Response to Referee #2

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 measurements of some aerosol properties and some trace gases in Missoula (US) during approx. one month in August-September 2017. During this period the measurement location was affected by several smoke plumes from wild fires. Some of the fire locations were identified, but several plumes represent aged regional smoke containing emissions from various sources. Altogether this data set contains approx. 500 h of in-plume measurements and can provide valuable information on statistics of flaming vs. smoldering combustion on regional scale. However, the methods need to be described in more detail and different sources of uncertainty have to be assessed before this manuscript can be accepted in ACP.

A1. We appreciate the positive feedback and also briefly note that even periods dominated by individual fires were not "pure" and affected by some mixing of sources.

Major comments

R2. My main concern is that uncertainties in the analysis are not well quantified. Uncertainties for individual instruments are presented in Section 2, but uncertainty estimates are not presented for any of the data points in the graphs.

A2. We added representative error bars in the figures.

R3. Furthermore, it is not clear how "smoke-impacted" periods are distinguished from non-smoke periods. For instance for peak G in Fig. 1: the "smoke-impacted" BC and CO concentrations during afternoon hours are lower than during the following "non-smoke period". Reliable differentiation between "smoke-impacted" and background periods is essential for accurate definition of excess concentrations and excess mixing ratios especially for more diluted regional smoke (e.g. peaks M, N, R, T in Fig. 1).

A3. We did not apply a formal algorithm. Instead, for instance, when high PM levels decreased to a local minimum, or more sustained values, near or below the "good" air quality level (12.5 µg/m3) we took this as the end of the "event." In some cases a post-event "cleaner period" was sustained, but sometimes a single point is the end of one event and the start of another. We also elected not to integrate some small or brief peaks that sometimes occurred after adjacent larger peaks. For instance, a small peak after peak G, was not included because of low S:N. The last peak was integrated up to where the CO measurement failed. We verified several times that the integrals for events are dominated by the large values and insensitive to small shifts in the endpoints at lower levels.

P7, L25, new text: ~Sustained periods when PM2.5 was elevated well above 12.5 were designated as events and assigned a letter in Fig. 1 and Tab. S1.

R4. Many of the "smoke-impacted" periods last 24h or more. In such cases any diurnal variability in background CO, BC and PM2.5 will be a source of uncertainty, as background is apparently estimated with linear interpolation (see page 6, line 9). Can you estimate how large is

the uncertainty in excess mixing ratios due to assumed linear change in background during long smoke-impacted periods?

A4. We can only probe the variability in the smoke-free backgrounds by examination of the smoke-free periods in 2017 and now 2018. CO_2 doesn't have a repeating pattern and varies substantially so we don't attempt CO_2 integrals. CH_4 varies enough to add noise to the $\Delta CH_4/\Delta CO$ ratios, which is likely reflected in the large stdev, but not in a systematic way that we can use to justify a non-linear baseline assumption and not in a way that suggests systematic bias from a linear assumption. BC, PM, and CO "bottom out" at levels close to zero during smoke free periods with no evidence of significant background variability. Since we are in the midst of widespread impacts and not adjacent to distinct, "spatially small" plumes, there is no actual instantaneous background that could be measured by comparing inside and outside the smoke. Typically the nearest clean air was hundreds of miles away and probably not a valid background for our site. Using the linear assumption to generate a "calculated background" for estimated excess mixing ratios is standard practice in peak integration and the most complex assumption that we can justify. At the real-time level any single, point excess mixing ratio might have a substantial uncertainty especially on the peak edges, but we have no rigorous way to estimate that. Because the smoke concentrations are so much larger than background (except for methane), it's likely that the error in the peak integrated values are very small.

R5. One more source of uncertainty, which is not very well constrained, is the effect of 3.2km distance between PM2.5 measurements and other measurements. At 1h resolution and for regional scale smoke the distance is probably not an issue, but for the relatively fresh plumes (1-2 h) that distance can make a difference. Is there any difference in the correlation between scattering and PM2.5 for diluted and fresh plumes?

A5. Even the freshest smoke was spread over wide areas and the concept of a well-defined plume, which we contributed to by using the word "plume" incorrectly is misleading here (vide infra). Both the BC vs PM and the supplemental MSC plots indicate good mixing across most of the concentration range, but with some increased scatter for higher values that could be due to concentrated pockets embedded in "smoke fronts" that arrived at the separated measurement sites at offset times. However, there are not enough of these high points to warrant a separate analysis nor do they provide evidence of bias from using the whole data set. The r-squared values are good in all these plots, they provide some idea of the uncertainty in the ratio, and we also added the uncertainty in the slopes. We've checked the text and tried to use the word "plume" more carefully.

The following text was changed:

P1, L29; P9, L33; P12, L10; P14, L17: "plume" to "smoke"

P11, L6: "…aging time for multiple plumes is…" to "…average age of mixed-age smoke…"

R6. It seems that at the moment only one integrated excess mixing ratio is defined for each smoke-impacted period (page 6, line 9-11). However, many of the smoke-impacted periods represent considerable temporal variability. I recommend calculating excess mixing ratio at e.g. 1h or 5min temporal resolution, which would allow presenting also standard deviation (or other measure of in-plume variability) in addition to mean values in Supplementary Table 1. I think

this approach would give also more representative study-average statistics. With the current approach short smoke-impacted periods have equal weight to long periods in the study average.

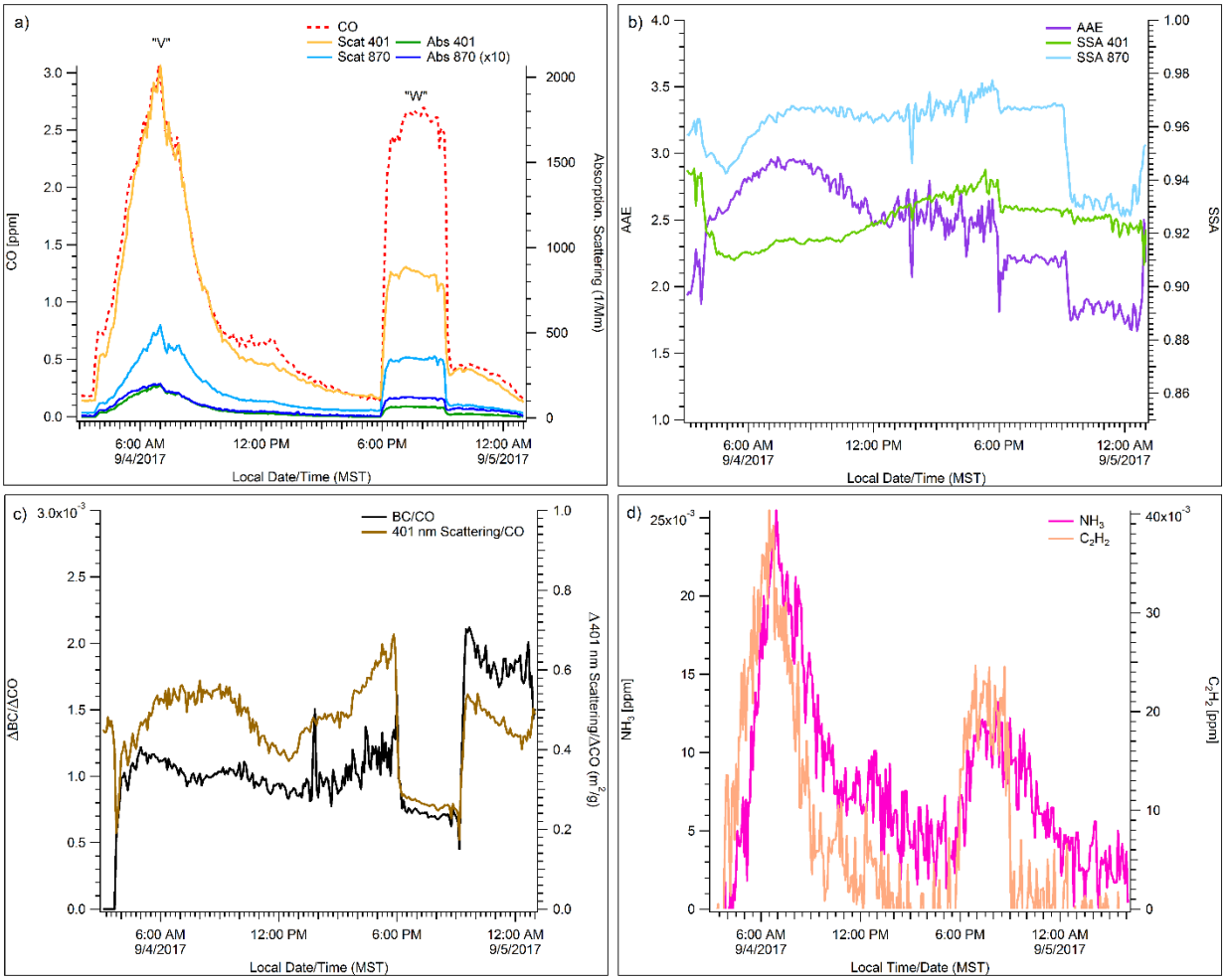
A6. We now specify that we used the time-weighted averages of the episode values in the text and in our tables, and note that they are essentially the same as the straight average.

New text:

P7, L28: “Table 1 reports study average ratios weighted by event duration (time-weighted)” old text: “Table 1 reports study average…”

For reasons given above we hesitate to compute real-time excess mixing ratios, but we have added some real-time absolute data to the Labor Day Weekend case study plots in Fig. 6. Again, the smoke levels are so dominant that the ratios between absolute values should be very close to the ratios between excess values.

New Figure 6:



We agree we are curious about the information content at the sub-episode level. However, our site is not in flat terrain impacted by one distinct plume at a time coming with a single wind

direction that allows “hour-resolution” age estimates based on distance to hotspot. In our valley site the flow is often slow to non-existent and highly variable in direction. It’s hard to know the relative extent to which transport time is changing during an event. Not only is the horizontal transport complex, but the vertical mixing is complex. For example, inversions are common and mixing smoky free troposphere air down into the boundary layer can’t be distinguished from arrival of smoke through the boundary layer a-priori. We can’t measure the smoke properties before or after our site. The big picture as far as advancing the interpretation is that we should soon have 3 summers of data to compare to a detailed model and are in discussions with modeling groups to eventually help us with more detailed interpretation as a separate paper.

R7. Please include also scattering/CO ratio in the analysis. I believe this would be a valuable reference in the future.

A7. We added scattering to CO to Fig. 6.

Minor comments

R8. Please indicate the units for excess mixing ratios. Are mass concentrations given in prevailing conditions or e.g. STP?

A8. P4, L4 we added “(ppmv)” after “mixing ratio”

P5, L2, before the reference: We added “at ambient temperature and pressure”

P5, L31, after “concentration”: We added “μg m^{-3} at ambient temperature and pressure”

We ensured that units are specified everywhere.

R9. Page 5, line 4. It seems that no truncation error correction was applied to the scattering coefficient. Please discuss shortly the uncertainty in SSA.

A9. As shown in the reply to Referee #1, the truncation error is believed to be 1-2.5% with about ten times smaller error in the SSA. New text was added to summarize a few error sources:

P5, L24: A few other sources of uncertainty in the measurements and/or calculations are poorly characterized; MAC increases due to coatings, potential particle losses in the drier or scrubber, and truncation error in the nephelometer. Mie calculations provided by the manufacturer suggest the scattering could be underestimated by about 1% at 870 nm and 2.5% at 401 nm due to truncation error (J. Walker, private communication). This would reduce the mass scattering coefficients (Sect. 3.4) and typically. a 1% reduction in scattering would imply approximately a tenth of a percent of value underestimate of SSA. Miyakawa et al. (2017) reported a size-independent particle transmission up to 400 nm of 84±5% in their diffusion drier. Larger particles may be transmitted more efficiently. We did not measure size distribution or transmission efficiency in this study and thus, we did not adjust the data. Size-independent particle losses would reduce scattering, absorption, and derived BC, but should have only a small impact on SSA or AAE. Unlike particle losses, an increased MAC due to “lensing” via coatings would inflate BC values by up to ~30% (Pokhrel et al., 2017).

R10. Page 5, line 8. Please define SSA based on scattering and absorption coefficients (Babs, Bscat defined on page 4, line 12).

A10. Done.

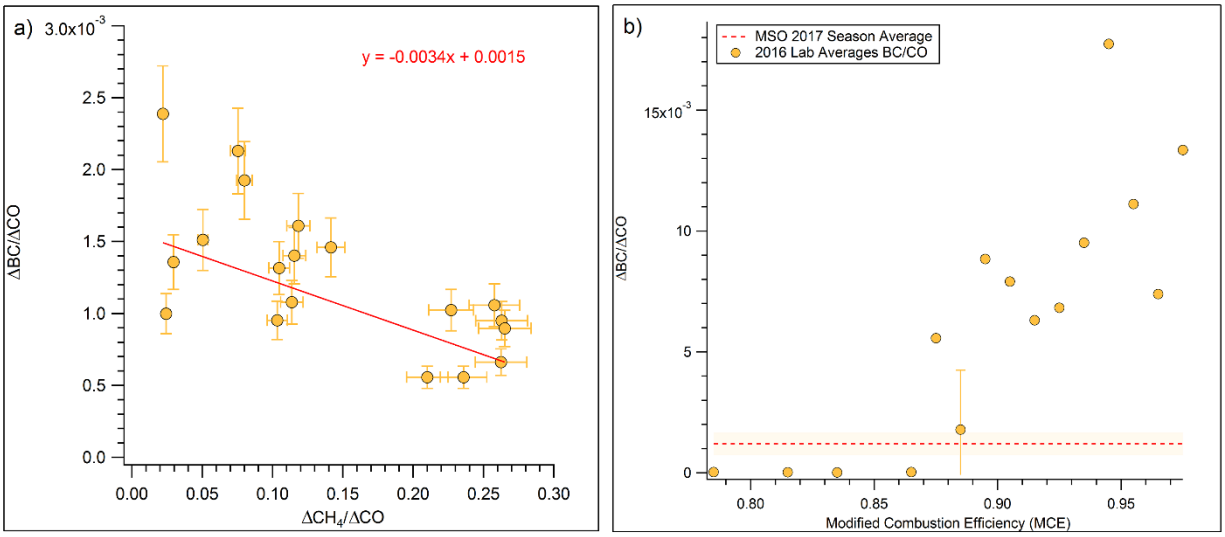
R11. Page 6, line 20-21: “Other approximate metrics of the relative amount of flaming to smoldering such as BC/CO or CH4/CO can still be used”. Are these ratios calculated as excess mixing ratio or plain concentration ratio? Please make sure that excess concentrations are always indicated with a delta (also in Figures) - now it seems that most excess mixing ratios are written without delta, i.e. as plain concentration ratio.

A11. We’ve implemented the “Δ” notation consistently throughout the paper text and figures now

R12. Page 8, line 3 and Fig. 2. Are there any previous studies to compare CH4/CO vs. BC/CO dependency?

A12. Good comment. We think the most valid previous study to compare dependence on MCE to comes from burning western wildfire fuels in the lab where mixing cannot distort MCE (Selimovic et al., 2018). We’ve added a BC/CO vs MCE plot to Fig. 2. and used it to roughly estimate average MCE for the regional surface level smoke. This topic continues below.

New Fig. 2 plot:



R13. Page 9, line 9. I agree, but the relationship between MCE and BC/CO is not linear (e.g. Vakkari et al., 2018). Can you estimate the MCE range from BC/CO in your case?

A13. Our BC/CO vs MCE plot is non-linear and qualitatively similar to that in Vakkari et al. It also roughly suggests an MCE below the aircraft value of 0.91.

P9, L17 Old text: “Taken together, this suite of observations is consistent with our ground-based site being impacted by relatively more smoldering combustion compared to the other, mostly airborne, studies.”

New text: “Taken together, this suite of observations is roughly consistent with our ground-based site being impacted by relatively more smoldering combustion (MCE ~ 0.87±0.02, based on Fig. 2) than the airborne studies (MCE 0.91 Liu et al., 2017; 0.90 Sahu et al., 2012).”

R14. Page 9, line 15. “The Selimovic et al. lab average” Year missing in reference, please check.

A15. Done.

R16. Page 9, line 24-25. “Changes in the PM/CO ratio as a plume ages can be used as a metric for the net effect of secondary formation or evaporation of organic and inorganic aerosol (Yokelson et al., 2009; Akagi et al., 2012; Jolleys et al., 2012; Vakkari et al., 2014).” This method was recently applied by Vakkari et al. (2018) as well; you may consider adding a reference.

A16. We added the suggested reference on P9, L25.

R17. Page 9, line 28. “Further our lower BC/CO ratio suggests enhanced smoldering, which should increase the PM/CO.” The observations by Vakkari et al. (2014, 2018) seem to indicate the opposite: fresh emission PM/CO decreasing with increasing smoldering. PM emission factor does increase with increasing smoldering, though.

A17. This is a valid point. DX/DCO typically increases for smoldering gases (such as CH4) as MCE decreases, but a quick check of the data in several papers shows that PM/CO can increase, stay the same, or even decrease slightly as MCE decreases. We revised the text to indicate that a large “factor of two” drop in PM/CO is not consistent with the known increase in EFPM with MCE.

P9, L28 new text: “Further our lower □BC/□CO ratio su
should preclude a large drop in □PM/□CO (Reisen et al., 2018).”

R18. Page 10, line 2-3. “The BC/PM ratio also allows for an estimate of ambient BC from ambient PM data when BC isn’t measured, but caution is needed since PM may not be conserved as long as BC.” BC fraction may also depend on combustion characteristics (c.f. Vakkari et al., 2014).

A18. We changed “an estimate” to “a rough estimate” and (at the end of the sentence) appended “and □BC/□PM is also variable at the source.”

R19. Page 10, line 7-8. “A previous study found that smoldering combustion emits anywhere between 4-49 times more PM than flaming combustion (Kim et al., 2018),” It seems that Kim et al. (2018) measured total PM (no size cut in inlet), which could be pointed out here. I would expect PM2.5 or PM1 emission variability be a bit less than TSP.

A19. The fine mode could vary with MCE more if the super-micron is dominated by entrained dust or vegetative debris. We added more references that make a similar point with fine PM and updated the range to 2-49 in the text.

References

Jen, C. N., Hatch, L. E., Selimovic, V., Yokelson, R. J., Weber, R., Fernandez, A. E., Kreisberg, N. M., Barsanti, K. C., and Goldstein, A. H.: Speciated and total emission factors of particulate organics from burning western US wildland fuels and their dependence on combustion efficiency, Atmos. Chem. Phys., 19, 1013-1026, https://doi.org/10.5194/acp-19-1013-2019, 2019.

Reisen, F., Meyer, C. P., Weston, C. J., and Volkova, L: Ground-Based field measurements of $PM_{2.5}$ emission factors from flaming and smoldering combustion in eucalypt forests, J. Geophys. Res-Atmos., 123, 8301-8314, https://doi.org/10.1029/2018JD028488, 2018.

Yokelson, R. J., Burling, I. R., Gilman, J. B., Warneke, C., Stockwell, C. E., de Gouw, J., Akagi, S. K., Urbanski, S. P., Veres, P., Roberts, J. M., Kuster, W. C., Reardon, J., Griffith, D. W. T., Johnson, T. J., Hosseini, S., Miller, J.W., Cocker III, D. R., Jung, H., and Weise, D. R.: Coupling field and laboratory measurements to estimate the emission factors of identified and unidentified trace gases for prescribed fires, Atmos. Chem. Phys., 13, 89–116, doi:10.5194/acp-13-89-2013, 2013a.

R20. Page 12, line 12-13. “Figure 5 shows a moderate increasing trend in the SSA at 870 nm, but no significant trend in the SSA at 401 nm.” Please state how you checked for statistically significant trend.

A20. We’ve added the uncertainty in the slopes to the figure. The slope is only larger than the uncertainty for the 870 nm data (the longer time series).

R21. Page 12, line 29. “smoke was mostly sourced from a local fire (Rice Ridge).” How far was the fire? Can you estimate the smoke age?

A21. We added an estimated range of hours after the fire name in parentheses: “smoke was mostly sourced from a local fire (Rice Ridge) and about 2-4 hours old.

R22. Page 12, line 29. “Our peak-integrated proxy for particle size (4.02, smaller particle size)” Please describe the “peak-integrated proxy for particle size” in Section 2. Figure 6 (case study). Please add a second panel with high-resolution excess mixing ratios (BC/CO, PM2.5/CO, scattering/CO, trace gases/CO) so that the reader can compare the two peaks.

A22. Is the first part a suggestion to move the proxy to experimental section? We’d like to keep it in results since it is not a standard product. We’ve added most of the higher resolution data that has reasonable signal/noise to Fig, 6; subject to the caveats discussed above.

R23. Page 13, Section 3.6 Diurnal Cycles. I would expect diurnal cycle to be important for near-fire measurements due to diurnal variation in the emissions (e.g. Saide et al., 2015), oxidation and dilution. However, I would not expect much difference in aged regional smoke, whether it is observed during morning or evening hours. Here, focusing on extensive properties (PM2.5, BC, CO) is problematic as they depend mostly on dilution. I wonder if the diurnal cycle in Figure 7 has a small increase in morning only because more fresh plumes happened to reach the measurement site during morning hours. I recommend removing this section or concentrating on fresh plumes (e.g. CO > 0.5 or 1 ppm) and intensive properties (excess mixing ratios).

A23. We understand that multiple factors influence the diurnal profiles. Nevertheless, we think they are useful on several levels. They provide a relaxed, averaged case for model evaluation compared to strict point by point agreement in real time. Curiosity about the diurnal profiles reflecting real-time partitioning and general curiosity are some of the first questions we had and the diurnal cycles characterize the typical regional impacts even if the underlying reasons are not completely clear. Also our loose association of BC in evening and BrC in AM is probably relevant for a "typical "source to Missoula" delay. Our response to Referee #3 further develops the potential applications of our data.

R24. Page 14, line 11-13. "Despite our lower BC/CO ratio our PM/CO ratio was about half that measured in fresh smoke from aircraft. This suggests that OA evaporation, at least near the surface, may typically reduce PM air quality impacts on the time scale of several days." I do not think you can draw such a straightforward conclusion, as PM/CO ratio decreases with decreasing BC/CO. If both fuel and BC/CO are equal, then a lower PM/CO in aged smoke would suggest primary aerosol evaporation. Please check also abstract (page 1, line 18-22).

A24. We addressed part of this above. The broader conclusion comes from considering all available data for wildfires on page 10. We see that PM/CO dropped after aging on the Rim Fire (Forrister et al) to a value similar to ours, but not in Collier et al further north and higher altitude. In response to referee #1 we noted that a similar evaporation of PM was observed for a prescribed fire in a coniferous ecosystem. We agree we need to revise the text for people who may read only the conclusions and did not see on page 10 that POA volatility might vary by fuel type, the G-1 flights were further north than the Rim Fire, and that higher ambient temperature for smoke aging, as opposed to aging in general, may increase smoke evaporation rates.

Old text: "Despite our lower BC/CO ratio our PM/CO ratio was about half that measured in fresh smoke from aircraft. This suggests that OA evaporation, at least near the surface, may typically reduce PM air quality impacts on the time scale of several days."

New text: P14, L11: Despite our lower $\Delta BC/\Delta CO$ ratio our $\Delta PM/\Delta CO$ ratio was about half that measured in fresh smoke from aircraft. Taken together with aircraft measurements in aged wildfire smoke, this suggests that OA evaporation at higher ambient temperatures nearer the surface may typically reduce PM air quality impacts on the time scale of several hours to days."

R25. It seems that all linear fits are calculated with ordinary least squares method, which assumes that there is no uncertainty in x-direction. At least for Figs. 2, 3 and S1 a bivariate method would be more appropriate (see e.g. Cantrell et al., 2008).

A25. The requirement for linear regression is not quite as strict as "zero" uncertainty in the x value (a case which may not exist) and the rigorous requirement is perhaps summarized in simple terms a bit closer to ~ "linear regression is most accurate when ΔX is significantly smaller than ΔY." We did switch to orthogonal regression for Figure 2, which is updated and has a slightly changed slope. Orthogonal regression was not satisfying for Figure 3. The BC/PM plot had a visually inappropriate fit that weighted a single high value too much and gave an unrealistic intercept that was much larger than the near zero value clearly implied by a glimpse at the data. The effect on the slope was about a 20% reduction, but we elected to keep the linear regression figure here and in 4b and the supplement; in all cases the x-error is smaller than y-error.

R26. Please combine Tables 1 and 5 to avoid repetition. Please also check that you have defined the values in parenthesis in all Table captions. Is the study average a mean of enhancement ratios defined for each plume?

A26. We planned to do this, but ended up adding to Table 5 (per Referee #1) and electing to keep it separate.

References

Cantrell, C. A.: Technical Note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems, Atmos. Chem. Phys., 8(17), 5477–5487, doi:10.5194/acp-8-5477-2008, 2008.

Saide, P. E., Peterson, D. A., da Silva, A., Anderson, B., Ziemba, L. D., Diskin, G., Sachse, G., Hair, J., Butler, C., Fenn, M., Jimenez, J. L., Campuzano-Jost, P., Perring, A. E., Schwarz, J. P., 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, Geophysical Research Letters, 42(9), 2015GL063737, doi:10.1002/2015GL063737, 2015.

Vakkari, V., Beukes, J. P., Dal Maso, M., Aurela, M., Josipovic, M. and van Zyl, P. G.: Major secondary aerosol formation in southern African open biomass burning plumes, Nature Geosci., 11, 580–583, doi:10.1038/s41561-018-0170-0, 2018.