject to oxidation may, at a given time, be defined as 'SV-OOA,' while by the next time step the same particle may technically be 'LV-OOA'; under such circumstances, the delineation between SV-OOA and LV-OOA – purely in terms of oxidation (as stated in the text) - do not indicate a major difference in particle source or content. The next sentence goes on to describe how differentiation in sources can be determined from associations between differing levels of oxidation and inorganics, meteorology, etc. We are merely stating that oxidation level as measured by mz43/mz44 is somewhat fluid and, by itself, incomplete indicator of sources and processing.

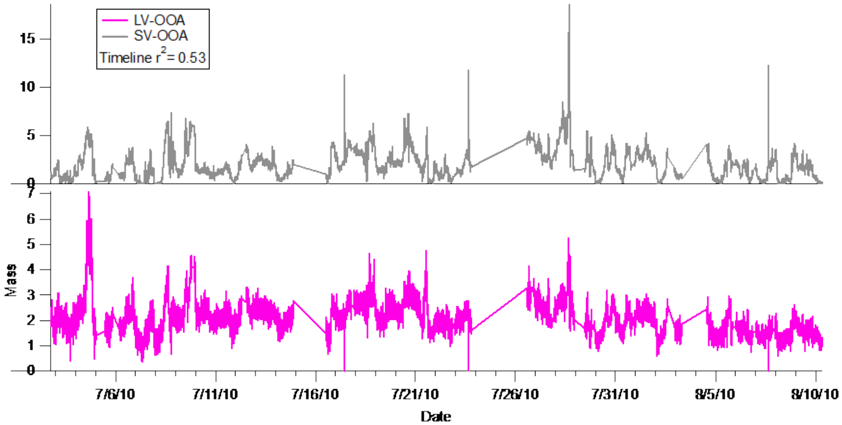
Page 19886, the organic nitrogen results are very interesting. It might be interesting to report the comparison of the AMS total CHN signal to the total WSON measurements from PILS, e.g., correlation coefficient and scaling factors etc.
AR: Unfortunately, we have only weekly filter-based PM2.5 PON measurements; these comparisons may be explored in the future.

Page 19889, line 9-10, it is helpful to show the size distribution image results in the supplementary.
AR: This figure will be included in revisions to the supplement.

Figure 5, the huge m/z 29 peak in the BBOA factor is strange.
AR: We have noted 'unusually' high signal at *m/z* 29 in all of the datasets gathered using this instrument; after exploring possible causes in the data analysis processes, peak fitting, ion choices, etc. appear to be correct (i.e. the signal is real), so we must conclude that our instrument tends to fragment more than others; it is established in the literature that fragmentation for various species is inconsistent between instruments (as discussed in, e.g. Farmer et al., 2010).

Figure 10, the purple trace on NO3 plot is hard to see.
AR: The blue (NO_3 data) trace is now somewhat lighter for greater contrast; thank you for noting this.

Figure S3, how do the time series of the two OOA factors derived from data with f60<0.003 look like? What are their correlation behaviors with nitrate and sulfate?
AR: The timelines are included below; they resemble the SV- ad LV-OOA timelines from the 6-factor recombinant solution. As shown in the table below, they retain the pattern of better correlation between LV-sulfate and SV-nitrate, as in the other solutions, though the coefficients of determination are weaker (like those in the 6-factor recombinant solution). This information is omitted from the main text and supplement for brevity, but is part of the public record in the form of this communication.



	SV-OOA’	**NO_3**	**SO_4**	**NH_4**
LV-OOA’	0.53	0.35	0.46	0.38
SV-OOA’		0.46	0.23	0.30

Figure S4, is this the solution of PMF performed on the entire org. matrix?
AR: yes; the captions are now more specific.

Thank you again for your comments.