Response to Referee #3

We thank the Referee for all their comments, which have helped improve the paper as described below. The Referee suggestions are shown in full along with our detailed response/revisions in an "R#, A#" format next.

R1. This manuscript presents a major wildfire aged smoke measurement of some aerosol properties and trace gases in Missoula (US) during August-September 2017. During this period the measurement location was affected by several smoke plumes from wild fires, more importantly a smoldering and nighttime fire chemistry case is presented. Model back trajectories and satellite retrievals allowed for some of the fire locations to be identified and investigated. In summary, this data set presented here contains approx. 500 h of ground-based plume measurements and can provide valuable information on statistics for modeling and emission factors based on flaming vs. smoldering combustion on a regional scale. The prescribed burning comparisons are an interesting start to a much-needed solution. I think this paper is acceptable but could benefit from a deeper look into the implications for modeling use via smoldering and nighttime chemistry.

A1. Referee #3 shares our desire for more insight into flaming vs smoldering and day vs night chemistry as evidenced by the comment above and several below. We therefore discuss this goal in detailed context at the outset of this response. Even in a lab where fire emissions mix with a constant background, once the flame front moves, flaming and smoldering are mixed. Finding the separate contributions requires a mathematical analysis such as in Yokelson et al., (1996). Even that is approximate because the relative contribution of pyrolysis and glowing to smoldering can vary over time and space, and both processes are themselves a complex mix. Sekimoto et al., (2018) show how the pyrolysis itself can be broken down into two complex factors. In the field, a real fire can mix with multiple different layers of the atmosphere or other fires during transport, which can distort some signatures of flaming vs smoldering as discussed in detail in Yokelson et al., (2013b). One scenario that is not uncommon is smoke traveling slowly at low altitude from nearby fires being older and initially stratified from smoke above it that traveled faster from fires further away. This can be followed by vertical mixing that blends smoke of different ages from different fires at some distance from the sources. MCE is a pretty good rough indicator of flaming vs smoldering (F/S) if no mixing effects distort it as discussed in Yokelson et al., (2013b). BC/CO can also be used as an F/S indicator and it should be preserved with less distortion if mixing only occurs with background since BC is rare in background air unlike CO_2. If BC/CO_2 was constant for flaming then BC/CO would be essentially a proxy for CO_2/CO or MCE by rearrangement. However, BC/CO_2 can vary a lot for flames perhaps mostly because turbulence in diffusion flames has a small effect on the CO_2 yield but a much larger effect on the BC yield (Shaddix et al., 1994). In a near-field study of fires there is some chance to resolve flaming vs smoldering or day vs night differences. In addition, most prescribed fires are less than a day long and most of the smoke is lofted in a way that is accessible to airborne sampling. However, wildfires can burn 24/7 for months with dynamic/shifting dispersion scenarios that may be accompanied by changes in emissions chemistry. Thus, it is difficult to assess how well the emissions sampled from any platform represented the overall fire output (Yates et al., 2016; Saide et al., 2015). In this study we monitor smoke mixtures at a distance and we are not best positioned to separately characterize pure flaming and smoldering or pure night and day chemistry. However, we can measure the net integrated downwind impact of a

huge number of regional fires, including mixing. This provides an opportunity to check if our observations of conserved tracers are consistent with the data being used to represent wildfire sources in models. I.e. the data can help evaluate measurements, emissions inventories, and models. Comparisons are possible to our exact time series or diurnal cycles for a more relaxed test. Also, for example is BC/CO at a heavily impacted surface site generally consistent with BC/CO in the emissions inventories that serve as model input, or do our results suggest some changes are worth considering? We also provide actual values of dynamic ratios (e.g. PM/CO) that can help elucidate the nature of plume evolution. We have reached out to several modeling groups interested to compare their model output to our "ground truth." We've also recently joined collaborative efforts to institute ground-based near-field sampling as an approach to sample a greater fraction of the total output from wildfires than can be done from the air alone. Modeling, near-field and downwind airborne sampling as well as ground-based sampling at various altitudes (e.g. surface through mountain-tops) all have a key role to play.

Yokelson, R. J., Andreae, M. O., and Akagi, S. K.: Pitfalls with the use of enhancement ratios or normalized excess mixing ratios measured in plumes to characterize pollution sources and aging, Atmos. Meas. Tech., 6, 2155-2158, doi:10.5194/amt-6-2155-2013, 2013b.

Saide, P. E., Peterson, D., da Silva, A., Anderson, B., Ziemba, L. D., Diskin, G., Sachse, G., Hair, J., Butler, C., Fenn, M., Jimenez, J. L., Campuzano-Jost, O., Perring, A., Schwarz, J., Markovic, M. Z., Russell, P., Redemann, J., Shinozuka, Y., Streets, D. G., Yan, F., Dibb, J., Yokelson, R., Toon, O. B., Hyer, E., and Carmichael, G. R.: Revealing important nocturnal and day-to-day variations in fire smoke emissions through a multiplatform inversion, Geophys. Res. Lett., 42, 3609-3618, doi:10.1002/2015GL063737, 2015.

Sekimoto, K., Koss, A. R., Gilman, J. B., Selimovic, V., Coggon, M. M., Zarzana, K. J., Yuan, B., Lerner, B. M., Brown, S. S., Warneke, C., Yokelson, R. J., Roberts, J. M., and de Gouw, J.: High- and low-temperature pyrolysis profiles describe volatile organic compound emissions from western US wildfire fuels, Atmos. Chem. Phys., 18, 9263-9281, https://doi.org/10.5194/acp-18-9263-2018, 2018.

We've modified text in various places as described in response to more detailed comments below:

Major comments

R2. Page 3 line 15: The author indicates that this can be used to inform model mechanisms; however, outside of presenting numbers for ratios (which can and is helpful) without context of in what way to use these ratios. Meaning, all numbers are not created equal, in what modeling scenario should these new numbers or measurements be applicable?

A2. We agree with Referee that more than three words are valuable here early on in the paper to summarize the value and potential applications of our data and made the following change:

P3, L14: truncate the sentence by deleting ", which can be compared to changes in aerosol optical properties and inform model mechanisms." Add new text before "We present…"

The main goals of this work are to document the net, combined effect of numerous fires from a heavily impacted surface site embedded in the region and thus, also help assess the

representativeness of field measurements, emissions inventories, and models. In more detail; we characterize the smoke impacts on a population center and we document the real-world regional significance of brown carbon. Comparisons are possible to our time series of BC, CO, PM, etc or diurnal cycles for these species for a more relaxed test. Our real-time through study-average ratios for "inert" tracers such as ΔBC/ΔCO are compared with ΔBC/ΔCO in the field measurements that are available to build emissions inventories that serve as model input. The time-resolved and study-average values of dynamic ratios (e.g. ΔPM/ΔCO) help elucidate the net effect of secondary aerosol formation and evaporation. Our measurements provide real-world aerosol optical properties (e.g., SSA, AAE, etc.) and can be used with the aerosol mass data at real-time through study-average resolution to probe multi-step, bottom-up calculations of climate-relevant aerosol optical properties.

R3. Are these numbers for nighttime generated smoke? Can one use these numbers when a fire is detected at night or during the day and expected to be smoldering? E.g. page 6 line 5: "time series of mixing ratios" is helpful to point out in detail. E.g. BC/CO as a function of distance would be helpful.

A3. While we can't measure pure night-time emissions (see above), the text here needed to be rephrased to clarify that time series of multiple data types, ratios and other parameters are useful.

P, L4, old text: "We converted the time series of mixing ratios for each analyte measured into a form that is broadly useful to others for implementation in local to global chemistry and climate models. To do this, we produce emission ratios (ERs) and enhancement ratios."

New text: "Time series are useful to characterize impacts and evaluate models, but we also used the time series of mixing ratios or concentrations for each analyte measured to derive other values that are broadly useful for study comparisons and implementation in local to global chemistry and climate models. As part of this, we produced emission ratios (ERs) and enhancement ratios."

R4. Page 4 line 3-5; brief discussion of the uncertainties; there needs to be more in this paper about those uncertainties associated with each calculation and its use in a modeling platform or intended use.

A4. Referee 1 and 2 also shared this concern and we agreed. Error bars and uncertainties in slope were added to figures and the error discussion was expanded in the text. We hope the improvements described in detail in those responses will address the concerns of Referee 3 also.

R5. Page 6, line 18-21 MCE is not a good indicator of flaming vs smoldering compared to BC and CH4 ratios to CO, needs a citation, unless you are planning on providing evidence in this paper of this using the data collected?

A5. What we mean is MCE can be distorted at a distance as discussed above and at length in Yokelson et al., (2013). We have added text to clarify that we meant MCE is distorted *in this particular study*.

P6, L20: We added "in this study" before "as in measurements…" and the citation to Yokelson et al 2013b.

R6. Page 7, line 18-27 it seems that the authors had an opportunity with this data set to take a look into the various composition of fuels and impacts on transported chemistry. The small caveat to this is that hysplit will not likely give you 100% certainty on the origin, but with the fires that were identified, I would have liked to see an attempt to separate out measured emissions vs fuel types. This could potentially be a nice case study for Lolo Peak fire and Rice Ridge fire. As this fuels composition could be one explanation of the presented results differences between the other studies.

A6. This would be nice, but both nearby fires burned in complex mixed-coniferous ecosystems that had a strong variation in vegetation mix with altitude. The back-trajectories have limited vertical resolution and fuel consumption weighting by component varied with time in unknown ways. Thus, while the goal is worthwhile we feel it is best addressed in a near-field study. We made a text change to clarify the general probable lack of pure sources.

P7, L25, old text: "Many of the longer smoke impacts that spanned several days were necessarily integrated as a single event for calculating ratios between species, but also probed as smaller "sub-events" to explore their source attribution, which could be mixed (Tab. S1)."

New text: "Many of the longer smoke impacts that spanned several days were necessarily integrated as a single event for calculating ratios between species, but we also initialized back trajectories from local maxima to further explore the source region of the smoke, which was probably always mixed to some extent (Tab. S1)."

R7. Page 8, line 17 "time since emission" I would have like a deeper dig into this as the results all hinge upon the accuracy of this. The authors claim the smoke came from late afternoon to nighttime but do not show this anywhere outside of the supplemental materials. And since hysplit does not include full chemistry it seems odd to use it to look at full chemistry transported, but as you indicated the ratios compared to the relatively conserved CO should be okay.

A7. What we meant was, in general, smoke may have a greater transport age or time since emission than may be indicated by a "photochemical age". This can always occur, but is perhaps most likely for wildfires which tend to blow up late in the day.

P8, L17 now reads: "However, the "time since emission" is potentially longer than indicated by a "photochemical age" since,"

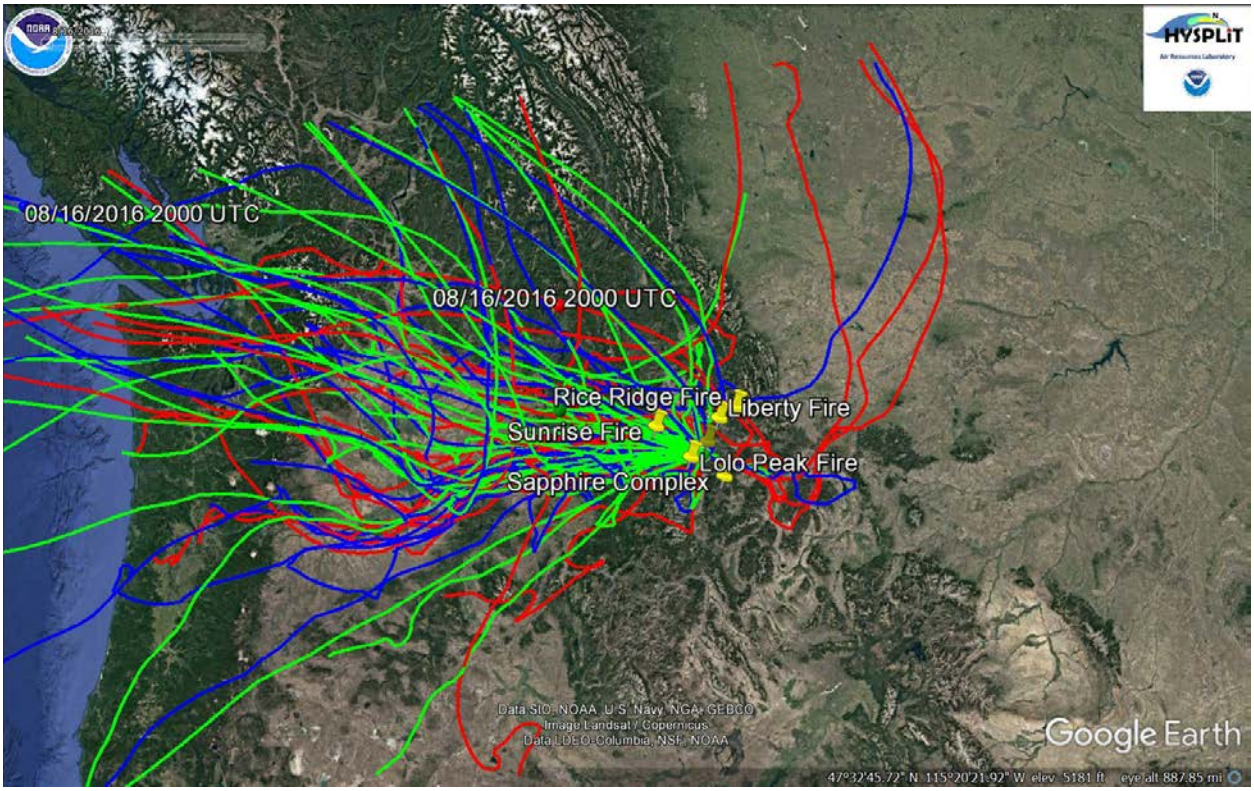
R8. Page 8, line 35 the separation of smoldering vs flaming vs residual smoldering is difficult, particularly in modeling and source attribution. If there was a ratio or tracer method that was found to actually indicate one of the other this was not clear to me reading this. It appears the distinction was made based off time of day (and one case presented grew at night), knowledge of fires state, and measured chemistry. Which is nice but going forward most cases wont have all that information.

A8. We don't fully understand this comment, but our point on P8, L35 was, for one example, a measurement of furan/CO from a different study measuring initial emissions close to a fire source could be used with our CO data to estimate the initial furan for a model simulation.

P8, L36: We changed "when emission ratios to CO" to "if those gases emission ratios to CO"

R9. Page 9, line 17. It appears that this study used only three heights to initialize hysplit, but did not indicate why those heights where chosen (if it was based purely on the elevation of the terrain then that makes sense). However, it does not include the effects of plume rise? As smoldering smoke tends to pool near the surface but can reach higher elevations, and vice versa for flaming smoke.

A9. The heights for back trajectories roughly indicate the following: 500 m AGL (height of frequently-observed elevated morning smoke layers that then mixed down into the Missoula valley at circa 11 AM to cause a mid-day PM peak); 3000 m AGL (common injection altitude for wildfires, e.g. assume maximum possible transport at injection altitude before mixing down), 1200 m AGL (intermediate point). In retrospect a lower starting elevation near 50-100 m AGL could also be useful, but the accuracy would likely be lower. Valley flows, up/downslope, and local vertical mixing are difficult to model in complex terrain. We often don't know if smoke arrived at ground level or mixed down and wind direction varies with altitude, so we initialize the back trajectories at several heights to generate possibilities. The sum of all the exploratory back trajectories is consistent with complex, but impressive regional coverage



R10. Consider the references

Wilkins JL, Pouliot G, Foley K, Appel W, Pierce T (2018) The impact of US wildland fires on ozone and particulate matter: a comparison of measurements and CMAQ model predictions from 2008 to 2012. International Journal of Wildland Fire, https://doi.org/10.1071/WF18053.

Zhou L, Baker KR, Napelenok SL, Pouliot G, Elleman R, O'Neill SM, Urbanski SP, Wong DC (2018) Modeling crop residue burning experiments to evaluate smoke emissions and plume

transport. Science of the Total Environment 627, 523-533, https://doi.org/10.1016/j.scitotenv.2018.01.237.

A10. These are both good examples of modeling and impacts as we added the citations on P1, L37.

R11. Page 9, line 33 aging and/or higher average temperatures at lower elevation may encourage some OA evaporation and reduce downwind PM impacts. This line is very interesting and should be expanded upon, as it's a critical finding from this study. What here is indicated as higher average temperatures? Is this flaming stage or just hot temperatures in the atmosphere as the plume ages? (page 10, line 12-15 also are confusing for the same reason "and thus strongly cooling"). Furthermore, can a statement be made in this section about smoldering plumes traveling in hotter temperatures or temperature of plume on evaporation of PM? This point would be good to attempt to relate to prescribed burns, as the emissions tend to be more toxic (or higher for PM) from the incomplete combustion and lower temperatures of burns and therefore longer smoldering time periods.

A11. Because temperature tends to decrease with altitude, smoke transported closer to the surface, or that mixes down, may experience higher ambient temperature, which could drive enhanced evaporation compared to measurements made higher in atmosphere or at high surface elevations. This comment reminded us that higher PM in early AM could have some contribution from gas-particle partitioning. We don't address relative toxicity of smoke from PF and WF, but note that PF are typically designed to have less smoldering than wildfires.

Changes:

P9, L33: We added "ambient" after "higher average"

P10, L10: we changed "some net evaporation of PM is occurring between the wildfire sources and our surface site." To "some net evaporation of PM is occurring at lower, warmer altitudes during transport between the wildfire sources and our surface site."

R12. Also, for the section 3.2 (page 10, line 3-5) are the authors discussing BC on average or BC for smoldering cases. It seems from the way its written that this ratio is for smoldering and the one presented in Liu et al. is for flaming? Could there be a statement made such as BC/PM < x is expected to be from smoldering while BC/PM > x is expected to be flaming?

A12. P10, L3 & 4: we added "study-" before "average" in two locations to clarify. We don't have a great lab data set for wildfire fuels for BC/PM as a function of MCE and in our downwind study BC/PM can be altered by PM evolution. BC/PM initial emissions are also variable as discussed above and explored in other responses.

R13. Page 13, line 20 It states that a possibly explanation is that more BC is being generated during the day, however it transported to the site overnight in order to arrive by 5am. Or is this statement meant to mean, the transported plume that remained over Missoula cooked during the daytime hours and generated more BC during the daytime while at Missoula?

A13. In-situ BC generation is not possible and time delays between emission and arrival in Missoula vary. Our thought was that more BC may be generated by increased flaming during the

day at the fire sources less than several hours upwind and that signal could survive and could contribute to higher (less diluted) levels in general in an evening peak.

P13, L20, old text: “One possible explanation for this is that despite variation in mixed layer height there is “typically” an increase in the flaming to smoldering ratio that produces more black carbon during the day. ”

New text: “One possible explanation for this is that despite variation in mixed layer height there is “typically” an increase in the flaming to smoldering ratio that produces more black carbon and less brown carbon during the day. If nearby (less diluted) fires with shorter transport times strongly influence the peak times a signal of diurnal variation at the source could be partially evident at our site. ”

Minor comments

R14. There is a need for a careful defining of terms. Some terms are used before they are defined, and others are never defined. And I believe all terms should be defined that are used in the abstract. E.g. BrC is used on page 1 line 23 and defined later on line 28; “US” is used on page 1 line 37 and is not defined. The authors need to decide whether or not to abbreviate which terms and remain consistent, e.g. Biomass burning appears as BB sometimes and other times not, also Air quality is sometimes AQ.

A14. We proofread and tied to eliminate the errors.

R15. A through grammar check is needed. There are some run on sentences and some missed placed commas and periods. E.g. page 2 line 3-10 very long run-ons.

A15. We proofread and tied to eliminate the errors.

R16. Page 10, line 35 does this ratio come with a trend or can expect numbers be inferred?

A16. What we meant was that even though our smoke was aged, BrC was still important. That implied that aging decreases BrC, which may not be obvious.

P10, L35: We changed “in our moderately aged smoke.” to “despite some aging of the smoke at our site.”

R17. Page 11, line 36 what is meant by “870 nm is unity to a good approximation “ the transitions at the end of paragraphs in my opinion are not needed (e.g. Page 13, line 12) “ which we examine next”

A17. We changed “unity” to “one” and deleted some transitions.