Author changes to acp-2018-1063-ms in order of Referee comments with minor voluntary changes described at the end of Referee #1 changes

Response to Referee #1

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. GENERAL COMMENTS: This study reports emission ratios and optical properties observed in smoke from wildland fires of various ages. The study measured ~500 hours of smoke impacts, making it very thorough in terms of sampling different ages, a variety of origins, and presumably a diversity of fire behavior. The study methods were appropriate, the presentation and discussion is thorough, yet concise. The authors have been careful to properly qualify their conclusions and have clearly pointed out limitations of the data. The discussion and conclusions are supported by the data presented. I found only one general issue that must be addressed. The comparison with prescribed fires somewhat overstates the prescribed fire versus wildfire PM differences. The authors have compared their measurements versus all aircraft measured prescribed fire measurements in May et al. (2014), which were mostly SE coastal plain understory burns or California chaparral. Only two of the May et al. (2014) aircraft prescribed fires, the Shaver fire and Turtle fire in Montane forest seem to be similar ecosystems / fuel types to the source fires that impacted Missoula during their study. From a smoke/air quality impact perspective, the wildfire vs. prescribed fire tradeoff issue is largely a matter of forest fires in the western US. The duration, fuel loading, and total emissions involved with western forest fires significantly exceeds that of chaparral and sagebrush systems (see e.g. French et al., 2011 San Diego County fires). Therefore, in the context of a wildfire vs. prescribed smoke/air quality comparison the authors should compare their wildfire results with the Shaver fire and Turtle fire from May et al. (2014), for which the forest PM1/CO = 0.011+/- 0.01, about 40% higher than the 0.08 value presented in Table 5 and used the discussion. Likewise the Shaver / Turtle fire BC/PM1 is 0.006, much closer to that observed in the current study and similar to Liu et al. (2017).

French, N. H. F., et al. (2011), Model comparisons for estimating carbon emissions from North American wildland fire, J. Geophys. Res., 116, G00K05, doi:10.1029/2010JG001469.

A1. This is a good comment though we assume the Referee meant a PM/CO of 0.11 and a BC/CO of 0.006. The Turtle and Shaver Fires comprise a small data set and it is not clear that brush, chaparral, or grass fires did not impact us in Missoula. E.g. The Rim Fire burned coniferous forests in the Sierras, but also oak and chaparral. In addition, the SE-US prescribed fires in May et al (2014) were also in coniferous ecosystems and help make a larger prescribed fire data set. The Turtle and Shaver prescribed fires may have burned more understory and less overstory than wildfires in the same ecosystem. We also have to be careful because the prescribed fire frequency (time since last burn) could impact emissions and, most of all, we are comparing fresh prescribed fire smoke (May et al, 2014) to more aged wildfire smoke (Missoula 2017) and prescribed fire emissions typically occur at lower air temperatures. In fact, May et al., (2015) observed a significant decrease of OA/CO after five hours of aging for one of the prescribed fire smoke plumes in their 2014 paper. However, we agree that it is worth acknowledging that the geographic location may combine with vegetation type to influence EF so we have added a discussion of the impact of comparing wildfires to a smaller, potentially more relevant, subset of prescribed fires as suggested by the referee.

Changes:
We added a column to Table 5 that shows the data averaged over just the Turtle and Shaver fires.

P 13, L36 Old text: The available PM/CO data for wildfires is consistently higher than for prescribed fires, which has air quality and land management implications.

The available PM/BC ratios are consistently ~20 times higher for wildfires, than prescribed burns, confirming that wildfire smoke is overwhelmingly more organic, which is important partly because many optical properties scale with the BC/OA ratio. In general, our ground-based wildfire study confirms the earlier airborne indications that prescribed fires are less smoky but also less cooling than wildfires.

New text: The ΔPM/ΔCO values for fresh wildfire smoke in Liu et al. (2017) and aged wildfire smoke (this study) are about three and 1.5 times higher than ΔPM/ΔCO for fresh smoke from prescribed fires in May et al. (2014) when comparing to all their US prescribed fires (Tab. 5). For only prescribed fires in western US mountain coniferous ecosystems (last column Tab. 5), the ΔPM/ΔCO for fresh smoke is close to our value for aged wildfire smoke. However, May et al. (2015) noted that ΔPM/ΔCO decreased by about a factor of two after several hours of aging on at least one prescribed fire.

The ΔBC/ΔCO for prescribed fires is higher than the wildfire average by a factor of ~9 (all prescribed fires) or ~4 (last column), roughly suggesting a higher MCE for prescribed fires. Ignoring smoke age, the ΔBC/ΔPM for prescribed fires is higher than the wildfire average by a factor of ~20 (all prescribed fires) or ~6 (last column). The ΔBC/ΔPM observations suggest that wildfire smoke is overwhelmingly more organic, which is important partly because many optical properties scale with the BC/OA ratio (Saleh et al., 2014). In general, our ground-based wildfire study confirms the earlier airborne indications that prescribed fires are less smoky but also less cooling than wildfires. Differences in smoke production and chemistry between wild and prescribed fires should be researched more and have air quality and land management implications.

Reference

May, A. A., Lee, T., McMeeking, G. R., Akagi, S., Sullivan, A. P., Urbanski, S., Yokelson, R. J., and Kreidenweis, S. M.: Observations and analysis of organic aerosol evolution in some prescribed fire smoke plumes, Atmos. Chem. Phys., 15, 6323-6335, doi:10.5194/acp-15-6323-2015, 2015.

SPECIFIC COMMENTS

R2. P4, Ln 27-37: Was calibration conducted using the same flow set-up as ambient data, i.e. through scrubber and diffusion drier? Any estimate of particle loss based on other studies?

A2. All the calibrations were done with the same sample line, cyclones, drier, and scrubber in the same location. We only report data where instrument pressures, flow rates, leak checks, etc passed QC checks, and for 401 nm, data that was collected between calibrations where the AAE was within +/- ~2-3 percent of one for fresh propane torch soot. We did not have the specialized equipment to measure any particle losses in the diffusion drier, but using the same drier and scrubber in 2018 with a PM2.5 cyclone gave mass-scattering coefficients for 2.5 micron scattering divided by 2.5 mass that were very close to the middle of the range of numerous other studies indicating that minimal losses are occurring in the drier and scrubber. However, this was an important comment. At the time we set up the PAXs we were aware of websites (at least 3) that suggested drier losses were “minimal.” However, upon re-investigating, only two of the three websites still make this claim and a recent paper briefly includes a somewhat relevant measured size-independent particle transmission efficiency (Miyakawa et al., 2017) for their diffusion drier of 84 +/- 5%. We have not applied a correction to our data because we did not measure anything specific to our setup. Referee #2 also brought up one more source of uncertainty; truncation error in the nephelometer. We added new text at P5, L25 to address several poorly characterized sources of error together after defining the relevant parameters.

New text:

P4. L30-32 text changed to: “The scrubber and drier were refreshed before any signs of deterioration were observed (e.g. color change). The diffusion based designs will cause small particle losses, but losses were not explicitly measured.”

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).

Reference: Miyakawa, T., Oshima, N., Taketani, F., Komazaki, Y., Yoshino, A., Takami, A., Kondo, Y., and Kanaya, Y.: Alteration of the size distributions and mixing states of black carbon through transport in the boundary layer in east Asia, Atmos. Chem. Phys., 17, 5851-5864, https://doi.org/10.5194/acp-17-5851-2017, 2017.

R3. P6, L4-21: Please state the criteria used to define smoke impacted periods of sampling?

A3. Any sustained period with $PM_{2.5}$ well above 12.5 µg/m^3, which EPA defines as the upper limit for good air quality, was included in one of the smoke events. Referee #2 commented on the divisions between events. 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, L20: Added: Sustained periods when $PM_{2.5}$ was elevated well above the 12.5 µg/m^3 EPA standard for "good" air quality were designed as events and assigned a letter in Fig. 1 and Tab. S1.

R4. P6, L4-21: Was a diurnal variation observed in CH4 for background conditions (e.g. due to constant source + varying mixed layer depth)?

A4. From 2017 and 2018 there is some variability in CH_4 during smoke-free periods, but it is not well-defined enough to confidently calculate a new baseline under peaks and we have no evidence that it contributes overall bias to the integrals. Most likely the variability contributes to a higher standard deviation for our measured ΔCH4/ΔCO ratios than we might have seen otherwise. This topic is also addressed in some detail in the response to Referee #2. Basically, the concept of a measureable background was usually not applicable due to the widespread (often synoptic scale) impacts.

R5. P7, L33-38 & Table 2: The authors should include CH4/CO ratios form Urbanski (2013) as the wildfires reported on in that study are most similar to the MT/ID/BC fires that impacted Missoula.

A5. We added the Urbanski CH4/CO (0.0946 +/- 0.0108) to Tab.1. Note: we were also impacted by fires in WA, OR, CA.

R6. P7, L 37: "Our higher study average ER of CH4 is indicative of smoldering, or specifically glowing combustion (Yokelson et al., 1997)." This statement implies CH4/CO for glowing combustion is different from smoldering pyrolysis, which is at odds with ground-based field study of Reisen et al. (2018). Please comment on this apparent discrepancy. (Reisen, F., Meyer, C. P., Weston, C. J., & Volkova, L. (2018). JGR - Atmospheres, 123, 8301–8314. https://doi.org/10.1029/2018JD028488)

A6. Reisen et al "visually" "broadly" sorted samples into glowing or pyrolysis, but pure pyrolysis cannot actually occur alone since pyrolysis requires heat. Glowing can occur "alone" briefly in a lab if no fresh fuels are left to pyrolyze. Yokelson et al., (1997) reported that CH_4 was enhanced from glowing compared to other organic gases, but CO could have also been enhanced from glowing so the Referee is correct that additional analysis would be needed to scope out effects on the ⍰CH_4/⍰CO ratio due to glowing/pyrolysis. That is beyond scope of this study, especially since fuel type may have an impact and authentic field conditions make it harder to isolate processes than in lab. We decided to remove any speculation about smoldering sub-types since the sub-type of smoldering is secondary here to our main point that ⍰CH_4/⍰CO tends to increase with smoldering. We do note that ⍰CH_4/⍰CO increased with smoldering (lower MCE) in Reisen et al (as in many other studies), which supports our interpretation of our Figure 2.

Change in text: We deleted ", or specifically glowing combustion" and added the Reisen et al reference on line 38.

R7. P9, L1: Reference needed.

A7. The references on line 2 supported both of the first two sentences. We moved Bond 2004 reference to the previous line to clarify that literature support exists for both sentences.

R8. P9, L14-15: Should note that Hobbs et al. (1996) were mostly prescribed fires of logging slash.

A8. We compared specifically to the subset of fires described a wildfires as now noted:

Old text: "The Hobbs et al. (1996) is notably"

New text: "The Hobbs et al. (1996) average value for their two fires specifically identified as wildfires is notably"

R9. How robust is BC = f(MCE) from Selimovic ?

A9. BC/CO correlates with MCE, but with considerable noise and in non-linear fashion. To acknowledge this, on page 9, line 16 we appended ", which tends to enhance BC emissions." We added a plot of BC/CO versus MCE from the Selimovic study to Fig. 2 in response to this comment and Referee #2 and some brief new text described in that response

R10. Fig 5. Adding date labels to a few ticks on the x-axis would be helpful.

A10. Done.

R11. P9, L16-23: Does "annual" refer to 2011 or average over some period of time?

A11. We changed "Liu et al. (2017) calculated an annual CO production from western US wildfires of 5240 ± 2240 Gg, which they reported was in good agreement with an EPA estimate from the 2011 National Emissions Inventory (4894)."

to "Liu et al. (2017) calculated an average annual CO production from western US wildfires for 2011-2015 of 5240 ± 2240 Gg, which they reported was in good agreement with an EPA estimate based on a similar burned area in the 2011 National Emissions Inventory (4894)."

On line 23 we added the year (2006) for the Mao et al (2015) study.

R12. Section 3.5. Please note the value of PM2.5/CO over these periods.

A12. Unfortunately, the PM monitor had its few missing hourly values during peak "W".

R13. P13, L29-30: This should be restated, prescribed fires do not allow control over dispersion conditions, but allow one to ignite fires when dispersion conditions are favorable and/or manipulate ignition in a manner that enhances dispersion, e.g. mass ignition that puts smoke above mixed layer.

A13. This sentence now ends "… and can be ignited when conditions are favorable for minimizing air quality impacts (Liu et al., 2017)"

TECHNICAL

R14. Mixing of units notation, superscripts and "/", e.g. L min^-1 and L/min, throughout paper

A14. Fixed

R15. P4, L36: missing "nm" after 401

A15. Fixed

R16. P5, L13: “BrC” should not be subscript

A16. This could be OK or could be parenthetical format, but be consistent.

R17. P10, L35: missing “nm” after 401

A17. Fixed

Voluntary updates.

We made three additional voluntary minor changes (described next). We did some very light editing (updating references, added a missing word, etc) that is indicated in “track changes.”

P2, L29: Added Tomaz et al., 2018 reference.

P6, L37: Changed “British Columbia experienced a record fire season…” to “Over 1.2 million ha burned in British Columbia in 2017.” The previous record was broken in 2018.

P12, L24, after Ansmann citation: We re-inserted a link that had been accidentally removed to a NASA website that described how Labor Day weekend smoke from the NW US reached Europe.

Table 4. The MSC and MAC values between 870 and 401 nm were adjusted slightly using a more accurate method of extrapolation. We note that both calculation methods produce MSCs in excellent agreement with the literature when used with our 2018 data that was collected with PM2.5 cyclones on the PAXs. With both procedures, the MSC values are lower with PM1 cyclones on the PAXs. We think the PM1 cyclones likely do a good job of isolating the combustion generated aerosol, but that super-micron dust and vegetative debris gets entrained in smoke plumes, transported, and affects the optical properties, which has prompted us to switch to PM2.5 cyclones for continued monitoring. Change “linear” in text to indicate based on power law fit.

P11, L35: Old text: “…were calculated using a linear regression using the calculated averages.”

New text: “…were calculated with a power law fit using the calculated average.”

Figure 3. Added caption: “b) Lab averaged BC/CO ratio versus modified combustion efficiency (MCE) separated into bins by 0.1 of MCE.

Figure 4. We had the caption for parts a and b reversed and that has been corrected.

Figure 7. Added “shown for the entirety of the monitoring period” to caption.

Figure 8. Added “BC and PM shown for the entirety of the monitoring period, but %401-Absorption by BrC only shown for when the PAX 401 was operational.”

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 ▯CH_4/▯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.

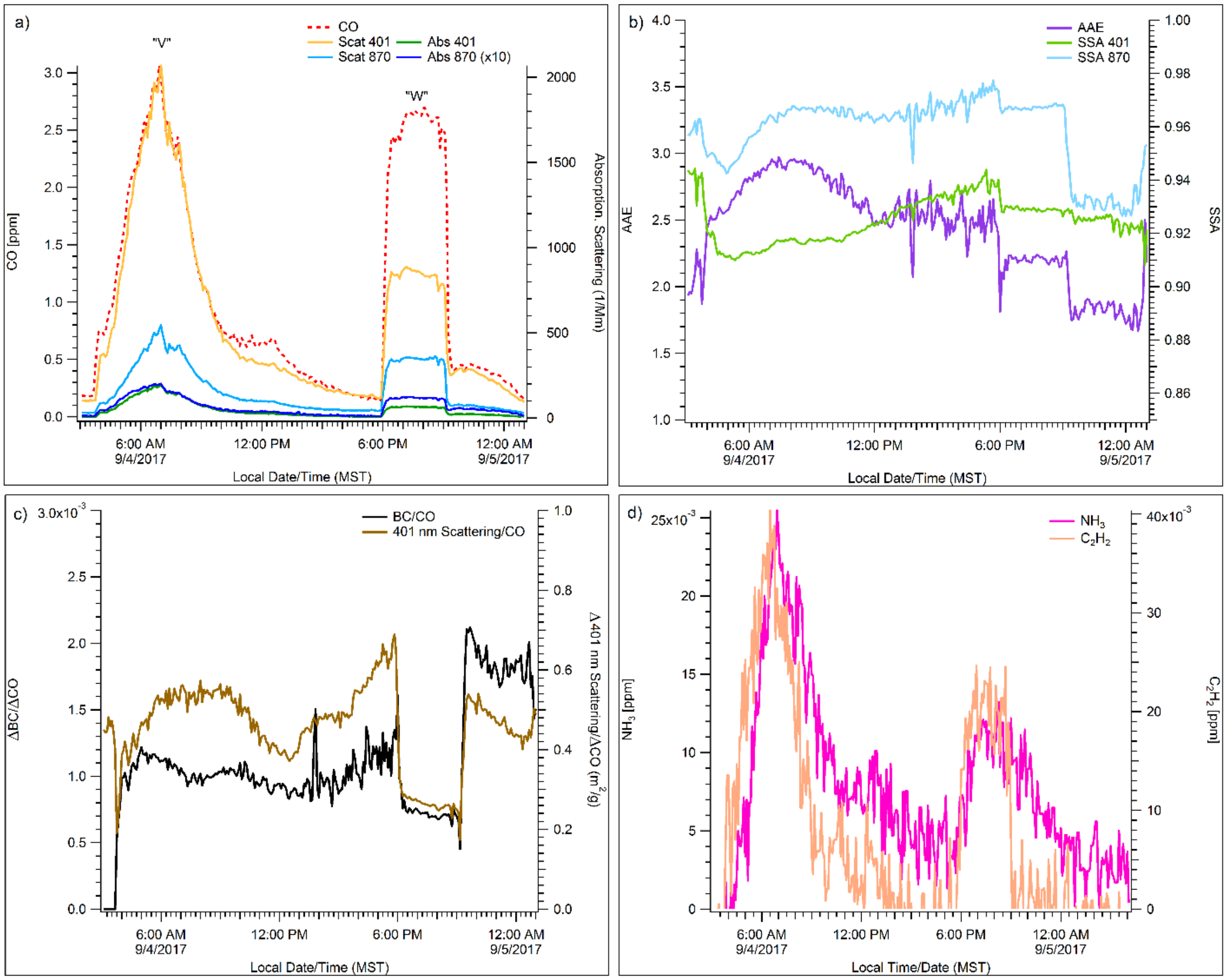
A6. We now specify that we used the time-weighted averages of the episode values in the text and in our tables, and note that they are essentially the same as the straight average.

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.

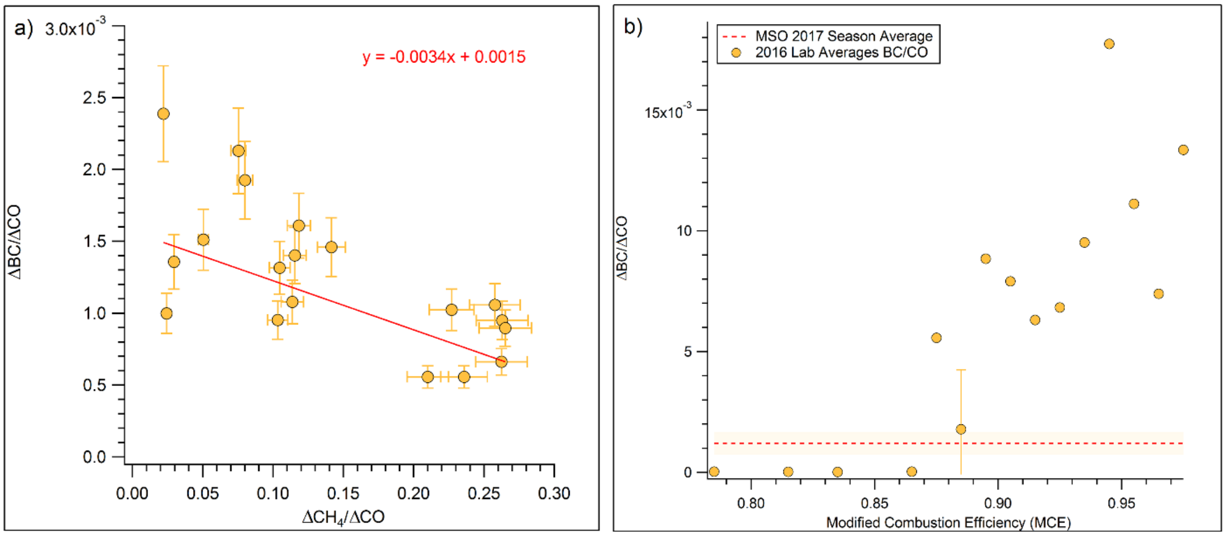
R11. Page 6, line 20-21: “Other approximate metrics of the relative amount of flaming to smoldering such as BC/CO or CH4/CO can still be used”. Are these ratios calculated as excess mixing ratio or plain concentration ratio? Please make sure that excess concentrations are always indicated with a delta (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 suggests enhanced smoldering, which 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 ΔBC/ΔPM 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

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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 ΔBC/ΔCO ratio our ΔPM/ΔCO 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.

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.

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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,"

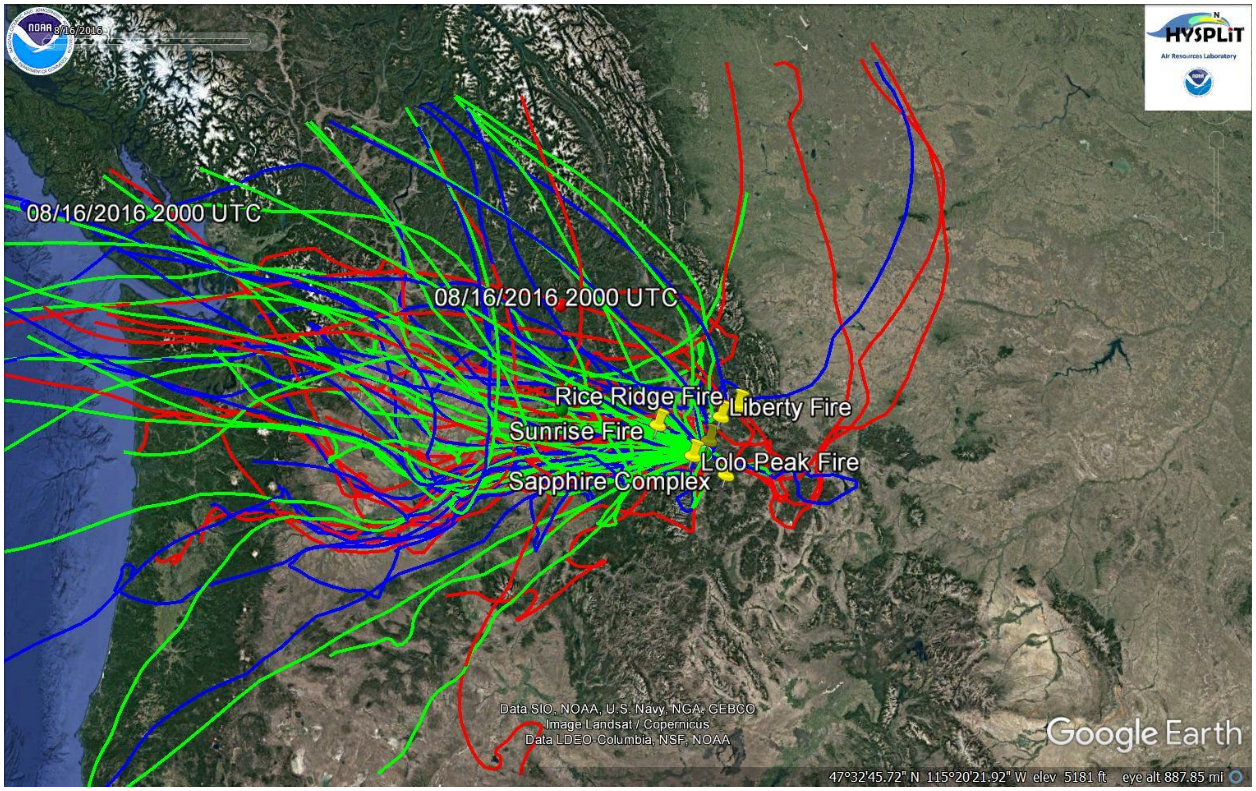
R8. Page 8, line 35 the separation of smoldering vs flaming vs residual smoldering is difficult, particularly in modeling and source attribution. If there was a ratio or tracer method that was found to actually indicate one of the other this was not clear to me reading this. It appears the distinction 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.

In-situ measurements of trace gases, PM, and aerosol optical properties during the 2017 NW US wildfire smoke event

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Abstract. In mid-August through mid-September of 2017 a major wildfire smoke/haze episode strongly impacted most of the NW US and SW Canada. During this period our ground-based site in Missoula, MT experienced heavy smoke impacts for ~500 hours (up to 471 µg m^{-3} hourly average $PM_{2.5}$). We measured wildfire trace gases, $PM_{2.5,}$ and black carbon and sub-micron aerosol scattering and absorption at 870 and 401 nm. This may be the most extensive real-time data for these wildfire smoke properties to date. Our range of trace gas ratios for $\Delta NH_3/\Delta CO$ and $\Delta C_2H_4/\Delta CO$ confirmed that the smoke from mixed, multiple sources varied in age from ~2-3 hours to ~1-2 days. Our study-average $\Delta CH_4/\Delta CO$ ratio (0.166 ± 0.088) indicated a large contribution to the regional burden from inefficient "smoldering" combustion. Our $\Delta BC/\Delta CO$ ratio (0.0012 ± 0.0005) for our ground site was moderately lower than observed in aircraft studies (~0.0015) to date, also consistent with a relatively larger contribution from smoldering combustion. Our $\Delta BC/\Delta PM_{2.5}$ ratio (0.0095 ± 0.0003) was consistent with the overwhelmingly non-BC, mostly organic nature of the smoke observed in airborne studies of wildfire smoke to date. Smoldering combustion is usually associated with enhanced PM emissions, but our $\Delta PM_{2.5}/\Delta CO$ ratio (0.126 ± 0.002) was about half the $\Delta PM_{1.0}/\Delta CO$ measured in fresh wildfire smoke from aircraft (~0.266). Assuming $PM_{2.5}$ is dominated by PM_1, this suggests that aerosol evaporation, at least near the surface, can often reduce PM loading and its atmospheric/air-quality impacts on the time scale of several days. Much of the smoke was emitted late in the day suggesting that nighttime processing would be important in the early evolution of smoke. The diurnal trends show BrC, $PM_{2.5}$, and CO peaking in early morning and BC peaking in early evening. Over the course of one month, the average single scattering albedo for individual smoke peaks at 870 nm increased from ~0.9 to ~0.96. $B_{scat401}/B_{scat870}$ was used as a proxy for the size and "photochemical age" of the smoke particles with this interpretation being supported by the simultaneously-observed ratios of reactive trace gases to CO. The size/age proxy implied that the Ångström absorption exponent decreased significantly after about ten hours of daytime smoke aging, consistent with the only airborne measurement of the brown carbon (BrC) lifetime in an isolated plume. However, our results clearly show that non-BC absorption can be important in "typical" regional haze/moderately-aged smoke~~plumes~~ with BrC ostensibly accounting for about half the absorption at 401 nm on average for our entire data set.

1 Introduction

Biomass burning (BB) emissions are an important source of trace gases and particles that can influence local, regional, and global atmospheric chemistry, air quality, climate forcing, and human health (Crutzen and Andreae, 1990). BB is one of the largest sources of fine primary organic aerosol (OA), black carbon (BC), brown carbon (BrC) **(**Bond et al., 2004, 2013; Akagi et al., 2011), total greenhouse gases, and non-methane organic gases (NMOG) (Yokelson et al., 2008; 2009), which are precursors for the formation of ozone and OA. While the majority of BB occurs in the tropics, the small fraction of the global BB in the western US is responsible for a significant portion of US air quality impacts (Park et al., 2007; Liu et al., 2017; Wilkins et al., 2018; Zhou et al., 2018) and contributes to increasing health concerns. Wildfire smoke has been shown to have adverse respiratory and cardiovascular health effects, is associated with mortality and morbidity, and exhibits lung toxicity and mutagenicity (Le et al., 2014; Liu et al., 2015; Reid et al., 2016; Adetona et al., 2016; Kim et al., 2018). In some cases, long range transport of biomass burning emissions can cause air quality standards to be exceeded hundreds or thousands of kilometers downwind of the fire source (Jaffe et al., 2013; Wigder et al., 2013). In addition to health concerns, particulate matter from wildfires can reduce visibility, which can have impacts on safety and transportation **(**United States Environmental Protection Agency, 2016), and is a concern in protected visual environments such as national parks and wilderness areas, most~~much~~ of which are in the western US, where a majority of wildfires occur. The Interagency Monitoring of Protected Visual Environments (IMPROVE) program initiated in 1985 implemented long term monitoring that establishes current visibility conditions and has helped to improve visibility in protected areas. However, record high temperatures, drought, and fire-control practices over the last century have culminated into a situation in which we can anticipate more frequent fires of a larger size and intensity in the Western US and Canada (Yue et al., 2015; Westerling et al., 2006). These fires~~that~~ are expected to impact all aspects of air quality in the US—and have other impacts, including on visibility. In fact, over the last few decades, the annual number of wildfires in the US has not changed significantly, but the annual area burned has increased by a factor of about 3 (United States National Interagency Fire Center, 2017), and many of the highest burned-area years have coincided with many of the warmest years on record (United States Environmental Protection Agency, 2016). Despite these important issues, much of the emissions from BB remain either understudied or completely unstudied. To date, most of the research on the emissions and evolution of smoke from US fires in the field has targeted prescribed fires (Burling et al., 2011; Akagi et al., 2013; Yokelson et al., 2013a; May et al., 2014; Müller et al., 2016), and while there are studies that probe trace gas and optical property emissions of wildfire smoke sampled in the field (Liu et al. 2017; Lindaas et al., 2017; Landis et al., 2017; Collier et al., 2016; Eck et al., 2013; Sahu et al., 2012; Lack et al., 2012), much of the information is limited in temporal extent or incomplete chemically, and fails to assess important issues such as the aging and evolution of smoke over varying and extended amounts of time, night time evolution and oxidation, or the contribution of constituents of increasingly recognized importance such as BrC (UV-absorbing OA), to name a few.

BrC emissions are typically mixed with co-emitted BC and non-absorbing OA, which can result in some measurement difficulties and uncertainty in isolating and evaluating the optical properties of BrC and its overall radiative impact (Wang et al., 2017; Tomaz et al., 2018). In lab-simulated wildfires, BrC was associated with smoldering combustion and accounted for about~~up to~~ 86% of absorption by particles in the UV in the fresh smoke, which has several implications in atmospheric chemistry, including impacts on radiative forcing, UV-driven photochemical reactions producing ozone, and the lifetime of NO_x and HONO (Selimovic et al., 2018). In addition, there are sources of BrC not directly emitted from BB, including the photo-oxidation of volatile organic compounds (VOCs) and aqueous-phase chemistry in cloud droplets. These processes produce BrC with optical properties and lifetimes that are not yet well-characterized (Graber and Rudich, 2006; Ervens et al., 2011; Wang et al., 2014; Laskin et al., 2015). In fact, several factors such as chemical transformation, mixing state, combustion conditions, photochemical aging, etc., can all influence the absorption of BrC (Wang et al., 2017). Most modeling studies have found that despite the multiple variables contributing to the absorption of BrC, including BrC in climate models would mean the net radiative forcing of biomass burning would move in a more positive direction. (Feng et al., 2013; Jacobsen, 2014; Saleh et al., 2014; Forrister et al., 2015). Unfortunately, observational constraints on BrC are scarce making it difficult to assess and enhance models based on observational evidence. Thus, more field measurements are required to get an accurate estimate of the impact of BrC both regionally and globally.

Most of the western US, including the Rocky Mountains, constitutes a large fire prone-region. Missoula, Montana is the largest city completely surrounded by the Rocky Mountains. Missoula is also located within a large region of the inland Pacific

Northwest where wildfires have caused air quality trends to deviate from the pattern in the rest of the US (McClure and Jaffe, 2018). Missoula frequently experiences smoke impacts typical of much of the urban and rural west due to local and regional western fires. A few airborne studies have sampled western wildfires and are most sensitive to lofted emissions (Liu et al., 2017; Yates et al., 2016), but wildfires may produce some unlofted emissions, especially at night. Ground-based studies could probe these unlofted emissions, but have difficulty to representatively sample lofted emissions unless advection accompanies transport. Despite these platform-based considerations, our laboratory on the eastern edge of Missoula is a relevant receptor for mixed-age (1-2 hours to 1-2 days) western wildfire smoke. In this study, we measured the wildfire smoke characteristics for 500 smoke-impacted hours during August-September of 2017, which constituted a prolonged period of record-breaking AQ impacts in Missoula. This very large sample of wildfire smoke helps address some of the afore-mentioned observational gaps in current wildfire field data. Specifically, two photoacoustic extinctiometers (PAXs), and a Fourier-transform-infrared spectrometer (FTIR) characterized the smoke that entered the Missoula valley. A Montana Department of Environmental Quality (DEQ) $PM_{2.5}$ (particulate matter ≤2.5 micrometers in diameter) monitor provided additional insight and verified some impacts. The PAXs provided measurements of scattering and absorption at two wavelengths (nominal 405, actual 401 nm; 870 nm), BC, and derivations of single scattering albedo (SSA), and Angstrom absorption exponent (AAE) for $PM_{1.0}$. The FTIR measured the BB "tracer" carbon monoxide (CO) and a few other trace gases that help estimate "effective average smoke age". ~~, which can be compared to changes in aerosol optical properties and inform model mechanisms.~~ The main goals of this work are to document the net, combined effect of numerous fires on 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 BrC. 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 $\Delta BC/\Delta CO$ are compared with $\Delta BC/\Delta CO$ 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. $\Delta PM/\Delta CO$) 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. We present our results and compare them to those previously reported for wildfire field measurements and prescribed fire field measurements.

2 Experimental Details

2.1 Site Descriptions

Trace gases and particles were measured through co-located inlets at the University of Montana (UM), ~12.5 m above the ground through the window of our laboratory on the fourth (top) floor of the Charles H. Clapp building (CHCB). The UM campus encompasses an area of ~0.89 km^2 and is located on the eastern edge of Missoula, with the CHCB located in the southeastern corner of campus. The CHCB is ~ 1.1 km from the nearest road that gets appreciable traffic during the summer, thus our measurements were not significantly influenced by automobile emissions (see Sect 3.1). $PM_{2.5}$ measurements were made by the Montana Department of Environmental Quality via a stationary $PM_{2.5}$ monitor located in Boyd Park, Missoula, which is ~3.2 km southwest of our UM laboratory, with both sites being located in the Missoula valley proper.

2.2 Instrument Details

2.2.1 Fourier transform infrared spectrometer

Trace gas measurements were made using an FTIR (Midac, Corp., Westfield, MA) with a Stirling cycle cooled mercury-cadmium-telluride (MCT) detector (Infrared Associates, Stuart, FL; Ricor USA Inc., Salem, NH) interfaced with a 17.22 m path closed multipass White cell (Infrared Analysis, Inc., Anaheim, CA) that is coated with a halocarbon wax (1500 Grade, Halocarbon Products Corp., Norcross, GA) to minimize surface losses (Yokelson et al., 2003). Although the system was designed for source measurements, and is described elsewhere in more detail (Akagi et al., 2013; Stockwell et al., 2016a, Stockwell et al., 2016b), the FTIR is convenient for ambient monitoring because the Stirling cooled detector does not require refilling of liquid nitrogen and thus allows for mostly autonomous operation. Ambient air was drawn through the 2.47 liter White cell at ~6 liters per minute via a downstream IDP-3 dry scroll vacuum pump (Agilent Technologies) using a 0.635 cm o.d. corrugated Teflon inlet that was positioned outside the window (~12.5 m above ground level). Cell temperature and pressure were also logged on the system computer (Minco TT176 TRD MKS Baratron 722A). Spectra were collected at a resolution of 0.50 cm^{-1} covering a frequency range of 600-4200 cm^{-1}. A time resolution of approximately 5 minutes was more than adequate and sensitivity was increased by co-adding scans at this frequency. Gas phase species (with their respective detection limits in parentheses), including carbon monoxide (CO, 20 ppb), methane (CH_4, 20 ppb), acetylene (C_2H_2, 2 ppb), ethylene (C_2H_4, 2 ppb), methanol (CH_3OH, 3 ppb), and ammonia ($NH_{3,}$ 2 ppb) were quantified by fitting selected regions of the mid-IR transmission spectra with a synthetic calibration nonlinear least-squares method (Griffith, 1996; Yokelson et al., 2007). The uncertainties in the individual mixing ratios (ppmv) varied by spectrum and molecule and were influenced by uncertainty in the reference spectra (1-5%) or the real time detection limit, whichever was larger. The procedure used to correct for gases outside of the spectrometer cell raised the uncertainty to ~20 ppb for background CO and CH_4, but did not affect the measured enhancements above background during smoke episodes. Calibrations with NIST-traceable standards indicate that peak CO values had an uncertainty of less than 5%. The FTIR system was designed for source sampling and the sensitivity was adequate to measure a significant amount of usable trace gas data, but not every species on every event. In addition, an FTIR system problem caused the trace gas data to terminate about one day before the smoke cleared.

2.2.2 Photoacoustic extinctiometers (PAX) at 870 and 401 nm

Particle absorption and scattering coefficients (B_{abs}, Mm^{-1}, B_{scat}, Mm^{-1}) were measured directly at 1 s time resolution using two photoacoustic extinctiometers (PAX, Droplet Measurement Technologies, Inc., Longmont, CO; Lewis et al., 2008; Nakayama et al., 2015), and single scattering albedo (SSA) at 401 (nominally a 405 nm system) and 870 nm, and the Angstrom absorption exponent (AAE) were derived using those measurements. Although the PAXs measured every second, data was averaged to 5 minutes, which was deemed adequate for the final analysis and matched the time resolution used by the FTIR for the same reason. A 1L min^{-1} aerosol sample flow was drawn through each PAX using a downstream IDP-3 dry scroll vacuum pump (Agilent Technologies) and split internally between a nephelometer and photoacoustic resonator for simultaneous measurement of light scattering and absorption. Both PAX instruments contain an internal pump, however these internal pumps were bypassed to improve measurement sensitivity, as the pumps can contribute an amount of acoustic noise that is noticeable in clean-air ambient measurements. Scattering of the PAX laser light was measured using the wide-angle (6º-174º) reciprocal nephelometer that responds to all particle types regardless of chemical makeup, mixing state, or morphology. For absorption measurements, the laser beam was directed through the aerosol stream and modulated at a resonant frequency of the acoustic chamber. Absorbing particles transferred heat to the surrounding air, inducing pressure waves that were detected via a sensitive microphone. Advantages of the PAX include direct in-situ measurements, a fast response time, continuous autonomous operation, and eliminating the need for filter collection and the uncertainties that come with filter artifacts (Subramanian et al., 2007).

The PAX sample line was ~4.7 m of 0.483 cm o.d. conductive silicon tubing positioned outside the window ~12.5 m above ground level and co-located with the FTIR inlet. The tubing transferred outside air to a scrubber to remove light-absorbing gases (Purafil-SP Media, minimum removal efficiency 99.5%) and then a diffusion drier (Silica Gel 4-10 mesh) to remove water, with post-drier relative humidity varying between 13 and 30%. The scrubber and drier were refreshed before any signs of deterioration were observed (e.g. color change). ~~and~~ T~~t~~he diffusion based designs ~~should incur minimal~~will cause small particle losses, but losses were not explicitly measured. After the drier, a splitter connected to the two instruments. After the splitter, each sample line featured a 1.0 µm size-cutoff cyclone and two acoustic notch filters that reduced noise. Both PAX instruments were calibrated before, during, and after the experiment using the manufacturer-recommended scattering and absorption calibration procedures utilizing ammonium sulfate particles and a propane torch to generate purely scattering and strongly absorbing aerosols, respectively. The 401 nm data was only used after August 27 because of frequent clogging of the $PM_{1.0}$ cyclone before that date. The estimated uncertainty in PAX absorption and scattering measurements has been estimated to be ~4-11% (Nakayama et al., 2015).

In the PAX, the incident laser light is absorbed in situ by light absorbing particles without filter or filter-loading effects that can be difficult to correct, particularly for samples with high organic aerosol loadings (Lack et al., 2008; Li et al., in prep). We directly measure aerosol absorption (B_{abs}, Mm^{-1}) and used the literature- and manufacturer-recommended mass absorption coefficient (MAC) (4.74 ± 0.63 $m^2\ g^{-1}$ at 870 nm) to calculate the BC concentration ($\mu g\ m^{-3}$) at ambient temperature and pressure (Bond and Bergstrom, 2006), but the BC mass can be adjusted using different MAC values if supported by future work. Because the PAXs also measured light scattering, scattering and absorption values can be combined to directly calculate the single scattering albedo (SSA, the ratio of scattering to total extinction). SSA is a useful input for climate models, where an SSA closer to 1 indicates a more "cooling" highly-scattering aerosol:

$$SSA = \frac{Bscat\cancel{Scattering}\ (\lambda)}{Bscat\cancel{Scattering}\ (\lambda) + Babs\cancel{Absorption}\ (\lambda)} \qquad (1)$$

To a good approximation, sp^2-hybridized carbon (including BC) absorbs light proportional to frequency (Bond and Bergstrom, 2006). Thus, the B_{abs} contribution from BC at 401 nm can be calculated from 2.17 times B_{abs} at 870 nm (an absorption Angstrom exponent of one), where BrC absorption is expected to be negligible, and any additional B_{abs} at 401 nm can be assigned to BrC ($B_{abs,}$ BrC) subject to limitations due to "lensing" by coatings discussed elsewhere (Pokhrel et al., 2016; 2017; Lack and Langridge, 2013; Lack and Cappa, 2010). Coating effects are very difficult to isolate from BrC direct absorption effects and this adds some uncertainty to the BrC attribution (±25%), but not to the absorption measurements themselves. Additionally, the absorption Ångström ~~absorption~~ exponent (AAE) (401/870) can be calculated from the 401 and 870 data, where the AAE of pure BC is usually close to one and larger values are indicative of smoke absorption more dominated by BrC emissions:

$$AAE = -\frac{\log\left(\frac{B_{abs,1}}{B_{abs,2}}\right)}{\log\left(\frac{\lambda_1}{\lambda_2}\right)} \qquad (2)$$

The AAE is useful as an indicator of BrC/BC, but in addition, the full aerosol absorption spectrum is often approximated with a power law function (absorption = C × λ^{-AAE}) and thus the AAE determined with any wavelength pair can be used to approximately calculate the shape of absorption across the UV-VIS range (Reid et al., 2005b). An equation similar to equation 2 provides the scattering Ångström ~~scattering~~ exponent (ASE), which can be used to calculate scattering at unmeasured wavelengths.

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 could inflate BC values by up to ~30% (Pokhrel et al., 2017).

2.2.3 Montana Department of Environmental Quality $PM_{2.5}$

The Montana DEQ uses beta attenuation monitors (Met One Instruments, Model BAM-1020) in accordance with US EPA Federal Equivalent Methods (FEM) for continuous $PM_{2.5}$ monitoring. At the beginning of each sample hour, a constant ^{14}C source emits beta rays though a spot of clean glass fiber filter tape. The beta rays are measured by a photomultiplier tube to determine a zero reading. The BAM-1020 then advances this spot of tape to the sample nozzle, where it filters a measured amount of outside air at 16.7 L min^{-1} ~~/min~~. At the end of the sample hour, the attenuation of the beta ray signal by the filter spot is used to determine the mass (and concentration µg m^{-3} at ambient temperature and pressure) of the particulate matter. Hourly detection limits for the BAM-1020 are <2.4 µg ~~/~~m^{-3} (1σ). Current and archived air quality data for the state of Montana can be accessed using the following link: http://svc.mt.gov/deq/todaysair/. More information on the BAM-1020 can be found at http://metone.com/air-quality-particulate-measurement/regulatory/bam-1020/. Note PAX size cutoff was 1.0 micron and the PM size cutoff is 2.5 µm. The mass in the 1.0-2.5 µm range is thought to be a small part of the total mass (e.g. 10-20% in Fig. 2 in Reid et al., 2005a), but the size range difference does affect data interpretation as detailed later. ($PM_{2.5}$ cyclones have now been obtained for the PAXs for ongoing studies.)

2.2.4 Emission ratios (ERs) and downwind enhancement ratios

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.~~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.~~ The calculation of these two types of ratios is the same, but an emission ratio is only the appropriate term for a ratio measured directly at a source or further downwind for relatively inert species such as BC or CO. First, an excess mixing ratio (denoted by "ΔX" for each species X) is calculated for all species measured by subtracting the relatively small background mixing ratio based on a sloping baseline from before to after a smoke impact. For example, the ratio for each species relative to

CO ($\Delta X/\Delta CO$) is the ratio between the sum of ΔX over the entire smoke impacted period relative to the sum of ΔCO over the entire smoke impacted period. Mass or molar ratios to CO were calculated for BC, PM, and all the gases measured by the FTIR that exhibited enhancement above background levels for each smoke impacted period. Emission factors (EF), which can be derived by including the molar ER to CO_2 in the carbon mass balance method were not calculated (Selimovic et al. 2018). The diurnal variation for CO_2 is considerable, and the smoke was mainly aged (not reflecting initial emissions for most species) in Missoula. The prolonged "small" ΔCO_2 peaks that persist for times similar to the natural, substantial variation that CO_2 has have uncertain values. E.g., for CO_2, the wildfire smoke impacts in Missoula are largely diluted and protracted enough to not completely dominate background variability as is the case for the other gases and for source sampling (Stockwell et al., 2016a, Stockwell et al., 2016b, Akagi et al., 2011, Akagi et al., 2012). Since ΔCO_2 are not as reflective of fire impacts, then by extension, the modified combustion efficiency (MCE) which is defined as $\Delta CO_2/(\Delta CO_2 + \Delta CO)$, is not as useful as an index of the combustion flaming to smoldering ratio in this study as in measurements closer to the source (Yokelson et al., 2013b). Other approximate indicators~~metrics~~ of the relative amount of flaming to smoldering such as $\Delta BC/\Delta CO$ or $\Delta CH_4/\Delta CO$ can still be used.

2.3 Investigating smoke origin and back trajectory calculations

To investigate the sources contributing to smoke events we used a combination of back trajectory calculations, satellite imagery, and local meteorological data that provided insights into mixing and smoke origin. Back trajectories were calculated utilizing the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT; Stein et al., 2015; Draxler et al., 1999; Draxler et al., 1998; Draxler et al., 1997) initialized from UM (46.8601º N, 113.9852º W) at 500, 1200, and 3000 m above ground level during the hour at which enhancements for that particular smoke event were at a maximum. Back trajectories were run using the High Resolution Rapid Refresh (HRRR) operational model, which uses the uses the Weather Research and Forecasting (WRF) modeling system combined with observational data assimilation and is run over the contiguous US at 3km × 3km resolution (Benjamin et al., 2016). For events that spanned multiple days, multiple back trajectories were initialized during the hour(s) at which enhancements for the sub-events were at a maximum. Because of the complex local topography and micrometeorology, the combination of back trajectories, satellite imagery (GOES "loops") and other evidence can only suggest a most likely smoke origin and cannot provide an exact smoke age. Our best guess at the smoke origin for each event is listed in Tab. S1.

2.4 Brief description of 2017 regional and selected local fires

Missoula experienced smoke impacts from local (western MT) and regional fires with regional fires including fires in California, Idaho, Oregon, Washington, and British Columbia. ~~British Columbia experienced a record fire season, with over~~Over ~1.2 million ha burned in British Columbia in 2017(BC Wildfire Service, 2017). More than 4 million ha burned in the US during the 2017 fire season, making it one of the largest to date. Idaho, Oregon, and Washington had burned areas over 263,000 ha, 283,000 ha, and 161,000 ha, respectively. California and Montana experienced their ~~worst fire seasons~~largest burned areas to date, with both states experiencing close to 526,000 ha burned each (National Interagency Fire Center, 2017). Although the complicated meteorology and topography of the Missoula valley makes attributing smoke sources somewhat difficult (as noted above), we can say with some degree of certainty that the majority of the fresh smoke impacting Missoula came from two local fires, the Lolo Peak fire and the Rice Ridge fire (Tab. S1). The Lolo Peak fire started at high elevation ~15 km SW of Missoula (46.674º N, 114.268º W) on 15 July 2017 and burned continuously (mostly at lower and lower elevations) until it eventually grew to over 20,000 ha. The fuel description as given by Inciweb (https://inciweb.nwcg.gov/incident/5375/) is summarized as containing generally sparse or patchy subalpine fir (*Abies lasiocarpa*) with dead Whitebark pine (*Pinus albicaulis*) above ~2100 m. Below 2100 m, fuels were mainly typical of a variety of coniferous-dominated ecosystems with major tree species such as ponderosa pine (*Pinus ponderosa),* sub-alpine fir (*Abies lasiocarpa)*, and lodgepole pine (*Pinus contorta)*. Lower elevations near containment lines were dominated by ponderosa pine with grassy understory. The Rice Ridge fire started 24 July 2017 ~52 km NE of Missoula (47.268º N, 113.485º W). The fire eventually burned over 64,000 ha, with a notable run on 3 September 2017, where it doubled in size from ~20,000 ha to ~40,000 ha. Fuels involved were timber (litter and understory), and brush (https://inciweb.nwcg.gov/incident/5414/).

3. Results and discussion

3.1 Overview of 2017 fire season smoke impact in Missoula

Figure 1 shows the hourly average mixing ratios of CO, BC, and $PM_{2.5}$ observed from 11 August to 10 September 2017, which includes nearly all of the 2017 Missoula smoke impacts. There were more than 20 distinct periods of major smoke-impacts that are readily identified by large simultaneous enhancements in CO, BC, and $PM_{2.5}$. Sustained periods when $PM_{2.5}$ was elevated well above the 12.5 ug m^{-3} EPA standard for "good" air quality were designated as events and assigned a letter in Fig. 1 and Tab. S1. The highest hourly values were observed on 4 September 2017, the morning after the Rice Ridge fire doubled in size ($PM_{2.5,}$ 471 ug m^{-3} ~~µg/m^3~~, CO 2.78 ppm, BC 3.62 ug m^{-3} ~~µg/m^3~~). This event is discussed in more depth as a case study in a later section (3.5). Numerous other $PM_{2.5}$ peaks exceeded e.g. levels of 100 ug m^{-3} ~~µg/m^3~~. "Cleaner" periods between smoke peaks became less extensive as the regional atmosphere became increasingly polluted until widespread clearing on 10 September 2017. Overall high correlation of CO and BC to $PM_{2.5}$ suggest that the smoke was normally well mixed on the spatial scale that separated the $PM_{2.5}$ and UM monitors. 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). ~~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).~~

3.1 Trace gas ratios

Table 1 reports study average ratios weighted by event duration (time-weighted) to CO for gases measured by the FTIR. These measurements are representative of moderately aged regional wildfire smoke. We interpret our results by comparing them to emission ratios measured in the lab (Selimovic et al., 2018) and other field studies mostly in fresher smoke (Liu et al., 2017; Landis et al., 2017; Radke et al., 1991). CO is a major pollutant in the atmosphere with BB as a main source. In Missoula, especially in the summer, the CO background is not strongly influenced by non-fire sources. CH_4 on the other hand has more background variability, but at these smoke levels the ratio of CH_4 to CO, while variable, yields a study average (0.166 ± 0.088) that mostly reflects the real average $\Delta CH_4/\Delta CO$ fire emission ratio. Yates et al. (2016) reported a smoldering stage $\Delta CH_4/\Delta CO$ ER of 0.095 (±0.023) for the Rim Fire, which is lower than our study average ER, but the ratio reported in Yates et al. (2016) comes from airborne measurements closer to the source and from a single fire source. Our higher study average ER of CH_4 is indicative of smoldering.~~, or specifically glowing combustion~~ (Reisen et al., 2018; Yokelson et al., 1997). Because the measurement was not in a direct downslope flow of smoke into Missoula, this ratio suggests that smoldering emissions from regional fires can be and were frequently transported to the Missoula valley. This may be why our study average is higher than observed in airborne studies. In a consistent observation, we find that ERs for $\Delta CH_4/\Delta CO$ are lower when the $\Delta BC/\Delta CO$ ERs are higher (Fig. 2), which is indicative of a flaming to smoldering ratio dependence (Christian et al., 2003). This is a useful result, because our two metrics for combustion characteristics at the fire source are consistent and it indicates that the variability in ratios between species observed at Missoula was partly due to variable combustion types at the regional fire sources along with the expected effects of variable aging that are discussed next.

Next, we compare other measured trace gas ratios, including some more reactive VOC, to the limited amount of data available from previous airborne and lab studies. Liu et al. (2017) sampled smoke between 1-2 h old on average, and did not report an ER value for NH_3. However, Liu et al. (2017) reported an average wildfire MCE that Selimovic et al. (2018) used with measurements of very fresh lab fire smoke to calculate an ER value for $\Delta NH_3/\Delta CO$ based on the average wildfire MCE reported in Liu et al. (2017). The predicted NH_3 value (0.0279) for wildfires based on an average wildfire MCE (0.91), is about twice our observed average $\Delta NH_3/\Delta CO$ (0.0133). Radke et al. (1991), measured an $\Delta NH_3/\Delta CO$ range from 0.037 for fresh smoke to 0.011 when including samples up to 48 h old. Our 2017 individual ratios span a range (Tab. S1). Near the high end we see $\Delta NH_3/\Delta CO$ of 0.0196 for relatively fresh smoke assigned to the nearby Lolo Peak Fire and 0.0216 for event “S” where the origin is unclear. Our lowest ratios are about ¼ of our highest ratios (0.0044) (Tab. S1). Akagi et al. (2012) measured a mid-day $\Delta NH_3/\Delta CO$ half-life of ~5h, which suggests that our average sample age is roughly equivalent to ~5h of mid-day processing and our oldest samples (with NH_3 data) are aged equivalent to about 10 hours of “mid-day processing” (Tab. S1). However, the “time since emission” is potentially longer than indicated by a “photochemical age” since, according to the GOES satellite, a lot of smoke was produced in the evening and OH processing may not have started fully until the next day. In addition, we note that the true processing ages have potential to be even longer, since the true initial $\Delta NH_3/\Delta CO$ may have been higher than our highest observed ratios as we were not immediately adjacent to sources. This possibility is supported by the fact that NH_3 and CH_4 emissions have been shown to be linked (Yokelson et al., 1997), and our “high” $\Delta CH_4/\Delta CO$ value for event “S” (~0.14) could indicate that the real initial $\Delta NH_3/\Delta CO$ was higher than ~0.022. Finally, the $\Delta NH_3/\Delta CO$ ratio is also related to the size and age of particles as will be discussed in future sections (3.3).

C_2H_4 has been observed to decay in isolated plumes with a similar half-life to ammonia (Akagi et al., 2012; Hobbs et al., 2003), and our study average $\Delta C_2H_4/\Delta CO$ ratio (0.011) is again about half that in the other wildfire studies in younger smoke reported in Tab. 1 (~0.02) or listed elsewhere (Akagi et al., 2011). Our lower $\Delta C_2H_4/\Delta CO$ ratios tended to occur when the $\Delta NH_3/\Delta CO$ ratio was also lower (Tab. S1), but unfortunately there are only two events with data for both gases and not enough measured values to warrant a detailed analysis. Methanol and acetylene react at least an order of magnitude more slowly with OH than C_2H_4. Our average methanol enhancement ratio (0.019) thus falls in the middle of the other wildfire values (0.0148 – 0.024) as might be expected when any aging effects are smaller than the natural high variability in initial emissions (Akagi et al., 2011). In fact $\Delta CH_3OH/\Delta CO$ has been observed to increase or decrease slightly or stay the same for several hours of aging (Akagi et al., 2012, Akagi et al., 2013, Müller et al., 2016). We have only a few data points for $\Delta C_2H_2/\Delta CO$, but their average is significantly lower than the other wildfire studies. Since C_2H_2 is associated with flaming combustion (Lobert et al., 1991; Yokelson et al., 2013a) this could be due to the prevalence of smoldering that was also indicated by the high average $\Delta CH_4/\Delta CO$ ratios as noted above. Another point about our trace gas data is that our mixing ratios for CO are valuable as an inert tracer for wildfire emissions for comparison to models and they can be useful for inferring the initial emissions of other gases ~~when emission ratios to Co~~if those gases emission ratios to CO have been measured elsewhere (Selimovic et al., 2018; Koss et al., 2018; Liu et al., 2017). CO can also be used as a scaling/normalizing factor for particle emissions, which is discussed in the next section.

3.2 $\Delta BC/\Delta PM_{2.5}$, $\Delta BC/\Delta CO$, $\Delta PM_{2.5}/\Delta CO$

BC is estimated to be the second strongest global climate warming agent and BB is the main BC source (Bond et al., 2004).~~.~~ Accurate BC measurements are challenging and aerosol absorption remains poorly understood in atmospheric models (~~Bond et al., 2004;~~ Bond et al., 2013). In contrast, CO is measured reliably at a network of surface sites and in aircraft campaigns, and can also be retrieved by satellite (MOPITT, IASI, AIRS, etc). As a result, CO emissions estimates are available for most sources, including fires, and the estimates are in reasonable agreement for western wildfires (Liu et al., 2017). BC and ΔBC/ΔCO measurements by modern methods for wildfires are rare, thus, our BC, CO, and ΔBC/ΔCO measurements from a large sample of wildfire smoke can be used with CO emissions to update BC emissions estimates from wildfires (see below). BC is made only by flaming combustion at a fire source and despite the fact that its production rate can vary strongly with flame turbulence, the ΔBC/ΔCO ratio can serve as a rough indicator of the fire's flaming to smoldering ratio (Vakkari et a., 2018; Christian et al., 2003; Yokelson et al., 2009; Shaddix et al., 1994) as exploited earlier in Fig. 2b. Table 2 reports our study average ratios (time weighted) of ΔBC/ΔCO, ΔBC/ΔPM$_{2.5}$, and ΔPM$_{2.5}$/ΔCO and compares them to the limited measurements of wildfire smoke available in the lab (Selimovic et al., 2018) and in the field (Liu et al., 2017; Sahu et al., 2012; Hobbs et al., 1996). Our ΔBC/ΔCO ratio (0.0012) is a bit lower than the aircraft measured averages of Sahu et al. (2012) (0.0014), and Liu et al. (2017) (0.0016), and the Selimovic et al. (2018) estimate at the field average MCE for wildfires from Liu et al. 2017 (0.0018). The Hobbs et al. (1996) average value for their two fires specifically identified as wildfires is notably higher than the other values and is actually an ΔEC/ΔCO measurement that could be biased high. The Selimovic et al. 2018 lab average is also higher, but obtained at the higher lab-average MCE. The uncertainty in our value is likely asymmetric because coatings in aged PM could inflate absorption and our BC value by a small amount. 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. 2b) than airborne studies (MCE 0.91 Liu et al., 2017; 0.90 Sahu et al., 2012). ~~compared to the other, mostly airborne, studies.~~ Liu et al. (2017) calculated an average annual CO production from western US wildfires for 2011-2015 of 5240 ± 2240 Gg, which they reported was in good agreement with an EPA estimate based on a similar burned area in the ~~from the~~ 2011 National Emissions Inventory (4894 Gg). Ratioing to the Liu et al. estimate with the average field study ΔBC/ΔCO in Tab. 2 (0.0014 ± 0.0002) suggests that western US wildfires emit 7.3 ± 3.3 Gg of BC per year. This is significantly lower than a previous estimate, but the other estimate is not strictly comparable since it is based on EC measurements and for a different year (2006) (Mao et al., 2015).

Changes in the ΔPM/ΔCO 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; Vakkari et al., 2018). Table 2 indicates that our ground-based ΔPM$_{2.5}$/ΔCO (0.126 ± 0.002) is about half that obtained at aircraft altitudes in fresher wildfire smoke (0.266 ± 0.134) as reported by Liu et al. (2017) and ~4 times less than that reported for very fresh smoke by Hobbs et al., (1996) (0.492). Further our lower ΔBC/ΔCO ratio suggests enhanced smoldering, which should ~~increase the~~preclude a large drop in ΔPM/ΔCO (Reisen et al., 2018). Liu et al. (2017) and Forrister et al. (2015) measured smoke aging for the Rim Fire (a large California wildfire) as the plume aged and found that the ΔOA/ΔCO ratio started high and then dropped to a value (0.125 ± 0.025) similar to our ΔPM$_{2.5}$/ΔCO. However, Collier et al. (2016) found no age dependence for ΔOA/ΔCO for plumes intercepted at Mount Bachelor or on the G-1 aircraft and obtained a value for ΔOA/ΔCO (0.25 ± 0.07) close to both the ΔOA/ΔCO and ΔPM$_{1.0}$/ΔCO of Liu et al. (2017) in fresh Rim Fire smoke. Taken together, these observations suggest that, on time scales up to ~1-2 days for the wildfire smoke~~plumes~~ studied to date, aging and/or higher average ambient temperatures at lower elevations may encourage some OA evaporation and reduce downwind PM impacts, Some studies in other fire types have found secondary formation to dominate at low elevation (Yokelson et al., 2009; Vakkari et al., 2014) so it is premature to generalize this observation to all BB and more study is needed. However, both of the latter studies measured smoke within a few hours of the source, and our lower $\Delta PM_{2.5}/\Delta CO$ indicates that evaporation of PM dominated over formation of PM as smoke was transported to the Missoula valley in smoke that was between several hours and several days old.

The climate impacts of smoke are strongly related to the $\Delta BC/\Delta PM$ ratio and also the SSA and BrC, which are described in more detail in other sections. The $\Delta BC/\Delta PM$ ratio also allows for a~~n~~ rough 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, and $\Delta BC/\Delta PM$ is also variable at the source. Our study average $\Delta BC/\Delta PM_{2.5}$ ratio (0.0095, Fig. 3) is higher than the study average $\Delta BC/\Delta PM_{1.0}$ in Liu et al. 2017 (0.006) but falls within the range observed for two wildfires measured in Liu et al. (2017), despite the differences in measurement techniques ($PM_{2.5}$ vs. $PM_{1.0}$, ~~etc~~etc.). It's possible that the $\Delta BC/\Delta PM$ ratio reported in this study is up to ~30% too high if we consider the effects of coating on BC and lensing as a positive error (Pokhrel et al., 2017). P~~A p~~revious studies~~y~~ found that smoldering combustion emits anywhere between 2~~4~~-49 times more PM than flaming combustion (Jen et al., 2019; Kim et al., 2018; Reisen et al., 2018; Yokelson et al., 2013a), so the combination of our $\Delta BC/\Delta CO$ ratio that is indicative of more smoldering combustion and a BC/PM ratio that is similar to or slightly above measurements closer to fire sources (Liu et al., 2017) again suggests that some net evaporation of PM is occurring at lower, warmer altitudes during transport between the wildfire sources and our surface site~~between the wildfire sources and our surface site~~. Again, this is worth more study since this could modify air quality and health effects.

OA is the main component of PM and the $\Delta BC/\Delta PM$ ratio is likely similar to the $\Delta BC/\Delta OA$ ratio. Our $\Delta BC/\Delta PM$ ratio (~1%) then suggests that the aerosol measured was overwhelmingly organic, and thus strongly cooling, especially if the impact of BrC or lensing was small. Further, the mass-absorption coefficient (MAC) for OA scales with the $\Delta BC/\Delta OA$ ratio (Saleh et al., 2014) so we anticipate a low MAC, which is explored more next.

3.3 UV-absorption by brown carbon

While the attribution of BrC is not exact and varies across studies (Pokhrel et al., 2017), BrC absorption will offset the climate cooling calculated for purely-scattering OA depending on the amount emitted, its MAC, and its lifetime (Feng et al., 2013). One field study of BrC lifetime suggests a significant decrease of BrC over the course of a day, but a prolonged persistence of BrC nonetheless (~6% above background even after 50h following emission) (Forrister et al., 2015), and studies of relevant chemical mechanisms involving BrC have shown both increases and decreases **(**Lin et al., 2015; Liu et al., 2016; Xu et al., 2018). Satellite retrievals employing reasonable a-priori aerosol layer heights indicate that BrC can have a strong impact in fresh BB plumes and a persistent significant impact in downwind regional haze (Jethva et al., 2011; Hammer et al., 2016). Here we present in-situ data showing persistent widespread regional impacts of BrC. Table 3 lists the study-average AAE and percent contribution to absorption at 401 nm by BrC. We interpret our results by comparing them to the limited measurements of wildfire smoke in the lab and field and measurements for "flaming dominated" savanna fires (Selimovic et al., 2018; Forrister et al., 2015; Eck et al., 2013). Theoretically, aerosol absorption that is dominated by black carbon would have an AAE close to 1.0 (Bergstrom et al., 2002; Bond and Bergstrom, 2006; Bergstrom et al., 2007), which is the case in Eck et al., 2013 where they report an average AAE of 1.20 for measurements of savannah fires in southern Africa. On the other hand, Selimovic et al. (2018) and Forrister et al. (2015) calculated AAEs for fresh smoke of 3.31 and 3.75, respectively, for various mixed coniferous fuels burned in a laboratory and in the field. Our study average AAE (1.96 ± 0.38) is almost 2 times lower than the average value recommended for fresh wildfire smoke (~3.5) in Selimovic et al. (2018), but higher than that reported in Eck et al. (2013). This is also the case for the percent contribution to absorption at 401 nm by BrC, where a lower AAE corresponds to lower BrC absorption. The AAE recommended for fresh wildfire smoke implies the %-absorption by BrC at 401 nm is close to 86%, but we still see significant (~50%) absorption by BrC at 401 nm, on average, ~~in our moderately aged smoke~~despite some aging of the smoke at our site.

Although we cannot determine precise smoke ages in this study, we can construct an analysis of our data that probes the trend in AAE and % absorption by BrC with aging. We start by noting that Mie scattering calculations (J. Walker, personal communication, 2017) imply that the ratio of $B_{scat}401/B_{scat}870$ should decrease as average particle size increases (e.g. Schuster et al., 2006; Eck et al., 1999; Kaufman et al., 1994) and average particle size is well-known to increase with particle age (Akagi et al., 2012; Eck et al., 2013; Carrico et al., 2016). We also show in Fig. 4a that the $\Delta NH_3/\Delta CO$ ratio decreases with $B_{scat}401/B_{scat}870$ and we know NH_3/CO decreased with aging with a ~5 hour half-life in the fall and under slower photochemical conditions in Tab. 2 in Akagi et al. (2012). Thus, the range in $B_{scat}401/B_{scat}870$ shown in Fig. 4a represents about 10 hours of day-time aging. We also see a weak trend, but significant decrease in AAE over a similar range of our size/age parameter in Fig. 4b. Our data for AAE versus a proxy for average age of mixed-age smoke~~aging time for multiple plumes~~ is more variable than the AAE versus known transport time for a single plume in Forrister et al. (2015), but still supports a similar conclusion: that the net effect of BrC aging is a substantial decrease in AAE over the course of ~10 hours of aging.

We also speculate that, in addition to aging, the time of day that smoke is formed may impact BrC and AAE. We motivate that hypothesis next and then explore the issue in subsequent sections. Selimovic et al. (2018) showed that BrC accounted for most of the absorption at 401 nm when MCEs were in a low range associated with dominant smoldering combustion. Benedict et al. (2017) further observed that smoke impacts from a nearby wildfire had a much higher smoldering/flaming ratio at night than during the day, which then suggests the potential for increased BrC formation at night. It is also known that smoldering combustion of biomass emits many precursors, including monoterpenes, furans, cresol, etc. (Stockwell et al., 2015); that can react quickly with the major night time oxidant, NO_3, and ostensibly form UV-absorbing organic nitrates that could augment BrC. In fact, estimates using current data strongly suggest that a substantial nighttime secondary BrC source could exist. The EF for primary organic aerosol (POA) produced by BB typically ranges from 3 to 30 g ~~/~~kg^{-1} (May et al., 2014; Liu et al., 2016, 2017). The EF for known plus unidentified non-methane organic gases (NMOGs) with intermediate to low volatility ranges from 3 to 100 g ~~/~~kg^{-1}. Converting even a small percentage of the co-emitted NMOGs that are known to react quickly with NO_3 could yield substantial amounts of BrC and build up a reservoir of BrC during dark hours. Once daytime commences, other studies show that some types of BrC, depending on the precursor, can experience rapid photochemical degradation or formation via both direct photolysis and oxidation (Zhao et al., 2015; Lee et al., 2014, Zhong and Jang et al., 2014; Sareen et al., 2013). In summary, our extensive in-situ measurements show that even after 1-2 days of aging, BrC remains a significant component of ambient smoke, and that the climate properties of the regional haze have a non-BC absorption contribution. However, the details of the formation and lifetime of BrC are complicated and probably vary diurnally.

3.4 Single Scattering Albedo, Mass Absorption Coefficient, Mass Scattering Coefficient

This section starts with an important reminder/caveat. Our scattering and absorption data is measured for particles up to 1.0 µm, but the PM mass reported by the Missoula DEQ site includes particles up to 2.5 µm. Thus, using our data to calculate mass absorption coefficients (MAC) and mass scattering coefficients (MSC) will produce lower limit values that are not directly comparable to those obtained when the range for both optical and mass measurements goes up to 2.5 µm. Nevertheless it is potentially useful to link PM$_{1.0}$ and PM$_{2.5}$ measurements since measurements at 1 µm cutoffs are common in field campaigns, but PM$_{2.5}$ still remains the common measurement in regional networks.

Our MAC and MSC values were calculated by plotting 1-hr averages of B$_{scat}$401, B$_{abs}$401, and B$_{scat}$870, B$_{abs}$870 versus the 1-hr PM$_{2.5}$ values to calculate an MSC(401), MAC(401), MSC(870), MAC(870), respectively (Fig. S1). Values at other wavelengths were calculated ~~using a~~with a ~~linear regression~~ power law fit using the calculated averages. Our (ΔPM$_{1.0}$/ΔPM$_{2.5}$) MSC values are lower than those reported for PM$_{2.5}$/-PM$_{2.5}$, but still potentially useful. For instance, the ΔPM$_{1.0}$/ΔPM$_{2.5}$ MSC at 870 nm is one~~unity~~ to a good approximation, which suggests a convenient way to estimate PM$_{2.5}$ directly from PAX-870 scattering data. Using a 1-micron cut-off probably isolated the combustion-generated OA and BC pretty well, but dust, ash and biological particles can be physically entrained in wildfire plumes (Formenti et al., 2003; Gaudichet et al., 1995; Hungershoefer et al., 2008). The particles in the 1.0-2.5 micron range are a small part of the total mass in smoke emissions (Reid et al., 2005a) but they contribute disproportionately to the scattering. The additional absorption that we might have measured with a 2.5 micron cutoff may be less significant. Our study average MAC at 401 nm is only 0.19 ± 0.08 m^2 g^{-1}, consistent with a low BC/OA ratio (Saleh et al., 2014).

SSA, AAE, and SA~~AS~~E are commonly used to calculate aerosol absorption and scattering in models and satellite retrievals. (Ramanathan et al., 2001; McComiskey et al., 2008). Uncertainty in the SSA is one of the largest sources of uncertainty in estimating the radiative effect of aerosols (Jiang and Feingold, 2006; McComiskey et al., 2008). Some models and satellite (e.g. MODIS) retrievals assume a constant value of SSA for fire aerosol throughout the biomass burning season and the entire year, which may be an inaccurate approach. Eck et al. (2013) found an increase in SSA at 550 nm from 0.81 in July to 0.88 in October in southern Africa. In Fig. 5 we present evidence for an increase in the SSA for moderately aged wildfire smoke~~plumes~~ over a prolonged period of biomass burning. While we did not directly measure SSA at 550 nm, we did measure SSA at 870 nm for the duration of the sampling period and SSA at 401 nm for the duration that the PAX 401 was operational. Figure 5 shows a moderate increasing trend in the SSA at 870 nm (change in SSA), but no significant trend in the SSA at 401 nm. It could be that because the sampling period of the PAX 401 nm only covers ~2 weeks, any trend that may be present is not apparent within this time frame. Tab.~~le~~ S2 in the supplement shows our study average SSA at 870 nm and 401 nm, both of which are ~0.93, which is similar to the SSA reported at 550 nm in McMeeking et al. (2005b) of 0.92. Our SSA and the SSA reported in McMeeking et al. (2005b) are higher than the sometimes quoted typical surface SSA of the earth (~0.9, Praveen et al., 2012) which suggests that the wildfire PM$_{1.0}$ in regional haze would contribute to regional cooling (Thornhill et al., 2018; Kolusu et al., 2015). Conversely, an SSA range like that reported in Eck et al. (2013) could contribute to warming, which could potentially contribute to a positive-feedback cycle associated with biomass burning (Jacobsen, 2014).

3.5 Case Study: Labor Day Weekend

Figure 6 highlights our data for Labor Day weekend (LDW), spanning ~50 hours from 4 September 2017 to 5 September 2017. We focus on this time period because it includes the largest impacts in Missoula, a regional smoke-production episode detected as far downwind as Europe (https://earthobservatory.nasa.gov/images/90980/an-american-aerosol-in-paris) (Ansmann et al., 2018), and an opportunity to compare what is likely smoke from one fire, subjected to different processing scenarios. Peak "V" is smoke that was likely primarily produced at night and transported to Missoula at night before subsequent photochemistry and dilution in the Missoula Valley. In contrast, peak "W" is smoke that was likely produced and transported during the day before aging in Missoula. Surface winds observed coming from the east, our back trajectory calculations, and satellite observations along with the high concentration values of peak V all imply that the smoke was mostly sourced from a local fire (Rice Ridge) and about 2-4 hours old. Our peak-integrated proxy for particle size (4.02, smaller particle size) and the peak-integrated $\Delta NH_3/\Delta CO$ ratio (9.66×10^{-3}) for peak "V" suggest that the smoke retained fairly fresh characteristics even factoring in the daytime tail on the peak (Tab. S2). The peak integrated AAE (2.88) is the highest observed value for AAE from this study for any peak where an AAE could be derived. The same is true for the %401-absorption by BrC (~77%). The UV absorption results are within the range observed for fresh smoke reported in Selimovic et al., 2018 and reiterated again earlier in Tab. 3, which lists average AAE values for fresh smoke between 2.80 and 3.75 (Forrister et al., 2015). Average values for %401-absorption by BrC in fresh smoke ranged between 64 and 86% (Selimovic et al., 2018), and again our integrated result for peak V falls in this range. In summary, the moderately-aged, strongly night-influenced peak has properties not inconsistent with significant amounts of BrC due to smoldering combustion or substantial nighttime BrC formation via reactions with NO_3 or O_3.

While not readily apparent via satellite observations due to stacked smoke layers, our back trajectory calculations, a similar peak shape on an upwind monitor, visual observations of a wall of smoke arriving from the northeast, and high concentrations of PM at the Missoula measuring site strongly suggest that peak "W", with an onset in the early evening, also mostly came from the Rice Ridge Fire as daytime produced/processed smoke. Peak "W" has a 401/870 scattering ratio (2.65) that implies larger particle sizes and an $\Delta NH_3/\Delta CO$ ratio (0.0044) that is ~50% that of Peak "V". The ratio of $\Delta C_2H_4/\Delta CO$ decreases by ~30% from peak V to peak W. The AAE for peak "W" is 2.00, which is ~30% less than the AAE for Peak "V", and corresponds to a lower %401-absorption by BrC for the evening-onset peak (~54%). Taken together, these values imply larger particles and more photochemically aged smoke. Interestingly, the ratio of $\Delta CH_4/\Delta CO$ and $\Delta BC/\Delta CO$ are essentially similar for peaks V and W. This implies the flaming/smoldering ratio at the source for these events was similar (NO_3 chemistry could still have been more important for peak V). While nighttime wildland fire combustion may be normally more smoldering dominated, LDW was marked by an unusual lack of nighttime RH recovery and an aggressive doubling of the fire size. Thus data from a different, more typical period is likely needed to probe diurnal differences in fresh smoke.~~, which we examine next~~.

3.6 Diurnal Cycles

Diurnal cycles of smoke measured in Missoula provide some insight into regional meteorological effects and have some potential to further probe the day versus night flaming/smoldering issues raised in the previous section (3.5). There is, however, a variable delay from production to receptor. Figure 7 shows the diurnal cycle of CO and the average hourly $PM_{2.5}$ measured across the entirety of the smoke sampling period. Levels of CO and $PM_{2.5}$ peak together from about 5 to 11AM, which is consistent with increased smoldering at night, but would also reflect the mixed layer height. Figure 8 shows the diurnal cycles of $PM_{2.5}$, hourly average BC, and hourly average %401-absorption by BrC (8 August 2017 to 10 September 2017). In this case we see that "potential" BrC absorption peaks in the early AM while BC peaks in the evening. 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. ~~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.~~ However, we can't rule out that an increase in photo-bleaching throughout the middle of the day impacts the peak position for absorption by BrC, but even then, the absorption by BrC remains about half of the absorption at 401 nm on average.

3.7 Brief comparison to prescribed fire data

Of the 718 hours we sampled during August and September 2017, 500.5 hours were part of a smoke event, which is close to three quarters (~70%) of the total monitoring time period. Of the total 718 hours of monitoring, over half (56%) violated the National Ambient Air Quality Standards (NAAQS) for allowable PM$_{2.5}$ averaged over 24 hours (35 µg ~~/~~m^{-3}). The hourly average for the entire sampling period of ~54 µg ~~/~~m^{-3} of PM$_{2.5,}$ is an average exceedance of the 24-hour NAAQS standard by 42%. One possible approach to minimizing wildfire AQ impacts is pre-emptive prescribed burning. Prescribed fires reduce hazardous fuels, burn less fuel per unit area, make less smoke per unit fuel consumption, ~~and allow controlled dispersion conditions~~and can be ignited when conditions are favorable for minimizing air quality impacts (Liu et al., 2017).

It is of interest to compare our large sample of ambient wildfire data to the comparatively rare data from airborne wildfire studies and prescribed fire data to see if our large sample size supports the earlier (Liu et al., 2017) conclusions regarding the nature of the smoke and emissions. More strongly supported conclusions can reinforce the land management implications. Table 5 lists the ΔBC/ΔCO, ΔBC/ΔPM, and ΔPM/ΔCO ratios for our ambient wildfire study, the airborne wildfire study from Liu et al., (2017), and prescribed fire values reported in May et al., (2014). The ΔPM/ΔCO values for fresh wildfire smoke in Liu et al. (2017) and aged wildfire smoke (this study) are about three and 1.5 times higher than ΔPM/ΔCO for fresh smoke from prescribed fires in May et al. (2014) when comparing to all their US prescribed fires (Tab. 5). For only prescribed fires in western US mountain coniferous ecosystems (last column Tab. 5), the ΔPM/ΔCO for fresh smoke is close to our value for aged wildfire smoke. However, May et al. (2015) noted that ΔPM/ΔCO decreased by about a factor of two after several hours of aging on at least one prescribed fire.

The ΔBC/ΔCO for prescribed fires is higher than the wildfire average by a factor of ~9 (all prescribed fires) or ~4 (last column), roughly suggesting a higher MCE for prescribed fires. Ignoring smoke age, the ΔBC/ΔPM for prescribed fires is higher than the wildfire average by a factor of ~20 (all prescribed fires) or ~6 (last column). The ΔBC/ΔPM observations suggest that wildfire smoke is overwhelmingly more organic, which is important partly because many optical properties scale with the BC/OA ratio (Saleh et al., 2014). In general, our ground-based wildfire study confirms the earlier airborne indications that prescribed fires are less smoky but also less cooling than wildfires. Differences in smoke production and chemistry between wild and prescribed fires should be researched more and have air quality and land management implications.

~~The available PM/CO data for wildfires is consistently higher than for prescribed fires, which has air quality and land management implications.~~

~~The available PM/BC ratios are consistently ~20 times higher for wildfires, than prescribed burns, confirming that wildfire smoke is overwhelmingly more organic, which is important partly because many optical properties scale with the BC/OA ratio. In general, our ground-based wildfire study confirms the earlier airborne indications that prescribed fires are less smoky but also less cooling than wildfires.~~

4 Conclusions

A major, prolonged wildfire smoke/haze episode impacted the NW U.S. and SW Canada during August through September of 2017. During this episode, we collected over 500 hours of data characterizing smoke/haze properties with FTIR and PAXs at 870 and 401 nm at a ground-based site in Missoula, MT. This is probably the most extensive real-time data on wildfire smoke properties to date. Our low ΔBC/ΔPM (0.0095 ± 0.0005) ratio confirmed the overwhelmingly organic nature of the smoke observed in the airborne studies of wildfire smoke to date. Our ΔBC/ΔCO ratio (0.0012 ± 0.0005) for our ground site was moderately lower than observed in aircraft studies suggesting a relatively larger contribution from smoldering combustion.

Despite our lower ΔBC/ΔCO ratio our ΔPM/ΔCO ratio was about half that measured in fresh smoke from aircraft. Taken together with aircraft measurements in aged wildfire smoke, t~~T~~his suggests that OA evaporation, ~~at least near the surface,~~at higher ambient temperatures nearer the surface may typically reduce PM air quality impacts on the time scale of several hours to days. B_{scat}401/B_{scat}870 was used as a proxy for size and age of the smoke particles with this interpretation being supported by the trace gas data. The size/age proxy implied that AAE decreased significantly after about ten hours of smoke aging, consistent with the single BrC lifetime measurement in an isolated plume. The results clearly show that non-BC absorption can be important in "typical" regional haze/moderately-aged smoke~~plumes~~ with BrC accounting for about half the absorption at 401 nm on average for the entire data set. The diurnal trends show BrC, PM, and CO peaking in early morning and BC peaking in early evening. Over the course of one month, the SSA at 870 nm increased from ~0.9 to ~0.96.

Data Availability

Raw data used to derive ERs and other quantities reported that are not included in the supplemental information can be obtained by contacting the corresponding author.

Author Contributions

VS and RY conducted the research and/or contributed to the data analysis. All authors contributed to the discussion and interpretation of the results and writing the manuscript.

Competing Interests

The authors declare that they have no competing interests.

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Table 1. Time-weighted s~~S~~tudy average enhancement ratios (ratioed to CO) compared to emission ratios reported in other studies.

Compounds	This Work	Selimovic et al., 2018[a]	Selimovic et al., 2018[b]	Liu et al., 2017	Landis et al., 2017	Radke et al., 1991[c]	Urbanski et al., 2013[SV1]
Methane (CH_4)	0.1661 (0.0884)	0.0741 (0.0698)	0.0870	0.0960 (0.0425)	0.104 (0.001)	0.0503 (0.0420)	0.0946 (0.0108)
Acetylene (C_2H_2)	0.0014 (0.0004)	0.0062 (0.0607)	0.0056	0.0028 (0.0022)	--	0.0023 (0.0018)	--
Ethylene (C_2H_4)	0.0114 (0.0022)	0.0209 (0.0193)	0.0199	0.0102 (0.0033)	--	--	--
Methanol (CH_3OH)	0.0199 (0.0013)	0.0148 (0.0152)	0.0176	0.0240 (0.0160)	--	--	--
Ammonia (NH_3)	0.0133 (0.0064)	0.0232 (0.0350)	0.0279	--	--	0.0219 (0.0099)	--

[a] Measured lab values at lab fire MCE

[b] Calculated from EF vs MCE fit based on average wildfire MCE reported in Liu et al.

[c] Averages of Myrtle Fall Creek and Silver Fire

Table 2. Time-weighted s~~S~~tudy average enhancement ratios (g g^{-1} ratioed to CO) compared to emission ratios reported in other studies.

Ratios	This Work	Selimovic et al., 2018[a]	Selimovic et al., 2018[b]	Liu et al., 2017[c, d]	Sahu et al., 2012	Hobbs et al., 1996[e]
BC/CO	0.0012 (0.0005)	0.0087	0.0018	0.0016 (0.0018)	0.0014	0.0103
BC/$PM_{2.5}$	0.0095 (0.0003)	--	--	0.0060 (0.0054)	--	--
$PM_{2.5}$/CO	0.1263 (0.0015)	--	--	0.2661 (0.1342)	--	0.4923

[a] Measured lab values at lab fire MCE

[b] Calculated from EF vs MCE fit based on average wildfire MCE reported in Liu et al.

[c] Average of Rim Fire and Big Windy Complex. BC data was analyzed for Liu et al. (2017) study, but not reported.

[d] PM values reported are $PM_{1.0}$

[e] PM values reported are $PM_{3.5}$

Table 3. Time-weighted s~~S~~tudy average AAE & %BrC contribution compared to other studies.

	This Work	Selimovic et al., 2018a	Selimovic et al., 2018b	Forrister et al., 2015	Eck et al., 2013
AAE	1.96 (0.38)	2.80 (1.57)	3.31	3.75	1.20
%BrC	50.72 (12.78)	64.19 (17.20)	78.00	--	--

[a] Measured lab values at lab fire MCE

[b] Calculated from average wildfire MCE reported in Forrister et al., 2015.

Table 4. Time-weighted s~~S~~tudy average SSA, MAC, and MSC compared to other work.

Parameter	λ (nm)	This Work	Selimovic et al., 2018[b]	Selimovic et al., 2018[c]	Eck et al., 2013	McMeeking et al., 2005	Reid et al., 2005b
SSA	401	0.93 (0.01)	0.79 (0.13)	0.9	--	--	--
	540	0.937~~3~~[a]	--	--	--	--	0.85 (0.03)
	550	0.938~~3~~[a]	--	--	0.81-0.88	0.92 (0.02)[d]	0.86-0.90
	870	0.94 (0.02)	0.64 (0.26)	0.92	--	--	--
MAC	401	0.23	--	--	--	--	--

		(0.01)					
	530	0.143~~78~~	--	--	--	0.37 (0.05)[e]	--
	540	0.138~~74~~					0.7 (0.4)
	550	0.132~~70~~	--	--	--	--	0.7-0.8
	870	0.04 (<0.01)	--	--	--	--	--
MSC	401	3.23 (0.06)	--	--	--	--	--
	530	2.13~~62~~	--	--	--	5.5 (0.5)[e]	--
	540	2.07~~57~~	--	--	--	--	3.2-4.2
	550	2.02~~52~~	--	--	--	--	3.6-3.8
	870	1.01 (0.02)	--	--	--	--	--

[a] Calculated values using fit based on 401 and 870 nm values.

[b] Measured values at lab fire MCE.

[c] Calculated from EF vs MCE fit based on averaged wildfire MCE reported in Liu et al., 2017.

[d] McMeeking et al., 2005b

[e] McMeeking et al., 2005a

Table 5. Comparison of wildfire emission/ enhancement ratios to prescribed fire emission ratios (g g^{-1})

Ratios	This Work	Liu et al., 2017[a, b]	May et al., 2014[b]	May et al., 2014[b,c]
BC/CO	0.0012 (0.0005)	0.0016 (0.0018)	0.013 (0.007)	0.006
BC/PM2.5	0.0095 (0.0003)	0.0060 (0.0054)	0.163 (0.019)	0.048

PM2.5/CO	0.1263 (0.0015)	0.2661 (0.1342)	0.080 (0.030)	0.11 (0.01)

[a] Average of Rim Fire and Big Windy Complex. BC data was analyzed for Liu et al. (2017) study, but not reported.

[b] PM values reported are PM1.0

[c] Values for the Shaver and Turtle fires (prescribed burns)

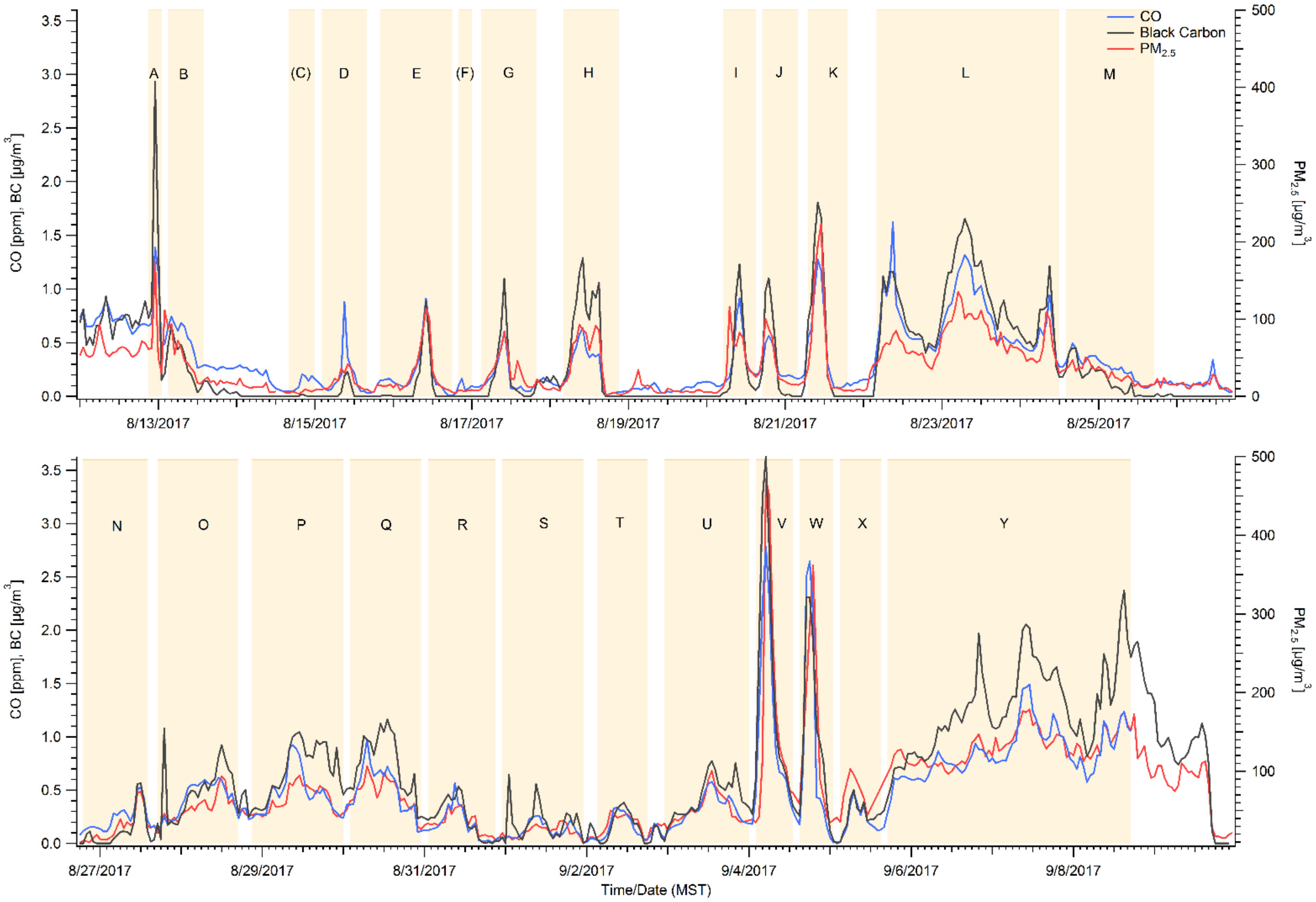
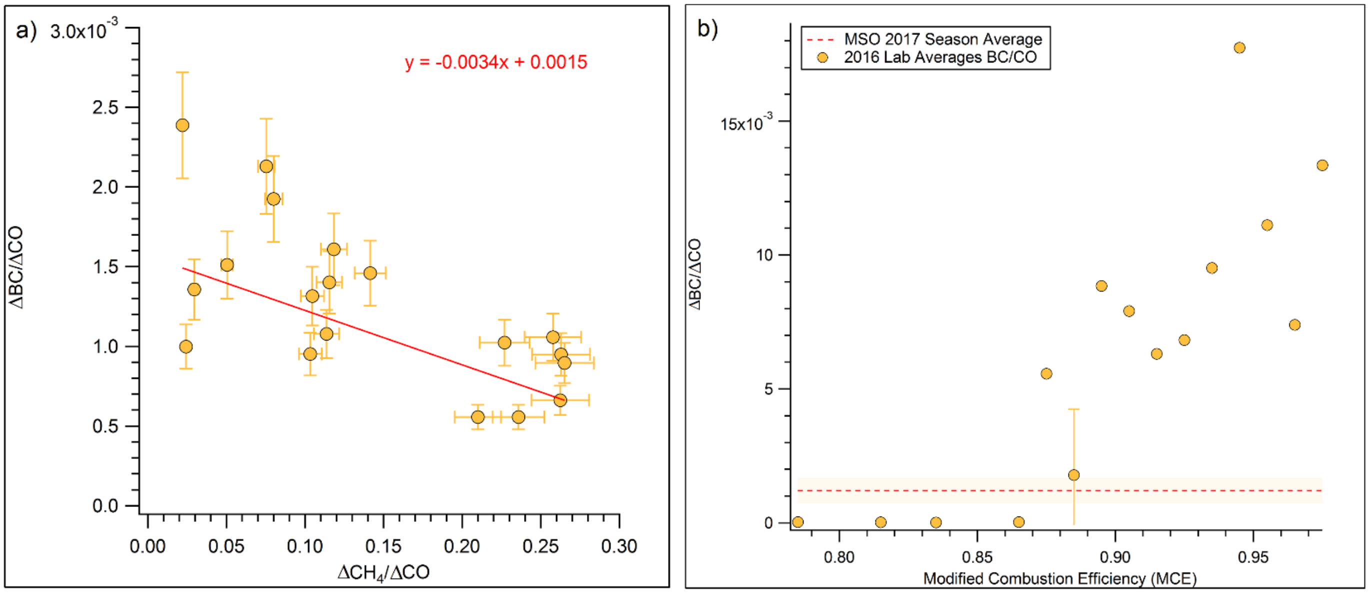


Figure 1. Time series of hourly CO, BC, and $PM_{2.5}$ measurements from Missoula. Sections highlighted in yellow indicated smoke-impacted periods. Peaks labeled with a parentheses indicated events that could not be attributed to biomass burning sources, and were excluded from analysis.


a)
3.0x10-3
2.5
2.0
1.5
1.0
0.5
0.0
ΔBC/ΔCO
y = -0.0034x + 0.0015
0.00
0.05
0.10
0.15
0.20
0.25
0.30
ΔCH4/ΔCO
b)
MSO 2017 Season Average
2016 Lab Averages BC/CO
15x10-3
10
5
0
ΔBC/ΔCO
0.80
0.85
0.90
0.95
Modified Combustion Efficiency (MCE)

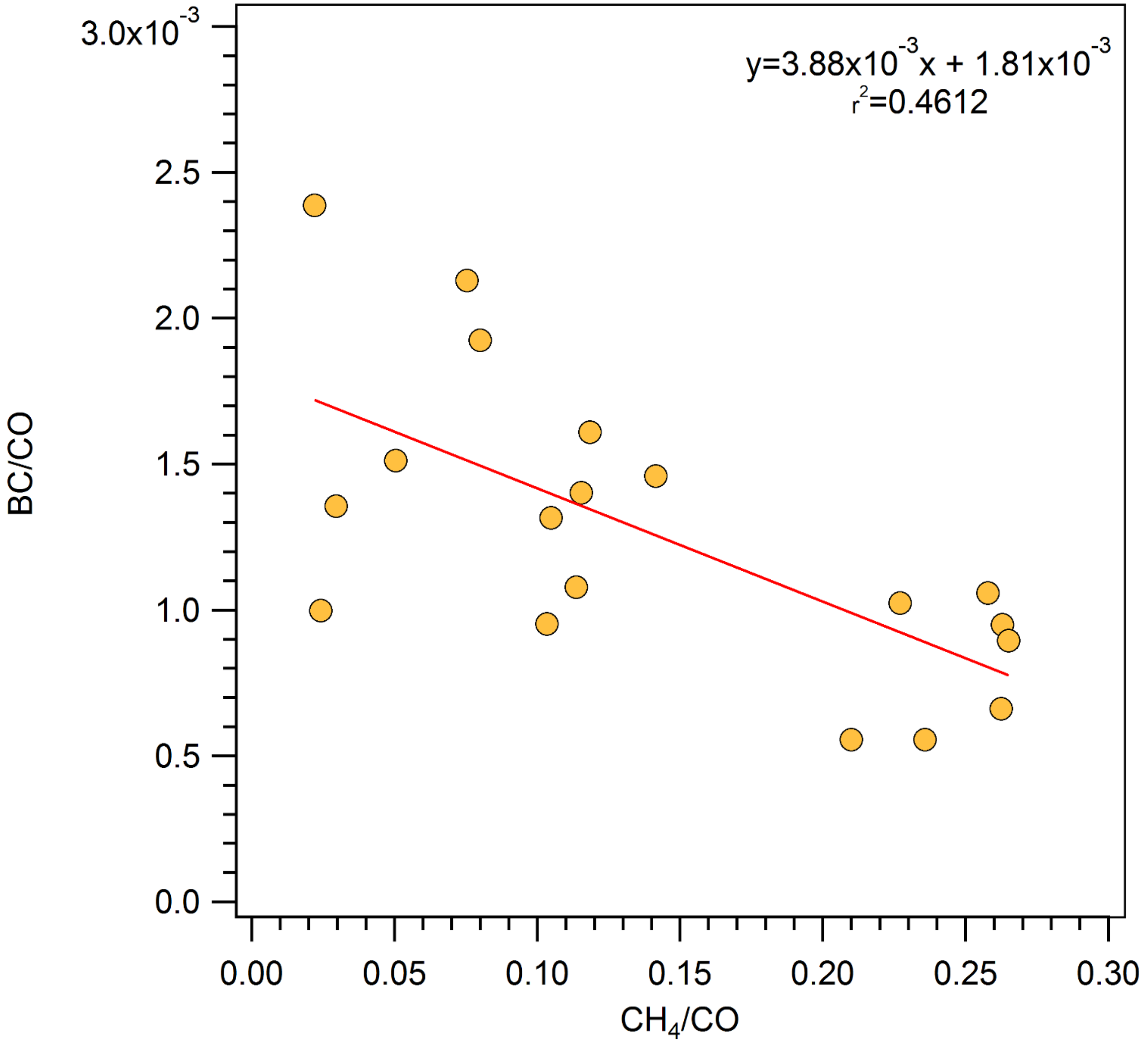

3.0x10-3
2.5
2.0
1.5
1.0
0.5
0.0
BC/CO
y=3.88x10-3x + 1.81x10-3
r2=0.4612
0.00
0.05
0.10
0.15
0.20
0.25
0.30
CH4/CO

Figure 2. a) Methane emission ratio versus black carbon emission ratio. Point shown are for events that have both a CH_4/CO ratio and a BC/CO ratio.b) Lab average (Selimovic et al., 2018) BC/CO ratio versus modified combustion efficiency (MCE), separated into bins by 0.01 of MCE.

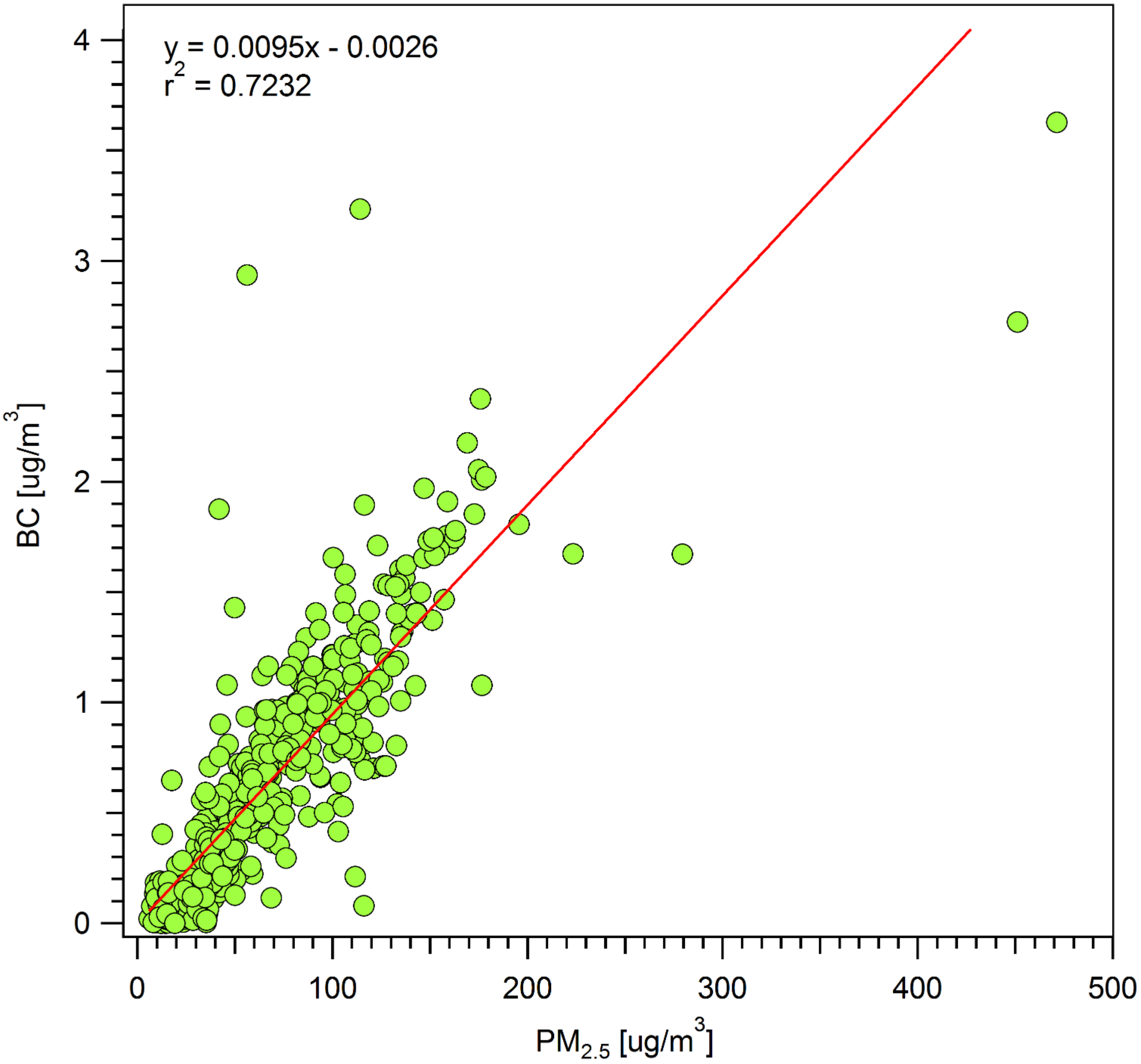
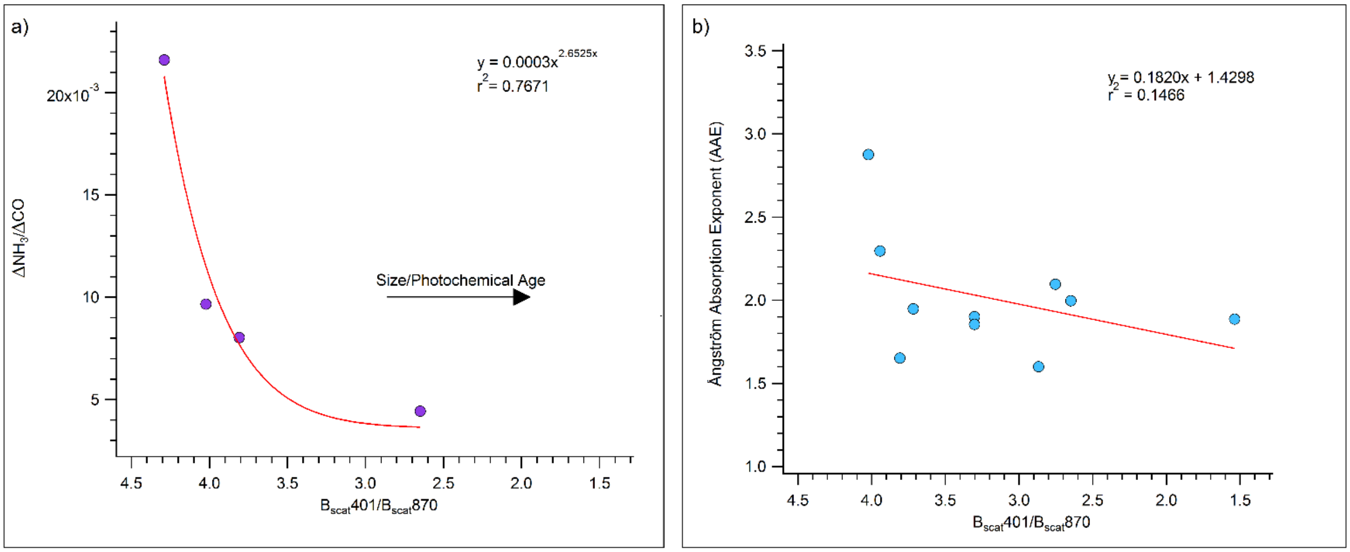


Figure 3. ΔBC/ΔPM ratio based on linear regression of 1-hour data.



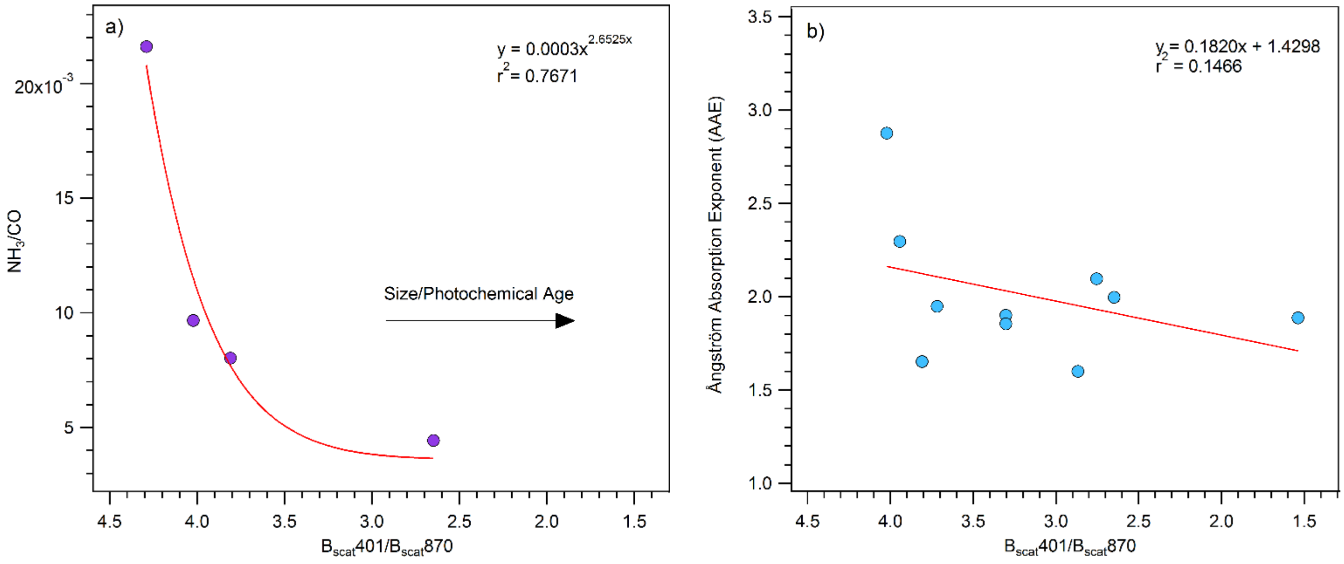
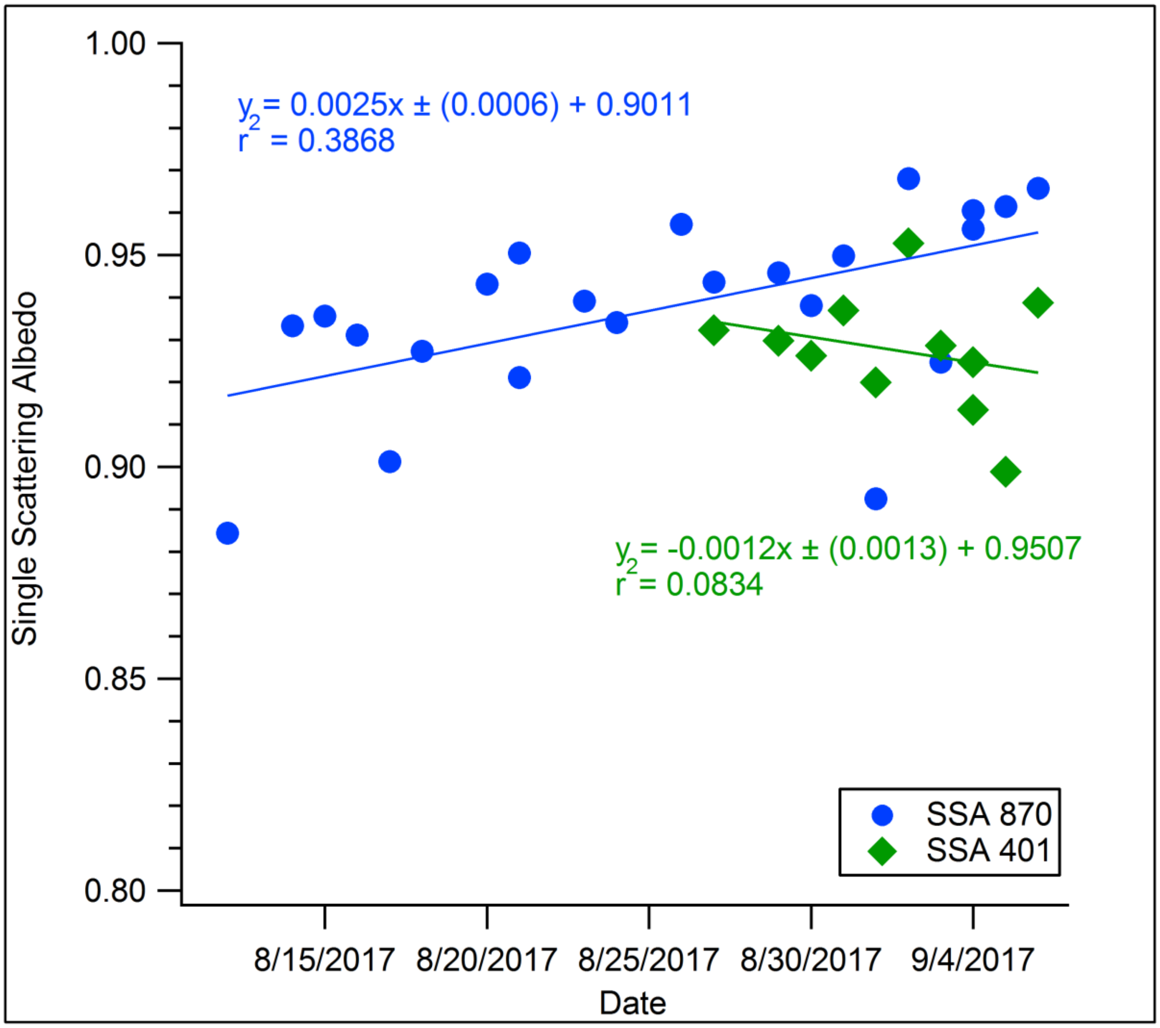


Figure 4: a. Plot of the peak-integrated $\Delta NH_3/\Delta CO$ ratio versus our size proxy (401 Scattering/870 Scattering)~~,~~ for smoke impacts that have an $\Delta NH_3/\Delta CO$ ratio. ~~versus the $\Delta NH_3/\Delta CO$ ratio. Points shown in both graphs are at 1-hr time resolution for smoke impacts that have an $\Delta NH_3/\Delta CO$ ratio and size proxy~~ (~~when both PAXs were operational~~). b. Plot of the peak-integrated absorption Angstrom exponent versus our size proxy (401 Scattering/870 Scattering) when both PAXs were operational. ~~versus the Angstrom absorption exponent. b. Plot of our size proxy (401 Scattering/870 Scattering), versus the NH_3/CO ratio. Points shown in both graphs are at 1-hr time resolution for smoke impacts that have an NH_3/CO ratio and size proxy (when both PAXs were operational).~~



1.00
0.95
0.90
0.85
0.80
Single Scattering Albedo
y = 0.0025x ± (0.0006) + 0.9011
r2 = 0.3868
y = -0.0012x ± (0.0013) + 0.9507
r2 = 0.0834
SSA 870
SSA 401
8/15/2017
8/20/2017
8/25/2017
8/30/2017
9/4/2017
Date

[SV2]

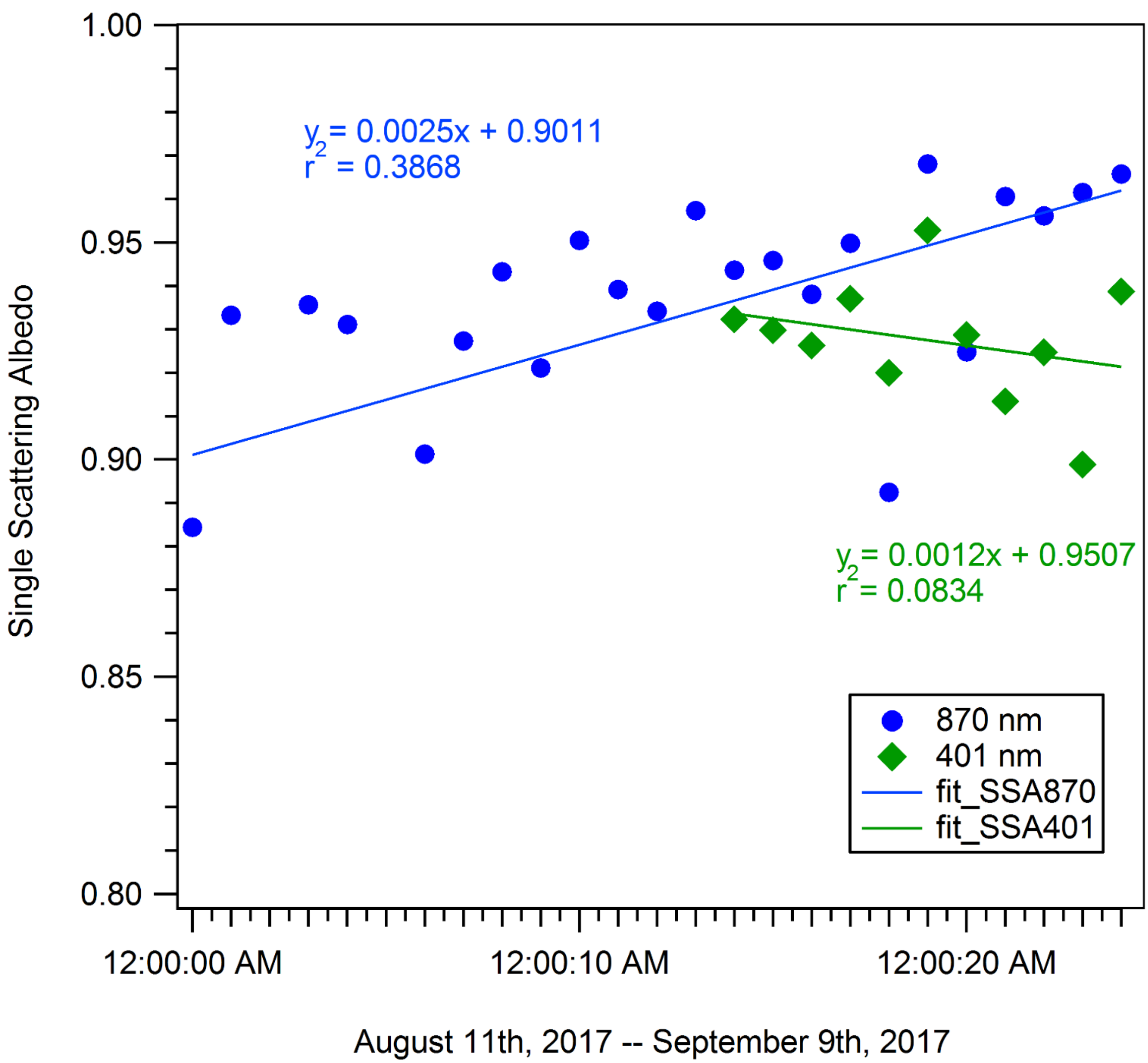
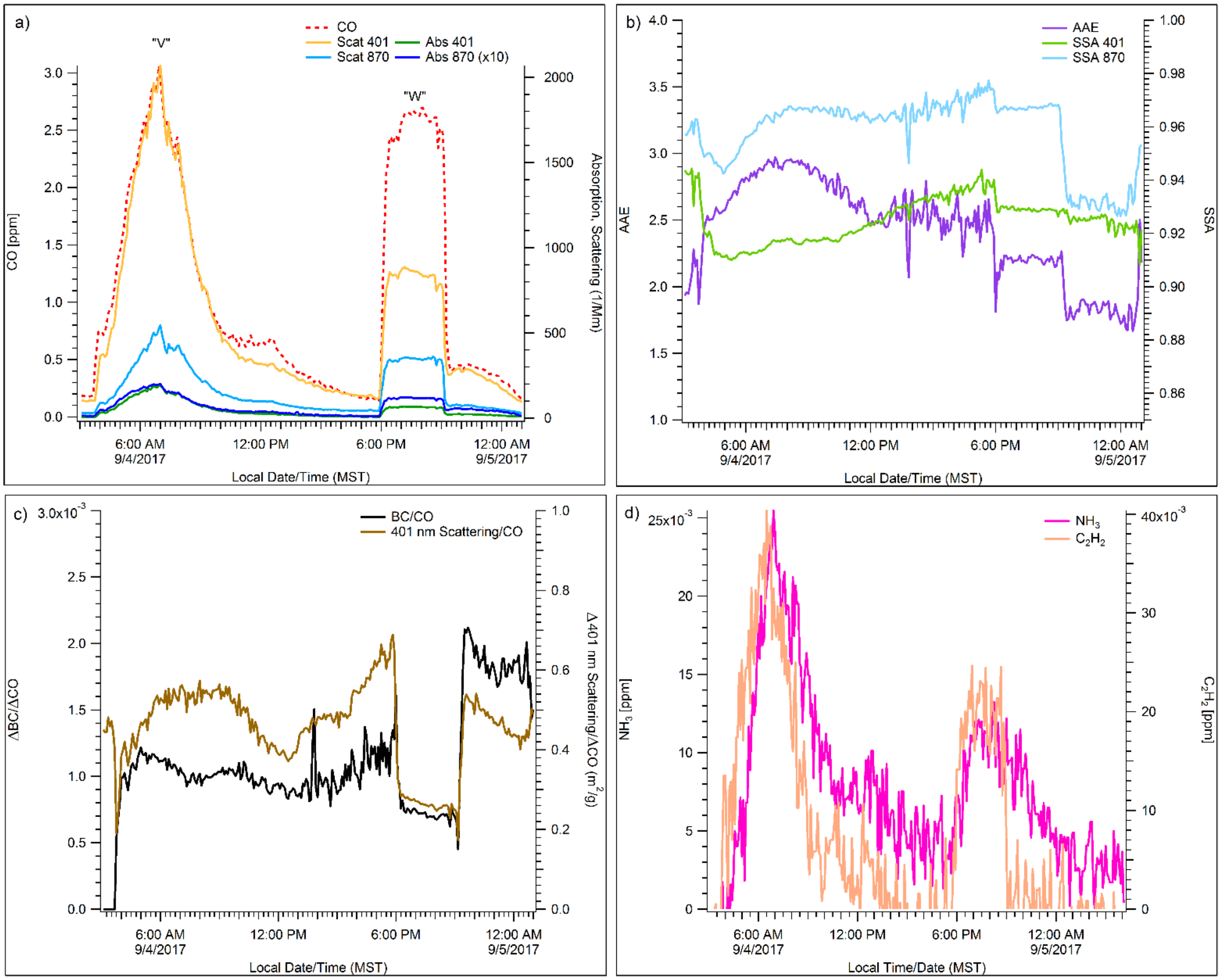


Figure 5. Plot of single scattering albedo over the course of the ambient smoke-monitoring period. Points represent SSA absorption and scattering integrated over ~~from~~ smoke-impacted events.


a)
"V"
"W"
CO
Scat 401
Abs 401
Scat 870
Abs 870 (x10)
CO [ppm]
Absorption, Scattering (1/Mm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2000
1500
1000
500
0
6:00 AM 9/4/2017
12:00 PM
6:00 PM
12:00 AM 9/5/2017
Local Date/Time (MST)
b)
AAE
SSA 401
SSA 870
AAE
SSA
4.0
3.5
3.0
2.5
2.0
1.5
1.0
1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
6:00 AM 9/4/2017
12:00 PM
6:00 PM
12:00 AM 9/5/2017
Local Date/Time (MST)
c)
BC/CO
401 nm Scattering/CO
ΔBC/ΔCO
Δ401 nm Scattering/ΔCO (m²/g)
3.0x10⁻³
2.5
2.0
1.5
1.0
0.5
0.0
1.0
0.8
0.6
0.4
0.2
0.0
6:00 AM 9/4/2017
12:00 PM
6:00 PM
12:00 AM 9/5/2017
Local Date/Time (MST)
d)
NH₃
C₂H₂
NH₃ [ppm]
C₂H₂ [ppm]
25x10⁻³
20
15
10
5
0
40x10⁻³
30
20
10
0
6:00 AM 9/4/2017
12:00 PM
6:00 PM
12:00 AM 9/5/2017
Local Time/Date (MST)

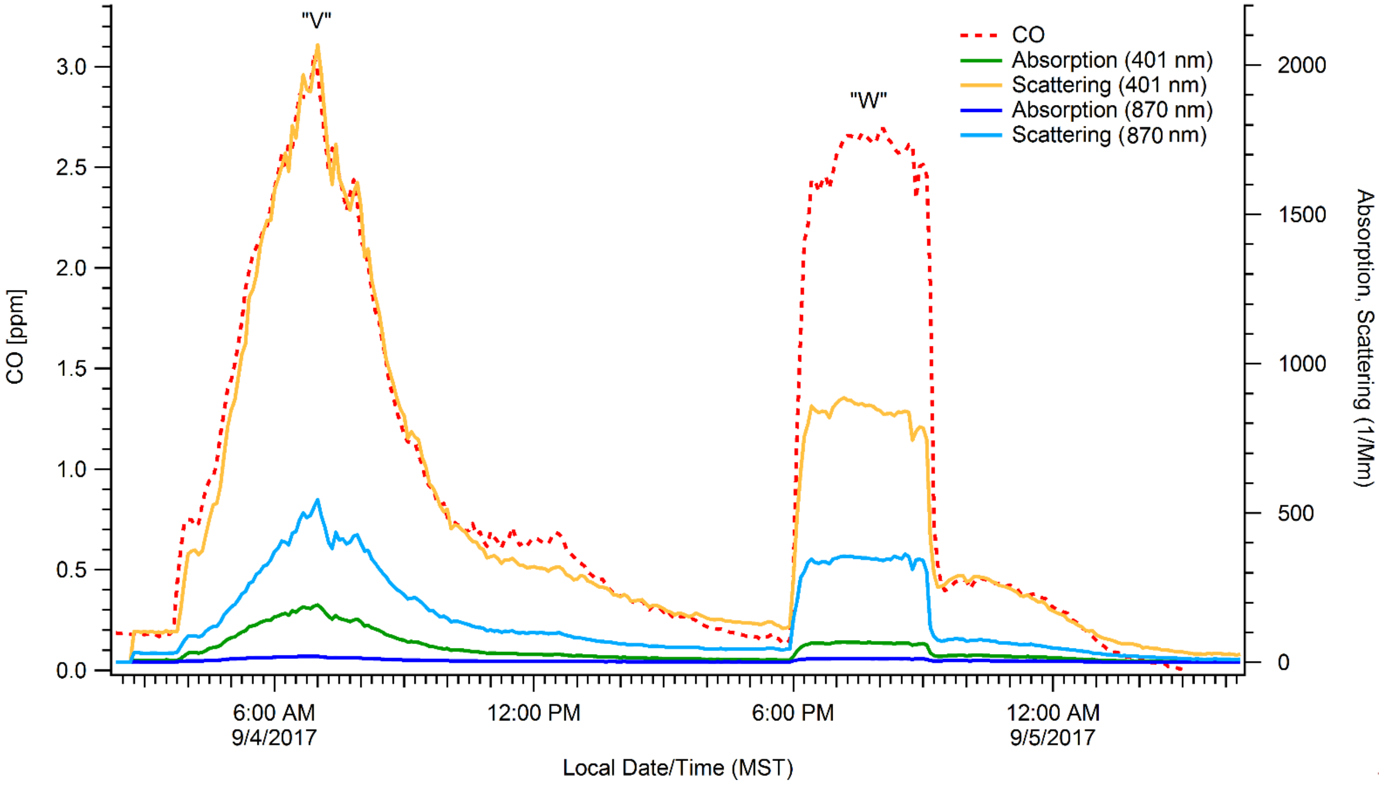


Figure 6. High resolution (5-minute) time series of smoke-impacts measured in Missoula over Labor Day weekend (see Sect.3.5).

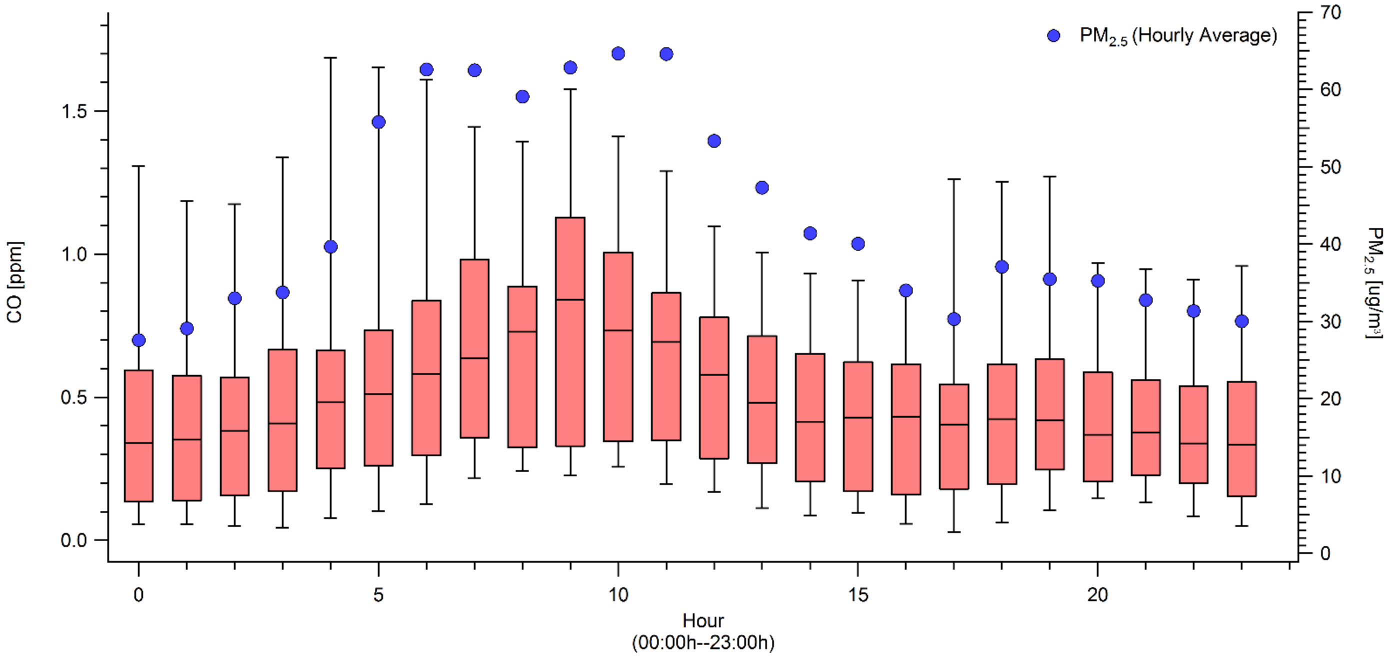


Figure 7. Diurnal plot of CO and PM$_{2.5}$, shown for the entirety of the monitoring period.~~.~~

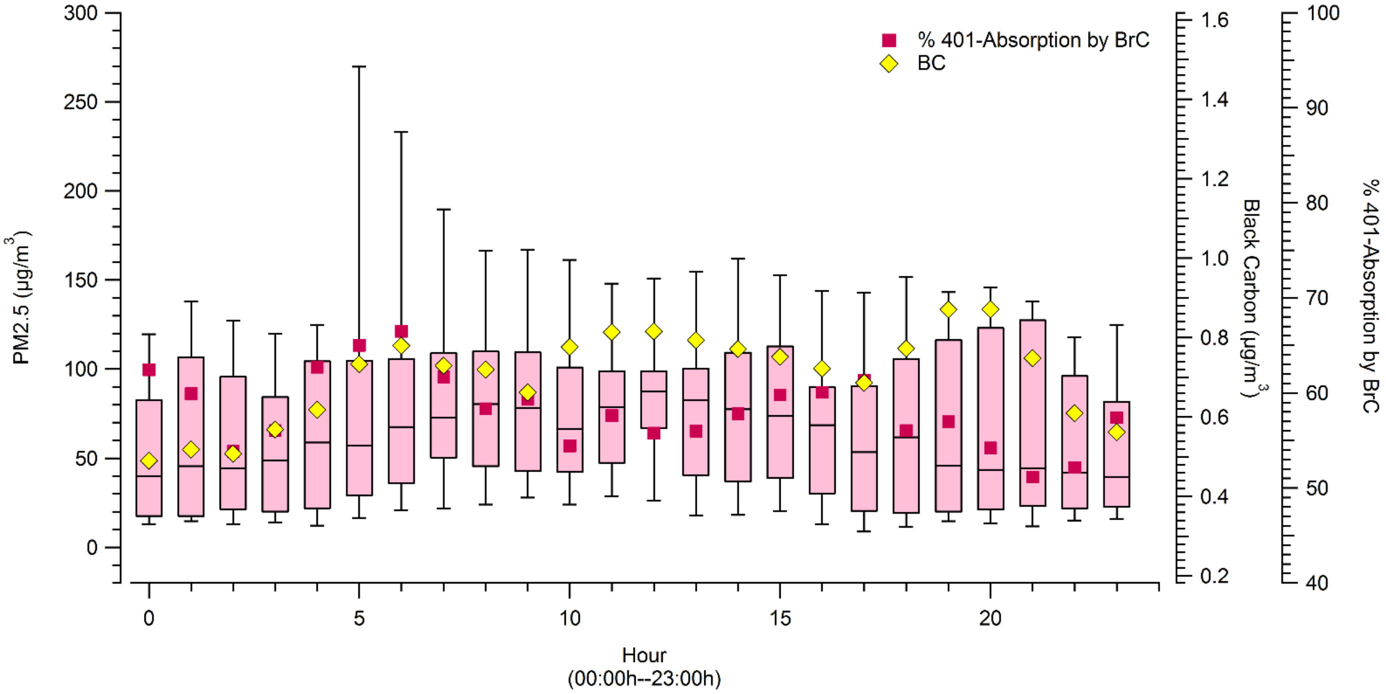


Figure 8. Diurnal plot of average $PM_{2.5}$, hourly average % 401-Absorption by BrC, and hourly average BC. BC and PM shown for the entirety of the monitoring period, but %401-Absorption by BrC only shown for when the PAX 401 was operational.