

In this manuscript, Zawadowicz et al. present analysis on a 3-year data set of aerosol chemical and physical properties measured at the Southern Grate Plains in the United States. They report seasonal behavior of aerosol chemical composition, source apportionment for organic and inorganic aerosol based on ACMS data, and impacts of wildfire emissions on aerosol chemical properties, optical properties, and CCN concentration. The results show that organic aerosol, NO_3 , NH_4 , SO_4 , and mineral dust have seasonal cycles with NO_3 and NH_4 peaking during winter and organic aerosol and SO_4 during spring and summer. With PMF, three organic aerosol types were identified, including semi-volatile and low-volatile oxygenated organic aerosol and biomass burning organic aerosol.

Overall, the dataset analyzed for this manuscript is extensive and mostly analyzed thoroughly, providing interesting insights on the topic. The language of the manuscript is good. However, the information given in methods section is not sufficient, the overall figure quality could be improved, and the novelty of the study is not clear. Based on these things and the other comments listed below, I suggest major revision for this manuscript.

Major comments:

- 1) The authors do not adequately acknowledge the similarity of their study to the one by Parworth et al. (2015) and compare the results of this manuscript to theirs. The authors should also highlight what new does this manuscript offer. Overall, in many places, the manuscript is lacking in comparison to earlier observations.
- 2) The methods section does not provide sufficient information to understand and replicate the study. Specific comments regarding this are listed below, but overall, please add measurement device models, adequate information on measurement device calibration and how often they were performed, and for some parts, data analysis (e.g. PMF information only appears in section 3.2).
- 3) The overall figure quality could be improved. Some specific comments are listed below, but please ensure that all figures have large enough font sizes and the captions provide enough information to the reader.
- 4) In two cases, it seems that the conclusions/interpretations of the authors were guided too much by the expected results and are not sufficiently supported by the presented data.
 - a. The contradictory argument about how the higher volatility of the “fresh” OA in spring explains the discrepancy to the filter data.

The authors state that the OA peak in spring that is not detected with the IMPROVE filters is caused by “fresh” OA which has higher volatility and thus will have a sampling artefact in the filter data. Careful inspection of Fig 2 A, E, and H shows that the OA peak in spring is almost exclusively caused by the increase of “LV-OOA”. The authors labeled this OOA factor as LOW volatility (based on the higher f44). If that label is true, spring shows an increase in LOW volatility material not in semi volatile one. This is the opposite what they claim to explain the lower values for the IMPROVE data.

Aside from the discrepancy from the filter data, the fact that summer and spring both have the main increase in LVOOA (the more oxidized OOA) is the interesting part here. This should be discussed in addition to finding a more suitable explanation for the discrepancy to the filter data.

- b. Interpretation that SVOOA is formed more locally while LVOOA has sources further away.

I do not understand how the authors conclude that the SVOOA sources are more localized than the LVOOA sources based on Figures 8 and 10. Based on the way that Fig 8 subplots are interpreted in the manuscript (high concentration close to center -> more local source), I take from this figure that SVOOA has the further away source region than LVOOA. Similarly, when looking at Figure 10, I detect more high concentration parts coming from far away in the SVOOA case than in the LVOOA case. This is counter intuitive to the assumption that fresh OA is usually less oxidized, and this needs discussion – or a rebuttal based on the available data

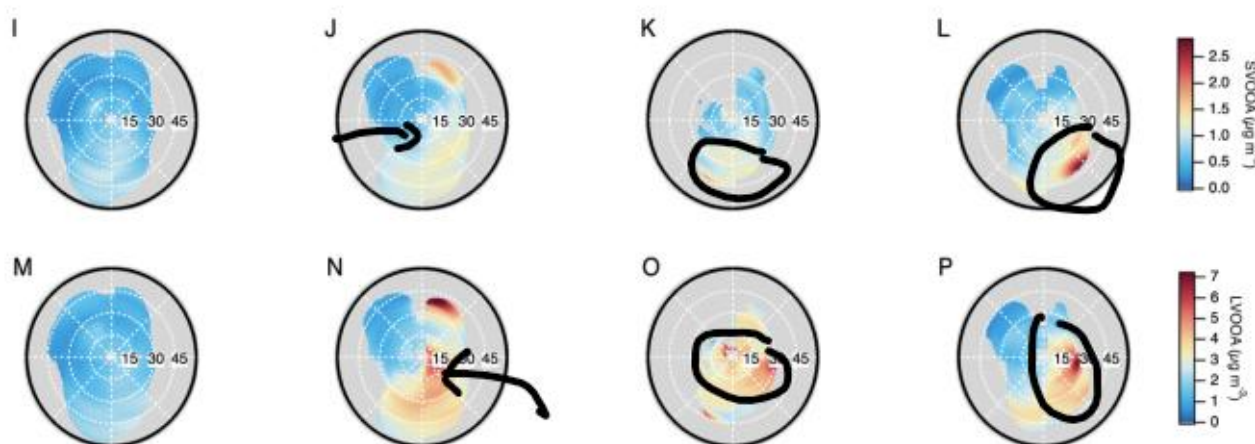


Figure R1: from Fig 8 in main manuscript. Hand drawn markings pointing out parts where the LVOOA data has higher concentrations closer to the center of the circle than SVOOA. This should indicate that the sources are closer to the measurement site.

- 5) From how I understand it, most of the results in the main text are from the rolling window data while the results of the seasonal PMF are buried in the SI. The purpose of the seasonal PMF is not clear to me. The authors did all this work and have interesting results but then they only extract the “SVOOA” and BBOA factor profile to use for the constrained rolling window PMF? They don’t even compare the occurrence of BBOA in the two PMF approaches. Since the identification of BB events is one of the main purposes of PMF in this context, a comparison between the two methods would be valuable to see the robustness of the identified periods. Especially, if no other tracer (e.g. BC) is available. Why did the authors choose to mainly discuss the less detailed rolling window PMF which has much more constraints and assumptions than discussion the more thorough seasonal data in the main text? If the aim was simplicity (having less factors, one could simply group the different LVOOA factors together and do the same type of analysis as now with the rolling window LVOOA factor.
- 6) The presentation of PMF results (especially seasonal) lacks important information. I find it problematic that no time series of factor contributions are shown for the seasonal PMF – PMF results are a matrix of factor profiles and factor contributions/time series. It is impossible to estimate the relevance of each factor if there is no information on how much it contributes to the total aerosol mass. Also, residuals are only shown for the rolling window case.

Specific comments:

The comments are in order of appearance, not of importance. S in line number refers to material in the SI.

- 1) The phrase “while OA and SO₄ peaked in spring and summer, reflecting enhanced photochemistry and biogenic precursor emissions” is ambiguous and implies that the enhanced photochemistry and biogenic precursor emissions are the reason for both elevated OA and SO₄.
- 2) Based on the introduction, the reader is left with an understanding that such measurements have not been published before from this site. However, some of the objectives of this manuscript have been covered before by Parworth et al. (2015), which the authors cite at line 40 but do not mention including long-term aerosol composition measurements. In addition, results of the current manuscript are never compared to those in Parworth et al. (2015). This feels like a missed opportunity since both data sets use comparable instrumentation, methods, and cover all seasons.
- 3) Lines 50-52: results should not be presented in introduction. Overall, most of the introduction consists of the author’s research objectives rather than providing context for the study and its results. A more thorough description of the measurement site (e.g. the expected sources) will be more valuable to the reader.
- 4) Section 2.1.1: a schematic of the measurement setup would help the reader to get a better picture of the setup. This could be put in the Supplemental Information.
- 5) Line S12: What is “DQA”? Also, this section provides very little additional information on ACSM data processing than what is written in main text. More information about the ACSM calibration should be provided. What compounds were used for the calibration and how often was the instrument calibrated? Was it stable throughout the measurements? The authors state that some linear interpolation was done between the calibration points. This suggests that there was some instrument drift. This should be shown to assure the reader about the stability and comparability of the long-term measurement.
- 6) Table S1: please provide references for all values in the table. The density values for the organic categories seem rather higher. Most studies I am aware of use values closer to 1.4g/cc. As an example, Figure S4 in (Hu et al., 2020) shows a typical distribution of density values for ambient data as well as the range of densities for specific organic compounds. Very few are above 1.5 g/cc.
- 7) Line S30-S31: with a slope of 0.62 and R² of 0.6 I would not say that the ACSM and nephelometer are consistent. Also, please provide information on how the ACSM-derived dry scattering estimates were calculated.
- 8) Figure S2: please mark the slope and 1:1 line to the figures.
- 9) I have couple concerns about the CCN closure. Firstly, the authors could provide more information on how $N_{\text{CCN,calculated}}$ was calculated. Did you calculate the actual compounds from the ACSM species using ion pair scheme (Gysel et al. 2007)? Secondly, ammonium concentration was omitted from this calculation as well as black carbon which can sometimes be an important component, especially to aerosol influenced by fire emissions. Was black carbon concentration measured at the site and if yes, why is it not included here? Thirdly, the offset from perfect closure is systematic for all SS, but there is no interpretation for this. Could there be missing aerosol components from the $N_{\text{CCN,calculated}}$ calculation as it takes into account

only the refractory ACSM species? Lastly, it seems very unlikely that the aerosol measured at the site would be fully externally mixed, given that the particles are relatively highly atmospherically processed. However, this is the implication that the reader gets from Supplementary Information lines 60-62. Could the authors comment on this?

- 10) In Figure 1A, the concentrations of the different aerosol components have been plotted starting from 0 but in Figure 1B, the different PMF factors have been stacked on top of each other. This is a bit confusing and should be stated in the caption. Also, in Figure 1C it is hard to distinguish between NH_4 and SVOOA as the colors are too similar. Please use different colors or switch the order of the components so that BBOA is between NH_4 and SVOOA.
- 11) Figure 1E: What is meant by reconstructed PM_{2.5} mass? Is there a reason it is included in this figure as it is not mentioned anywhere else in the manuscript?
- 12) Line 101: Is this data from a single SMPS unit, or was this a combination of a Nano- and long DMA? Please include the instrument models for all the instruments.
- 13) Line 114: Why wasn't the data with PM₁ impactor used and how comparable is the nephelometer data without impactor to ACSM and SMPS which are PM₁ and <500 nm? Can you comment on this?
- 14) Section 2.1.5: I assume that the CCN counter measured polydisperse particles? Was the CCN counter calibrated regularly during the measurement period? Was it stable throughout the measurements? Also, please elaborate on what is meant by "processed to .b1-level".
- 15) Line 126: Please provide more information on how the IMPROVE data was analyzed. How was total organic mass and inorganic compounds obtained? Comment on how this method compares to ACSM derived values. Which artefacts may be present that would impact closure between the methods? Note that the provided reference (Malm and Hand, 2007) does not contain the information about the method used at this specific station.
- 16) Sections 2.2.2 and 2.2.3 It is not clear how these methods compare to each other, i.e., what does one method show that the other does not? This is not sufficient to actually understand what was done.
- 17) Section 2.2.3: Why were the back trajectories calculated for 7 days but the dispersion mode was run for 5 days?
- 18) Information about fire data: the information about the origin of the fire data needs to be in the methods part.
- 19) The authors used two separate PMF calculations for their data interpretation. They ran an unconstrained version with 3-5 factors for the data grouped in 3-month intervals (seasonal PMF) and they conducted a rolling window PMF analysis with 2-3 factors with two constrained factors ("SVOOA" and BBOA). Both of these approaches are scientifically sound and can yield important insights into the composition of OA. But it is not always clear which PMF data was used at which place. This is mostly an issue with unclear description in the text and missing information in the methods part.
- 20) PMF sections in SI: Equally unclear are the exact settings for the PMF runs. Seasonal was run with averaging 3 data points (90min) but rolling window was not averaged. Why? Some ions were removed from rolling window but not from seasonal? Why?
- 21) Line S84: which version of SoFi was used?
- 22) Line S93: how was the clustering constrained? I do not understand how many clusters were set. Was the system forced to always find the same number of clusters? Was it allowed to put multiple factors into one cluster?

- 23) What criteria were used to determine the number of factors in the seasonal PMF case? Only the silhouette score as the text suggests? That is not the appropriate metric in my opinion. The silhouette score is more of a measure for the cohesion of the cluster analysis. I.e., how close the individual runs are in their results (which should be an indication of local vs global minimum). But this is not the primary indicator of the overall goodness of fit of a solution. E.g., what were the Q/Qexp values vs number of factors? Winter already shows the issue. The silhouette is slightly better for 5 factors than for 3 here, so the authors go with 5 which seems to make sense here (again, this needs the time series to fully evaluate the results). But how much better is this solution than the 3 factor one?
- 24) All factor profile figures need better labels for the mz. It is almost impossible to see which bar is 44 and which is 43.
- 25) Interpretation and labelling of seasonal PMF factors: I do not understand the criteria for labelling the factors. If the authors are using the presented f44, f43, and f60, I will make a strong case that the spring SVOOA factor is actually a LVOOA factor as f44 is twice as high as f43 (Fig S5). That qualified as a LVOOA factor in all other seasons. Furthermore, the "SVOOA" factor in summer (Fig S6) has higher f60 than the BBOA factor in autumn. Looking at the factor profile without expectations I cannot see why one is BBOA and the other SVOOA. In other words, I speculate that any BB related aerosol could not be split from the SVOOA aerosol in summer and is thus part of the SVOOA factor. I.e., there is BBOA but because of the chosen constraints it could not be identified. A comparison with other BB markers would be helpful to clarify this.
- 26) Lines 154-156: The authors state that inorganics (specifically NO_3 and NH_4) dominated in winter and organics in spring and summer. Was the NH_4 concentration so high that together with NO_3 their concentration was higher than that of the organics during winter or did the authors mean to include SO_4 in the inorganics here? Overall, the authors show NH_4 signals in Fig 1, but in all the further analysis and figures they only present data for SO_4 and NO_3 . They do claim several times that NO_3 is present as NH_4NO_3 . This is especially relevant as NH_4 can be paired either with NO_3 or with SO_4 and in the absence of NH_4 , SO_4 may be in the form of ammonium bisulfate or even sulfuric acid. The changes in correlations shown in Fig 4 already suggest that NH_4 is present in different compounds depending on the season. The pairing of these ions will impact on the physical properties of the particles (e.g. the CCN activity). Unless there is a very good reason, the authors should calculate the actual inorganic compounds using the ion pairing scheme in Gysel et al. 2007. This will provide a solid argument that NO_3 is indeed inorganic NH_4NO_3 as well as help with understanding the role of SO_4 better.
- 27) Lines 162-164 and 381-383: There is a contradiction between this and PMF results. Most of the increase in OA during spring is due to the increase in LVOOA, i.e. the lower volatility material, not higher volatility material. Hence, the difference in ACSM and IMPROVE cannot be explained with the evaporation of high volatility OA.
- 28) Line 183: What is meant by fractions of CCN aerosol budget?
- 29) Figure 3: There is a problem with the y axis labels of this figure: there are more rows in the figure than variables listed. Also, how was the data normalized? Did the authors just scale the values for the graphic representation? Or did they normalize the data of each day to e.g. the mean of that day before calculating the diurnal trend?
- 30) Line S160: Why was constraining SVOOA needed? If it is true that it showed up in every season (i.e. over the full time period), it should not need any forcing to be present.

- 31) The seasonal analysis shows that up to 5 factors are present. Unless the different factors show up exclusively in different time periods of those seasonal sections, I do not understand why they then reduce the total number of factors that drastically. Wasn't the seasonal stuff done to determine the number of factors? Also, if the average BBOA and SVOOA factor profile from 5 factor solutions is used, how can they be sure that those are still valid when using only 2 or 3 factors? This assumes that by adding more factors, only the LVOOA part of the data is split up more. Is that really the case? How much does the SVOOA factor change when looking at the 3, 4 and 5 factor solution for one season?
- 32) Line S173: if less than 30% of variability of 60 is explained by BBOA factor, there is no BBOA factor. But what is the source of mz60 at those times if it is not from BB?
- 33) Line S207: the highest residuals are observed for BB events with high concentrations. But isn't the special BBOA factor supposed to specifically capture the BBOA episodes? This reads like it may not be doing such a good job. I.e., there is systematic over/underestimation (the authors do not say which way) for high aerosol loadings. How much uncertainty will come from that when estimating the influence of e.g. BB events on the overall aerosol concentration?
- 34) Line 199: I do not understand this sentence "Special marker distributions..." What are individual BBOA solutions? The figure contains the f60 etc. for the BBOA factor profiles for cases when this factor was identified. How is that supposed to support the statement that summer has no BBOA? For this it would be more helpful to plot all f43 vs f60 data points and color code the markers by season to identify potential patterns.
- 35) Figure 4: The choice of color range is very unfortunate for this type of correlation figure. Both positive and negative R values are in shades of blue. It is almost impossible to see which variable pairs have positive and which have negative correlations. Adjust the color scale to have one (or more) color for the positive R values and another color for the negative ones. Additionally, the font size is too small.
- 36) Line 236: One important product of this study is the identification of the BB plumes at the site. The authors use rolling window PMF BBOA factor to identify the plumes, but the results are not checked against any other tracer, namely black carbon concentrations. Was there no BC measurements at the site?
- 37) Fig S17: this figure shows BB events in summer months. But the text states previously that there is no BBOA in summer. This seems contradictory.
- 38) Lines 245-246: "modest increase" is quite vague. Also, there are spikes in absorption in April and August, could you comment on why is that?
- 39) Lines 254-257: while it is widely known that biomass burning particles are usually not strongly hygroscopic and is likely the case also here, I don't think it is possible to draw this conclusion without information about the particle size. Please show comparison for size distribution during smoky and smoke-free periods. I.e., did the shape of the size distribution change due to smoke? Or was there only a general increase in particle number concentration?
- 40) Figure 7: Putting the PMF factor points into this figure is misleading and a comparison of unequal things. The figure can suggest that the BBOA in this data set is much more "fresh" (lower in f44) than the biomass burning material found in the other data sets. There are two issues.
 - a) the composition of the BBOA factors was constraint by the authors. Thus, it can only vary in the predefined range. So, the values displayed here display the expected range of BBOA

compositions. If the authors had selected a more “aged” BBOA factor profile, the values would reflect that.

b) The measurement data points are for the overall composition of the particles, which is a combination of the OA from different sources. The figure is supposed to give an idea how much impact there is from BB aerosol which is linked to high f60. The measurement data points are mixtures of all OA in the particles and thus reflect how much BB related material contributes to the overall composition. The green data points are the factor mass spectra that only represent BB related material for this specific data set. We do not know what the corresponding PMF factor profile would look like for the other studies. It might be similar or different. The position of the overall composition data points in the f44/f60 space depends on the mixture of BB related factor and the other factors in the PMF solution. In other words, the BBOA in the WE-CAN study (cyan colored points) may have been less fresh (lower f60) than in this current study. Or the BBOA PMF factor in the WE-CAN study was as “fresh” (high in m/z 60 contribution) as in the new study. But there is some contribution of OA factors with low 60 and high 44, the data points will remain higher in the f60 scale than the current study but lower than the PMF factor data points.

In short: the PMF factor data points that characterize the chosen BBOA factor profiles should be presented on their own.

- 41) Figure 8: What is the unit for the white circles? I assume those indicate wind speed?
- 42) Lines 320-321: is the difference in SVOOA significant between forest and other categories? To me, it seems that the difference in SO₄ may be larger, although not necessarily significant either.
- 43) Figure 11: could this data be presented in a way that the differences are more visible, e.g. with logarithmic y-axis? This applies to the other figures with box plots, too.
- 44) Figure 12: There are 16 colors in the color bar but 17 land use categories. Also, please move the labels so that the land use categories are next to the color, not at the interface of two colors.
- 45) Lines 344-349: Some of these stated differences seem very small, are they significant? To me, it seems that SSA is lower for cropland fires compared to forest and grassland fires, even though the authors state that they do not differ substantially.
- 46) Overall, the authors present several trends averaged over the whole data set (multiple years) and then draw conclusions about trends. E.g., they compare the average values of multiple parameters divided by the dominant fuel type (Fig 13) or compare average monthly values for the smoky and non-smoky times (Fig 5). With this type of data (many points and large spread) it is important to check if an observed difference (or trend) is actually statistically significant. The authors should use one of the established suitable statistic methods to verify that e.g. the higher concentration for SO₄ in the forest cases is indeed significantly different from the other cases or not.
- 47) Lines S231-S232: There is discrepancy between the text “High Org–MERRA correlation was interpreted as evidence of regional behavior, whereas low correlation indicated local influence. If the correlation was intermediate or missing, the algorithm next evaluated PBLH ...” and Supplemental Figure S18.
- 48) Lines 387-388: Based on Figure 10, I don’t think this is true for LVOOA, especially during spring and summer. Spring has the highest intensity from the northeast. This was not discussed.

- 49) Line 402-404: "... particularly the effects of fire emissions on particle number and size distribution." Since there is nothing shown about the aerosol size distribution or number concentrations in the whole manuscript, how can the authors draw this conclusion?

Technical comments:

- 1) Line 113: "and" should be "an"
- 2) Line 140: please write "AGL" out and add that also at line 144.
- 3) Figure 3: please replace "June-July" with "June-August".
- 4) Line 196: Should this be "solutions with 3,4, and 5 factors"?
- 5) Line 199: Instead of "summer does not contain BBOA" it would be better to write "no BBOA factor was identified in summer".
- 6) Line 280: Instead of "the strongest enhancements" should this be "the highest concentrations"?
- 7) Line 293: Should it be "Figures 9-10" instead of "Figures 10-11"?
- 8) At lines 365-366 it should probably say "Figures 14D and 14F" as there is no figure 15.
- 9) Line S77 the quantity "Q" is called "sum of scaled residuals".
- 10) Line S103: Should it be "Supplemental Figures S4-S7" instead of "Supplemental Figures 1-4".
- 11) Tables S2 and S3: Sage et al. (2007), Schneider et al. (2006), and Alfarra et al. (2004) are missing from the reference list.
- 12) Figure S5: Change scaling to scientific instead of engineering ($70\text{e-}3 \rightarrow 7\text{e-}2$)
- 13) Figure 12: Mark the location of the measurement site in the map.
- 14) Should Figure S13 caption start with "As in Supplemental Figure S12, ..." instead of "As in Supplemental Figure 8, ..."?
- 15) Figure S16: Please change y-axis labels from " $N_{CCN}N_{CN}$ " to " N_{CCN}/N_{CN} ".

References:

- Gysel, M., Crosier, J., Topping, D. O., Whitehead, J. D., Bower, K. N., Cubison, M. J., Williams, P. I., Flynn, M. J., McFiggans, G. B., and Coe, H.: Closure study between chemical composition and hygroscopic growth of aerosol particles during TORCH2, *Atmos. Chem. Phys.*, 7, 6131–6144, doi:10.5194/acp-7-61312007, 2007.
- Hu, W., Campuzano-Jost, P., Day, D. A., Nault, B. A., Park, T., Lee, T., Pajunoja, A., Virtanen, A., Croteau, P., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., and Jimenez, J. L.: Ambient Quantification and Size Distributions for Organic Aerosol in Aerosol Mass Spectrometers with the New Capture Vaporizer, *ACS Earth Sp. Chem.*, 4, 676–689, <https://doi.org/10.1021/ACSEARTHSPACECHEM.9B00310>, 2020.
- Parworth, C., Fast, J., Mei, F., Shippert, T., Sivaraman, C., Tilp, A., Watson, T., and Zhang, Q.: Long-term measurements of submicrometer aerosol chemistry at the Southern Great Plains (SGP) using an Aerosol Chemical Speciation Monitor (ACSM), *Atmospheric Environment*, 106, 43–55, <https://doi.org/10.1016/j.atmosenv.2015.01.060>, 2015.