

Anonymous Referee #1
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Author(s): Jakob Lindaas et al.
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We thank the reviewer for their time and thorough review of our manuscript. We have tried to address every comment and feel that doing so has resulted in a much improved manuscript. Our responses to the reviewer comments are below in italics, with text excerpts in quotes.

General Comments: Overall, this is a good example of a case study, with relevance specifically to Colorado air quality and which, more generally, speaks to air quality concerns relevant to the western United States, where wildfires are a substantive air quality issue. In Colorado, there is an active community of regulators at the State and Federal level who have been debating the very issues discussed in this paper for well over a decade. There is an extensive network of monitoring and also substantive photochemical modeling address this issue from a policy perspective. This case study has merit, but the danger here is that a paper will over generalize a case study and overstate its own importance. The authors should be careful in this regard. From a regulatory perspective, actual exceedances of ambient standards for ozone (70 ppbv for 8 hours) are relevant and anything below this is generally not relevant. Even so, a non-attainment designation is based on more than a single exceedance at a single location. The authors should demonstrate that knowledge and perspective in the body of this work. It is well established that wildfire smoke can enhance ozone formation, especially air masses that have been aged for several days. Despite an extensive monitoring network and a concentrated field study, measurements are sparse, as is evidenced here by the use of data from several monitors remote from the BAO tower. This paper would be strengthened immensely by the use of satellite imagery showing the wildfire smoke haze during the periods of interest and also by the use of additional State and Federal agency data to establish that wildfire smoke was the cause of the ozone enhancements observed. In my mind, this is not unequivocally established by the observations presented here. For example, could CO enhancements be caused by Asian airmass transport? I encourage the authors of this work make substantial improvements to this work before I recommend publication of this work in Atmospheric Chemistry and Physics. Also, in this work, the authors contrast data from two “smoke” events with that from nonimpacted periods during the same period. However, much of the data from the first fire plume is disregarded. It’s excluded from much of the text and the figures. In my opinion, the first fire plume should be included in all analyses, even if the results are diminished. If this is really a fire plume, it should not be dismissed and excluded. Fire plumes are variable, and that is an important point. Sometimes they make a case easier, sometimes more difficult, but this is a reality in a complex world.

We thank the reviewer for their perspective here. The strength of this paper is that it shows two examples of how a subset of ozone precursors changes in the presence of aged fire smoke. We are not able to probe changes in composition as extensively for the smoke-impacted period in July because that technically occurred before the start of our field campaign. We were fortunate that many of the “easy” measurements (i.e. ozone, CO) were running already at that time, but the more labor-intensive instruments (i.e. the gas chromatographs used for the VOC measurements) were not running. The dataset is interesting because of the high quality of the observations, but it is also interesting because the fires responsible for the smoke in August 2015 were extreme. The 2015 Washington wildfires season was the largest in history. There are a number of case studies, with high chemical specificity, of aged wildfire smoke. However, there are very few measurements of this duration (i.e. aircraft will only sample a plume over the course of a few hours) or within a polluted boundary layer. This paper does very carefully demonstrate that ozone during both the July and August smoke-impacted periods was higher than expected based on ambient temperatures (i.e. for a given temperature average hourly ozone is greater during the smoke-impacted periods than the smoke-free period). However, more importantly, it shows which ozone precursors also change in the presence of smoke. We do not understand the mechanisms driving all these changes. However, there are other papers demonstrating that state of the science air quality models cannot always reproduce observations of elevated ozone when smoke impacts urban areas (e.g. Singh et al., 2010). Our manuscript is an important contribution to our understanding of how aged smoke impacts air pollution mixtures, and our target audience is comprised of atmospheric chemists. In response to the reviewer’s comment that this paper is aimed at explaining ozone exceedances, we have revised the discussion substantially. Specifically, we now use the 95th percentile, rather than an MDA8 value, to subset elevated ozone. We agree with the reviewer

that satellite data is essential for validating our attribution of smoke periods – and this is exactly why we used the HMS smoke product, which is in fact based on satellite data. As this use of satellite data may have been unclear in our initial manuscript, we have substantially increased our explanation of that product. Finally we respectfully disagree that the CO enhancements observed in August 2015 over Colorado could have been due to transpacific transport. We present multiple lines of evidence that these enhancements were associated with the wildfires in Washington, as does Creamean et al. [2016 ACP].

Specific Comments

1) The Title and Abstract should more strongly indicate that this is a single case study showing influences from remote wildfire smoke on one location downwind

The authors agree that the title and abstract can be edited to be more specific. The title was revised to: “Changes in ozone and precursors during two aged wildfire smoke events in the Colorado Front Range in summer 2015”.

2) The Abstract should mention if nearby official monitors showed ozone exceedances to put this case study into context (see additional comments to this effect below).

As discussed above, our aim is not to identify exceptional events. Rather our goal is to carefully document significant changes in ozone and its precursors associated with the presence of smoke using high-quality observations. We believe that the most easily accessible summary for interested readers on ozone exceedances is available through the Regional Air Quality Council (<https://raqc.egnyc.com/dl/PwqCfyKZHM/2015%20Ozone%20Season%2010-21.pdf>), As we have tried to re-focus the introduction on the significance of these wildfire events, we have added the following information in the discussion of the ozone timeseries (Figure 7) rather than in the introduction.

“Several Front Range O₃ monitors recorded elevated ozone during the August smoke-impacted period. Specifically, the maximum daily 8-hour average ozone mixing ratio at Aurora East exceeded 75 ppbv on 21 August. This was the first highest maximum for this station for summer 2015. The second highest maximum for summer 2015 coincided with the August smoke-impacted period at Fort Collins West, Greeley, La Casa, Welby and Aurora East. The third highest maximum for summer 2015 coincided with the August smoke-impacted period at Aurora East, South Boulder Creek, Rocky Mountain National Park, and Fort Collins – CSU.”

3) Introduction. I recommend that the authors extend the background discussion to include policy relevant discussions and demonstrate knowledge of the extensive regulatory work that is ongoing on this topic in the west related to ozone exceedances. For example, only one exceedance of the NAAQS for ozone occurred for all of July and August at the measurement site. How does this compare to the exceedances for the entire State for 2015? Was the entire State in non-attainment this year? Was the event mentioned here a contributing factor? Or, did it fall much farther down the list other exceedances of the standard in the Front Range in 2015. These questions are very relevant to policy and should be discussed in some detail to place the study in a larger context.

We reiterate that the BAO ozone monitor is not an EPA Air Quality Monitor, and thus it is not used to determine ozone exceedances. We hesitate to add a comprehensive discussion of ozone exceedances for Colorado for 2015 as this will serve to focus the paper on policy, rather than atmospheric chemistry. Our aim is to show detailed chemical composition changes associated with the presence of aged smoke in the Front Range. However, we have added very specific information on which Front Range ozone monitors recorded elevated ozone during the smoke-impacted periods (see response to comment above). We are currently working on a second manuscript that provides detailed analysis of the elevated ozone observed at BAO that was not associated with the presence of smoke.

4) Introduction/Smoke events: How does the climatology of the study period compare to Colorado’s as a whole? Was it a cool year? A hot year? A wet year? Was there evidence of pollution transport besides fire smoke from other areas of the US and Internationally?

The key point is that the Washington 2015 wildfires were extreme. They were the largest in that state's history. We have added this information to the introduction. As a specific response to this suggestion, we have also added the following sentences to the manuscript.

“Front Range surface temperatures were not anomalously high in July and August 2015 based on a comparison of reanalysis data for this period to a 1981 – 2010 climatology. Surface precipitation, surface relative humidity, and soil moisture in the Front Range were all lower than this referent period. The extreme fires in Washington and Idaho were associated with warmer and dryer than average summer temperatures in the Pacific Northwest (Kalnay et al., 1996).”

Kalnay, E. and Coauthors, 1996: The NCEP/NCAR Reanalysis 40-year Project. Bull. Amer. Meteor. Soc., 77, 437-471.

We have not identified other clear transport events in our dataset for 2015 at this time.

5) It is not evident why values from the study site were compared with very select other monitoring sites (in this case CAMP, ROMO and Walden) and not others. This gives the impression that supporting evidence has been picked rather than evaluated broadly. Why, why for example, is the PM from the CAMP site (20+ miles from the BAO tower) used, while the CO measurements from CAMP have not? Why are other Front Range ozone measurements not evaluated? Why were Walden and Rocky Mountain ozone sites used, while other data (e.g. CO data from the Storm Peak Lab) were not? This needs to be address directly in the text.

Thank you for pointing out that all these choices seemed arbitrary. We have edited the text to make our criteria for selecting other sites besides BAO clearer.

BAO, ROMO, and Walden are on a gradient of more to less anthropogenic influence. We included measurements from ROMO and Walden in Figure 8 to illustrate that the ozone enhancements are observed in locations outside the Front Range. To our knowledge Storm Peak does not have regular CO measurements during this time period.

We did examine CO measurements from CAMP, and they do show an enhancement in ozone. Median CO during the smoke-impacted periods is 500 ppbv, as compared to 300 ppbv during the smoke-free periods. However, the CO measurement at CAMP is less precise than that at BAO, and thus this measurement is less ideal for identifying the exact start and end of the smoke-impacted periods.

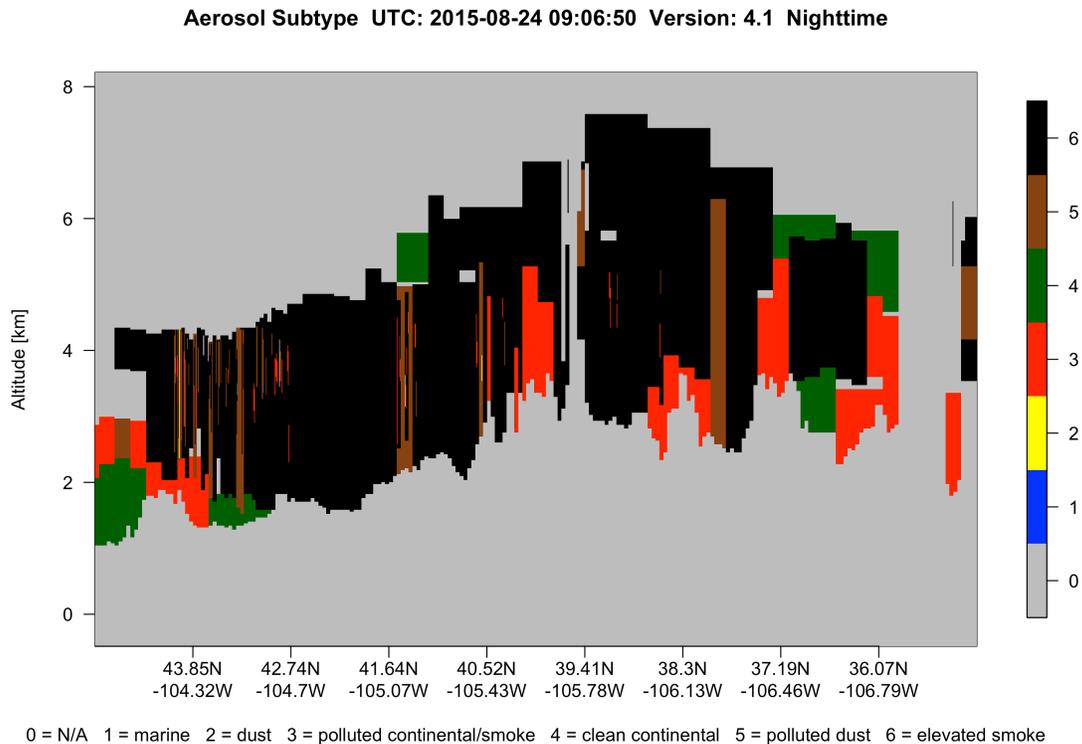
6) Was there satellite imagery from this period that showed the wildfire smoke haze? This data is often widely available, and so should be included if possible.

The HMS smoke product uses data from multiple NOAA and NASA satellites to identify smoke-plumes in the atmospheric column The smoke is detected using visible imagery assisted by infrared imagery, which allows clouds and smoke to be distinguished. A full description of the HMS smoke product is available in Brey et al. [2017], currently under review in ACPD. We have added this information to the text, see below.

“The NOAA Hazard Mapping System smoke polygons (grey shading) show that the smoke events observed at BAO were large regional events. The HMS smoke product is produced using multiple NASA and NOAA satellite products (Rolph et al., 2009). Smoke in the atmospheric column is detected using both visible and infrared imagery and is fully described in Brey et al. (2017). The extent of smoke plumes within the HMS dataset represents a conservative estimate, and no information is provided on the vertical extent or vertical placement of the plumes.”

Brey, S. J., Ruminski, M., Atwood, S. A., and Fischer, E. V.: Connecting smoke plumes to sources using Hazard Mapping System (HMS) smoke and fire location data over North America, Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-245>, in review, 2017.

The presence of smoke is also supported by lidar measurements from CALIPSO. Creamean et al. (2016) used CALIPSO data to investigate aerosol composition during the August smoke period. Below we have provided figure showing a CALIPSO overpass through the Front Range, close to BAO, and this data also shows clear contributions of wildfire smoke to the detected aerosol. For example black and red colors both represent possible smoke contribution to the aerosol detected by CALIPSO throughout the column. The plot also shows that smoke aerosol extends from the ground (the base of all the colors roughly follows the contours of the surface elevation) to the mid troposphere. It is clear that CALIPSO is sampling the widespread regional smoke plume that is also seen in the HMS smoke product during this same time period.



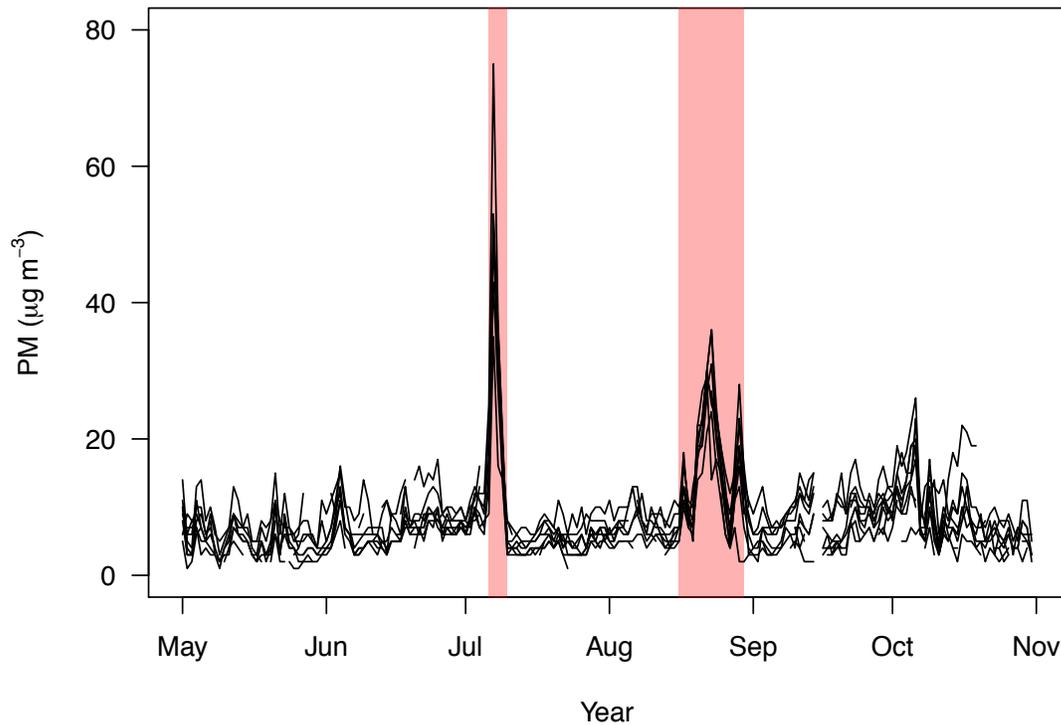
7) Line 102. The GC-method needs to be summarized in more detail. What is the integration period? What is the frequency of measurement? The overall method can be referenced from another paper, but those parameters are important and should be included here.

We have provided answers to the reviewers questions as edits to the text and continue to point to the full description of the GC instrument in Abeleira et al. (2017). The revised text is below.

“A custom 4-channel cryogen-free gas chromatography (GC) system (Sive et al., 2005) was used to measure selected non-methane hydrocarbons (NMHCs), $C_1 - C_2$ halocarbons, alkyl nitrates (ANs), and oxygenated volatile organic compounds (OVOCs) at sub-hourly time resolution; approximately one sample every 45 minutes. The inlet was located at 6 m a.g.l. with a 1 μm pore size teflon filter. Ambient air for each sample was collected and preconcentrated over 5 minutes, with a one liter total sample volume. A calibrated whole air mixture was sampled in the field after every ten ambient samples to monitor sensitivity changes and measurement precision. A full description of this instrument and the associated uncertainties for each detected species is provided in (Abeleira et al., 2017).”

8) Line 147 and Figure 1. CO and PM_{2.5} data from other surrounding monitors should also be included. Ozone data from other Front Range Non-attainment area monitors should be summarized and discussed.

Below we show a timeseries of daily average PM measurements for summer 2015 from 10 PM monitors in the Front Range: CAMP, BOU, CASA, CHAT, COMM, FTCF, GREH, I25, LNGM, NJH. All monitors show similar and consistent excursions during the same smoke-impacted time periods defined at BAO (shown in red shading).



In response to an earlier comment, we have added the following sentences on nearby ozone monitors in Section 4.3.

“Several Front Range O_3 monitors recorded elevated ozone during the August smoke-impacted period. Specifically, the maximum daily 8-hour average ozone mixing ratio at Aurora East exceeded 75 ppbv on 21 August. This was the first highest maximum for this station for summer 2015. The second highest maximum for summer 2015 coincided with the August smoke-impacted period at Fort Collins West, Greely, La Casa, Welby and Aurora East. The third highest maximum for summer 2015 coincided with the August smoke-impacted period at Aurora East, South Boulder Creek, Rocky Mountain National Park, and Fort Collins – CSU.”

The CO data at the other monitors are substantially less precise than that we collected at BAO, but all showed enhancements during the July and August smoke-impacted periods of between 60 and 150%, the same range of percentage increases as observed for CO at BAO.

9) Figure 1. Add CO from CAMP at minimum. There are other CO monitors nearby, do they agree? Add PM_{2.5} from locations closer than CAMP if possible. Address the latter points in text if they cannot be added to the figure.

See above.

10) Lines 147-157. CAMP also has O₃. The data from that station's O₃ needs to be included/shown here, and any place PM_{2.5} is used from that site, especially given the 35 km distance between sites. Also, there needs to be a space between 35 and km on line 150. The paper states, "PM_{2.5} was similarly elevated during the smoke-impacted periods at CDPHE monitoring sites across the Colorado Front Range (not shown)." Why is it not shown? It should be. Lastly, the spikes in figure 1 data are of equal magnitude as the spikes within the defined periods, why are these smoke free?

It is unclear why the reviewer is suggesting that we emphasize the CAMP site. This is just one of 14 ozone monitors that were operational in summer 2015 in the region. We have added a very specific description of which sites show elevated ozone during the fire impacted period based on Regional Air Quality Council analysis available here: <https://raqc.egnyte.com/dl/PwqCfyKZHM/2015%20Ozone%20Season%2010-21.pdf>

Yes, there are "spikes" in CO throughout the campaign; however, these are not accompanied by large increases in aerosol concentration and tend to be of very short duration (on the order of minutes). The enhancements in CO and PM_{2.5} during the smoke events are well correlated and last for hours to days.

11) Figure 2. Recommend that satellite imagery of smoke added as additional figure to make the case that the plume was smoke and widespread.

As discussed in response to an earlier comment, the HMS smoke product (shown in Figure 2) uses data from multiple NOAA and NASA satellites to identify smoke-plumes in the atmospheric column. The smoke is detected using visible imagery assisted by infrared imagery, which allows clouds and smoke to be distinguished. A full description of the HMS smoke product is available in Brey et al. (2017), currently under review in ACPD. We have added this information to the text, see below.

"The NOAA Hazard Mapping System smoke polygons (grey shading) show that the smoke events observed at BAO were large regional events. The HMS smoke product is produced using multiple NASA and NOAA satellite products (Rolph et al., 2009). Smoke in the atmospheric column is detected using both visible and infrared imagery and is fully described in Brey et al. (2017). The extent of smoke plumes within the HMS dataset represents a conservative estimate, and no information is provided on the vertical extent or vertical placement of the plumes."

Brey, S. J., Ruminski, M., Atwood, S. A., and Fischer, E. V.: Connecting smoke plumes to sources using Hazard Mapping System (HMS) smoke and fire location data over North America, Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-245>, in review, 2017.

We also note the CALIPSO data described in the answer to an earlier comment.

12) Section 4.1. Measured data, especially for VOCs, should be tabulated and summarized. Please insert a relevant table of species measured with relevant max, min, median values and standard deviations.

We have added a table in the SI that provides this information.

13) Figure 3. Labels not clear. Add text labels. Why is first fire period excluded?

We have added further labels to indicate that red signifies significant positive changes in the VOCs during the smoke-impacted period, and that blue signifies significant decreases in the VOCs during the smoke-impacted period. There are no VOC measurements during the July fire period. As discussed in response to an earlier comment, the first fire period occurred before our planned field intensive. We had simple instrumentation running (i.e. ozone, CO measurements), but the labor intensive GCs used for the VOC measurements were not running at this time.

14) Figure 3 is hard to understand without a table or plot of VOC concentrations.

We have added a table in the SI that provides this information.

15) Lines 178-181. The fact no biomass burning specific VOC speciation was done at all seems a bit off. This is surprising given the title, and conclusions, and likely impacts of this paper.

As discussed in the paper, the motivation for this field campaign was not associated with biomass burning. It is actually very difficult to plan such an experiment. The campaign was planned long before summer 2015, and was not initiated in response to the smoke. The GC was not optimized to be sensitive to biomass burning specific tracers such as HCN or acetonitrile. Were we to know we would get to sample this type of natural experiment again we would certainly make an effort to include measurements of such species.

16) Line 188. Section 4.1, Figure 2: Unclear how the statement “. . . suggests that the age of smoke impacting the Front Range during the August smoke-period was 2-3 days.” That is not apparent in the figure.

Thank you for noting that this was unclear – it looks like we accidentally lost some information from the caption for Figure 2. We have added the following text to clarify this point.

“The HYSPLIT backward trajectories shown in Figure 2 are 5 day backward trajectories.”

We have also added this to the caption for Figure 2, and we have added 24-hour markers to the trajectories plotted in this Figure.

17) Figure S1-S2. These plots are jumbled. Add legends. If your point is that the boundary layers at 0Z are more variable than the ones at 12Z, you should make that point in the text. The data contradict the conjecture you make around line 218. It's not clear why the sondes are included here. The surface temperature data is presented in Figure 8, so why show the sondes? Perhaps these figures should be revised to be simpler and more concise, or removed. If you must show the soundings then perhaps have two panels, one for smoke free and one for smoke and then a solid gray-area representing all the data, and a line for the average, or even a vertical box/whisker plot.

We agree with the reviewer that these figures are not necessary, and we had just included them for completeness. We have removed them from the supplemental material.

18) Line 216. “Not shown” in reference to the diurnal cycles. Diurnal cycles should be shown. 19) Line 218. A lower PBL height during the day is exactly the opposite of what is observed and this directly contradicts data from figures S1 and S2. This speculation should be removed.

Showing all the diurnal cycles associated with the VOC species would make an unmanageable number of figures, even for the SI. The changes to the alkanes were largely insignificant. We agree that this is a confusing detail, and with the removal of S1 and S2 as suggested above, we have also removed this text. The key point is the very high abundance of alkanes in our region, we agree that the discussion of the diurnal cycles is distracting and we have removed this section of text. In response to a later comment about diurnal cycles, we have shown them for the alkenes in the SI.

20) Line 231-2. This statement does not make sense. Abundances decrease over what time period? Please clarify the wording.

Thank you for pointing this out. This sentence has been clarified and pasted below.

“Surprisingly, we observed significant decreases in the abundance of isoprene, propene and ethene during the August smoke-impacted period compared to the smoke-free period: -64% (-143 pptv), -77% (-39 pptv), and -81% (-206 pptv) respectively (for summary statistics see Table 1).”

21) Line 232. Diurnals not shown. Conclusions in this section could use the support of the diurnal cycles and as is it's hard to follow without them.

We agree that this is a better use of SI figures than the soundings, so we have added plots of the diurnal cycles for the impacted alkenes (isoprene, propene and ethene) to the SI in Figure S1.

22) Paragraph including lines 230-246. Trends are not explained and speculation here is spurious. A table presenting the measured values could easily replace this table. Also, why would isoprene behave differently than other alkenes? Are the changes in alkenes even significant given that they are near their detection limits? A table would suffice here rather than trying to explain trends in ways that mean little. It is unclear what the conclusion of this paragraph is. It's also unclear what the take home point is or and how the evidence supports the conclusion.

We agree that we do not have an irrefutable mechanism to explain this observation, but the changes that we observed are significant. The mixing ratios were substantially suppressed, such that they were near their detection limits. To our knowledge, this is the first time this has been observed. This is very interesting because the aged smoke clearly changed either local emissions or oxidation rates in some way. To improve this paragraph, we have added a table as suggested by the reviewer. We have edited this section and have pasted the revised version below.

“The atmospheric lifetimes of the four alkenes we quantified (isoprene, propene, ethene, and cis-2-butene) range from tens of minutes to hours. Surprisingly, we observed significant decreases in the abundance of isoprene, propene and ethene during the August smoke-impacted period compared to the smoke-free period: -64% (-143 pptv), -77% (-39 pptv), and -81% (-206 pptv) respectively (for summary statistics see Table 1). The shape of the diurnal cycles did not change (Figure S1), though propene and ethene were near their respective limits of detection for the majority of each day during the smoke-impacted period. Given the short lifetimes of these species, this indicates that the presence of the smoke changed either local anthropogenic or biogenic emissions of these species, or their respective rates of oxidation by OH or O₃. We present several potential mechanisms here, but we do not have sufficient information to determine if one of these is solely responsible for the pattern we observed.

Our first hypothesis is that fewer anthropogenic emissions of these alkenes drove the observed decreases in alkene abundances. However, there is no evidence that anthropogenic emissions were different during the August smoke-impacted period. Specifically, the August smoke-impacted period encompassed both weekdays and weekends and did not contain any state or federal holidays. Therefore we move to our second hypothesis, that changes in the biogenic emissions of alkenes accounted for the decreased alkene mixing ratios. Isoprene is widely known to be emitted by broad leaf vegetation, and emission rates are positively correlated with light and temperature (Guenther et al., 2006). Recent measurements quantified ethene and propene emissions from a ponderosa pine forest near Colorado Springs, CO, with an inter-daily light and temperature dependence similar to isoprene (Rhew et al., 2017). Interestingly, emissions and mixing ratios of ethene and propene were not closely correlated with isoprene within the diurnal cycle, indicating they have different vegetative/soil sources than isoprene at that site. Ponderosa pine stands are present in the foothills on the western edge of the plains in the Front Range, and several species of broad leaf trees are present along waterways, in urban areas, and in the foothills of this region. Thus, biogenic sources of ethene, propene, and isoprene in the region around BAO are reasonable. Given the August smoke-impacted period was on average colder than the smoke-free period, and potentially saw a reduction in photosynthetic active radiation (PAR) at the surface due to the increased number of aerosols, it is possible that biogenic emissions of isoprene, ethane, and propene were suppressed. However, biogenic fluxes of these compounds are unavailable for the region around BAO during summer 2015, and extrapolating emissions from one ponderosa pine stand to the rest of the Front Range may be overly ambitious. Further, we note that a PMF analysis of the VOC data from this site did produce a ‘biogenic factor’ dominated by isoprene, but with negligible contribution of any other hydrocarbon, suggesting that the biogenic component of these C₂-C₃ alkenes was small (Abeleira et al...). Thus, while the hypothesis that smoke suppressed biogenic emissions remains feasible, we will consider other potential causes for the observed decrease in alkene abundances.

The alkenes we measured all have high reactivities with respect to OH ($> 8 \times 10^{12} \text{ molec}^{-1} \text{ cm}^3 \text{ s}$) and O_3 ($> 0.1 \times 10^{17} \text{ molec}^{-1} \text{ cm}^3 \text{ s}$) (Atkinson and Arey, 2003). Enhancements in OH abundances have been inferred in wildfire smoke plumes by several studies (e.g. Akagi et al. (2012); Hobbs et al. (2003); Liu et al. (2016); Yokelson et al. (2009)). If the August smoke-impacted period was characterized by higher than normal OH mixing ratios, then a third hypothesis is that the observed decreases in alkene abundances could be due to a higher oxidation rate by OH due to higher OH concentrations. However, other measured VOCs such as o-xylene or methylcyclohexane have similar OH reactivities to ethene (Atkinson and Arey, 2003), and we do not see associated decreases in abundances of these other VOCs. Thus, the hypothesis of increased oxidation by OH causing decreased alkene abundances in the August smoke period is not supported by the full suite of measurements at BAO.

Lastly, we move on to our final hypothesis. Alkenes have much higher rates of reaction with O_3 than the other VOCs we quantified. As we will demonstrate in Section 4.3, the August smoke-impacted period was characterized by higher O_3 abundances than would otherwise be expected. Therefore, the fourth hypothesis regarding decreased alkene abundances is that enhanced alkene oxidation by O_3 decreased the observed mixing ratios. Two factors complicate this hypothesis though. First, we do not observe a negative relationship between O_3 and alkene abundance during the smoke-free time periods (i.e. increased O_3 is not correlated with decreased alkenes when no smoke is present). Second, despite having a higher reaction rate with O_3 compared to propene and ethene, cis-2-butene does not decrease during the August smoke-impacted period.

After careful consideration, there is no strong evidence supporting any of these four hypotheses over the others (suppressed anthropogenic emissions, suppressed biogenic emissions, increased OH, increased O_3). It is possible that more than one of these processes could have contributed to the observation of decreased alkene abundances during the 2 week-long August smoke-influenced period. Future field campaigns and modeling work are necessary to understand how common suppressed alkene abundances may be in smoke-impacted air masses, and what processes might control this phenomenon.“

23) Figure 4. Include first fire period. This figure does not appear to be referred to in the text? It is unclear what 95th percentiles mean. In the legend says quantile and not percentile. Clarify. If it is not referred to in the text, it should be eliminated.

The legend has been fixed and the caption amended to clarify the meaning of 95th percentiles. This Figure is already referenced to in line 273 of the original manuscript.

24) Figure 5. Indicate what shaded regions are. Are they percentiles? Of which measurements? Note that almost never does red line leave the grey shaded area, except for PAN and NO_x. Discuss in text. Show solar noon on the plots for clarity.

We have tested the significance of the differences using a 2-tailed Student's t-test at the 95% confidence level, which describes the likelihood that two sets of data come from the same population. Shaded areas represent one standard deviation (67%) of a single population, assuming a normal distribution; overlap between standard deviations is not typically a metric for two datasets coming from the same population. The text has been edited to clarify this point. Solar noon varies throughout the summer, but the changes are quite small over our time period, and we have compared our data by hour. We have added this information to the caption:

“Solar noon on 1 July 2015 was at 1:03 PM, solar noon on 7 September 2015 was at 12:57 PM.”

25) Line 308. Please include more detail about the analysis you did related to traffic impacts.

In responding to this request we re-evaluated the analysis we had done previously, and took another detailed look at the time series. Previously we had searched for any consistent patterns in wind direction or speed during the large NO₂ peaks observed in the August smoke-impacted period, as well as looked at the correlation of NO₂ with NO. Our assumption was that since I-25 is within 2 miles of the BAO site that large NO₂ peaks coming from I-25 traffic would be freshly emitted NO_x and therefore closely correlated with NO. We did not find any consistent wind direction or correlation with NO, thereby we concluded that these

peaks were not related to traffic emissions. In revisiting this analysis we considered each large increase in NO_2 individually. We have added the following text to the manuscript to describe this additional analysis. We also pose an additional hypothesis for the changes that we observed that was suggested to us when this work was presented earlier this last month.

“Out of 7 morning peaks in NO_2 during the August smoke-impacted period, 3 had concurrent toluene and ethyne peaks. One of these days occurred on a weekend, and the others occurred on weekdays. Toluene and ethyne are common tracers of traffic/industrial emissions. However, 4 of the days did not have corresponding ethyne and toluene peaks. Thus, traffic may have impacted some of the NO_2 enhancements we observed, but there is also likely another contributing mechanism. There are a few potential hypotheses for a non-traffic related NO_2 enhancement during the August smoke period. One hypothesis is that the photolysis frequency (J_{NO_2}) was most impacted (i.e. reduced) by the smoke near sunrise and sunset.”

26) O_3 does indeed have a positive correlation with surface temperature as referenced often in this paper. However for the Front Range region, this should be tempered by the fact that the almost parallel rise in temperature and ozone starts dropping off after the air temperature hits about 86-90F (30C-32C). Some evidence of this can be seen in Figure 6. The reason for this is that once surface temperatures begin to exceed this threshold, a westerly wind component usually becomes dominant. These westerlies will often be gustier and not allow the cyclical terrain-driven circulations that normally enhance ozone concentrations across the Front Range. As referred to in this paper, the Reddy-Pfister study of 2016 expands on this and concludes that 500 mb heights and 700 mb winds hold a stronger correlation to ozone concentrations than surface temperature for Front Range locations. Perhaps this is irrelevant since the air temperature during the "smoke" periods did not get very hot, but maybe an explanation of this phenomena should be included if surface temperature is being emphasized as being more important than the other variables mentioned above.

Thanks for this note. We are happy to provide this context, and we already had supplemental figures showing the lack of correlation between 500 mb heights and 700 mb temperatures with MDA8 at BAO during 2015. This is not necessarily inconsistent with the Reddy and Pfister conclusion, as a key difference is that Reddy and Pfister’s conclusions are based on the interannual variability of monthly average conditions. There are also other chemical factors that could be contributing to this pattern, including a shortened thermal lifetime of PAN. This section of text now reads.

“ O_3 mixing ratios generally increase with temperature, and this relationship has been attributed to several specific processes including 1) warm and often stagnant anti-cyclonic atmospheric conditions that are conducive to O_3 formation, 2) warmer air temperatures that reduce the lifetime of PAN, releasing NO_2 , and 3) lower relative humidity that reduces the speed of termination reactions to the O_3 production cycle (Jacob et al., 1993; Camalier et al., 2007). Specific to the Front Range, Abeleira et al. (2017) show that ozone in this region has a temperature dependence, but it is smaller than other U.S. regions, consistent with the smaller local biogenic VOC emissions compared to many other locations in the eastern U.S. Finally, there is an additional meteorological factor in the Front Range that can impact the temperature dependence of ozone. Gusty westerly winds are often associated with high temperatures, and these winds serve to weaken or eliminate cyclical terrain-driven circulations that normally enhance ozone concentrations across the Front Range.”

Later in the paragraph we note:

“The increase in O_3 mixing ratios during the August smoke-impacted period compared to the smoke-free period is present across the entire range of comparable temperatures.”

27) Figure 6. Include first smoke impacted period on this chart in another set of colored box and whiskers if they are different from the second smoke period. Also, in this figure, the gray bars are indistinguishable from the gray circles, they blend together. Perhaps use black bars instead of gray. The same is true for Fig 8, S4, and S9.

We had originally included the July smoke-impacted period in the SI (originally S4). This figure also shows increased ozone at the low-end of the temperature distribution during the July smoke-impacted period, i.e.

it is consistent with Figure 6 from the second period, but there are lower ozone values and lower temperatures overall. We have combined Figures 6 and S4 into a new Figure 6. We have also outlined the boxes as suggested.

28) Figure 7. The point highlighted in mid-August where temperature is low and O₃ is high looks interesting, why is this not considered smoke influenced given the paper's hypothesis?

All elevated ozone periods are interesting, however, this particular point does not occur during a period with elevated CO or PM_{2.5}. Thus it is not smoke-impacted. We are working on another manuscript that will provide case studies of the elevated ozone events that were not associated with smoke. There is significant variability in the ozone temperature relationship in the Front Range, consistent with most other ground sites. We in no way intend to claim that all high O₃ events in the Front Range are linked to smoke. We have added this sentence to the conclusions to ensure that this is clear.

"This case study describes two distinct smoke events where the presence of smoke likely increased O₃ abundances above those expected by coincident temperatures. However, we do not intend to claim that all high O₃ episodes in the Front Range are caused by smoke, nor that smoke will always cause higher than expected O₃."

29) Figure S3. Clarify if the data shown is for one or both smoke free periods. Show both, using different are lines, if they are different from each other. It is hard to see what's happening at lower values due to so many points. Or figure could be revamped showing quantiles with error bars and all data in gray behind.

Data are only from the August smoke-impacted period. The PANs instrument was not operational during the July smoke-impacted period. We have removed this figure as it seemed to be confusing for the second reviewer, and does not show significant changes.

30) Figure S4. Combine this figure with Figure 6.

These figures have been combined. See our response to comment above.

31) Line 323. Figure 5d doesn't appear to show a very significant difference in ozone between the black and red shaded areas. Perhaps, the figure needs to be edited to make the true difference clearer; otherwise, it seems overstated in the text.

The purpose of the figure is to show the diurnal cycles of each species. To more easily visualize the differences in ozone abundances see Figure 6. The histogram in Figure 6 shows the difference in the distributions of all the data, and the boxplots show the difference as a function of temperature. As discussed above, we have tested the significance of the differences using a 2-sided Student's t-test. Significance is not indicated by non-overlapping standard deviations. Shaded areas are one standard deviation. The text has been edited to clarify this point.

32) Line 330-333. O₃ production with temperature levels off at high temperatures particularly in the Front Range due to the wind speed and direction associated with these high of temperatures. This should be addressed in the text.

Thanks for this comment, it is similar to the one above, and we have addressed it through this modified text.

"O₃ mixing ratios generally increase with temperature, and this relationship has been attributed to several specific processes including 1) warm and often stagnant anti-cyclonic atmospheric conditions that are conducive to O₃ formation, 2) warmer air temperatures that reduce the lifetime of PAN, releasing NO₂, and 3) lower relative humidity that reduces the speed of termination reactions to the O₃ production cycle (Jacob et al., 1993; Camalier et al., 2007). Specific to the Front Range, Abeleira and Farmer (2017) show that ozone in in this region has a temperature dependence, but it is smaller than other U.S. regions, consistent with the smaller local biogenic VOC emissions compared to many other locations in the eastern U.S. Finally, there is an additional meteorological factor in the Front Range that can impact the temperature

dependence of ozone. Gusty westerly winds are often associated with high temperatures, and these winds serve to weaken or eliminate cyclical terrain-driven circulations that normally enhance O₃ mixing ratios across the Front Range.”

33) Lines 334-335. Things like black lines or red lines descriptions should be in the figure legend and caption, not text body.

We thank the reviewer for catching this and have corrected the placement of the figure description.

34) Line 361-363. The chosen altitude limit makes sense, but the Denver cyclone and in-basin wind patterns do contribute to ozone and recirculation. This should be emphasized more and discussed. The authors should include the wind field reanalysis data to show surface winds on their chosen day of interest in each smoke period.

We agree that Denver cyclones and in-basin wind patterns do contribute to ozone production and re-circulation in the Front Range. We have added citations to two recent papers from the 2014 FRAPPE field campaign (Sullivan et al., 2016 and Vu et al., 2016), and more information on the two highest ozone days during the smoke-impacted period.

“Denver cyclones and in-basin wind patterns can also contribute to ozone production and re-circulation in the Front Range (see Sullivan et al. (2016), Vu et al., (2016) and references within). We examined surface wind observations (<http://mesowest.utah.edu>) on the highest ozone days during the smoke impacted period: 20 August and 25 August. There is no evidence of the establishment of Denver Cyclones on either of these days. Sullivan et al. (2016) point out that thermally driven recirculation can manifest as a secondary increase in ozone at surface sites. We did observe a secondary maxima at 17:00 MT on 25 August, but this feature was not present on 20 August.”

Sullivan, J. T., et al. (2016), Quantifying the contribution of thermally driven recirculation to a high-ozone event along the Colorado Front Range using lidar, J. Geophys. Res. Atmos., 121, 10,377–10,390, doi:10.1002/2016JD025229.

Vu, K. T., Dingle, J. H., Bahreini, R., Reddy, P. J., Apel, E. C., Campos, T. L., DiGangi, J. P., Diskin, G. S., Fried, A., Herndon, S. C., Hills, A. J., Hornbrook, R. S., Huey, G., Kaser, L., Montzka, D. D., Nowak, J. B., Pusede, S. E., Richter, D., Roscioli, J. R., Sachse, G. W., Shertz, S., Stell, M., Tanner, D., Tyndall, G. S., Walega, J., Weibring, P., Weinheimer, A. J., Pfister, G., and Flocke, F.: Impacts of the Denver Cyclone on regional air quality and aerosol formation in the Colorado Front Range during FRAPPÉ 2014, Atmos. Chem. Phys., 16, 12039-12058, doi:10.5194/acp-16-12039-2016, 2016.

35) Line 340. How did the weighting occur? Insert a reference or elaborate.

The weighting is described in the text: “weighted by the total number of hourly measurements within each bin”.

36) Does the "synoptic scale transport" discussed at the end of page 11 and start of page 12 also account for the possibility of Asian pollution influence? The HYSPLIT back trajectories on page 20 both suggest that at least a portion of the air mass may have originated in Asia. It would be interesting to see just how much, if any, influence Asian pollution may have had when comparing the smoke and non-smoke air masses.

We did not run backward trajectories of sufficient length to diagnose Asian transport. The transpacific transport of Asian pollution is more efficient in spring, though it can also occur in summer months. Diagnosing the contribution of Asian transport is beyond the scope of this paper, and would require the use (and careful evaluation) of a chemical transport model. We respectfully disagree with the reviewer that there is any evidence of Asian transport based on the data that we have.

37) Line 352. It is unclear how just referencing the geopotential height paper (include citation at this location) leads to the conclusion that was “no evidence” of meteorological factors in ozone enhancement. This is a very broad generalization and needs supporting evidence and specific discussion if it is to be included here. Is the point you are making that the lack of meteorological factors that correlate with ozone implies that all the ozone was due to fire? If so, make this case strongly and state it clearly. Is absence of evidence meteorological driven ozone production even acceptable evidence? I’m not so sure it is. At best, it is supporting evidence.

We agree that this wording might be confusing, and so have changed it to read:

“We tested the day-to-day variability in the relationship between O_3 and these meteorological variables during our study period using observations from the 0Z and 12Z atmospheric soundings conducted in Denver (<http://mesonet.agron.iastate.edu/archive/raobl/>). The positive relationships between MDA8 O_3 and 700 mb temperature, 500 mb geopotential height, and surface winds are very weak, $R^2 = 0.04$, and $R^2 = 0.08$, and $R^2 = 0.0009$ respectively. Thus, we did not find any evidence to support the hypothesis that differences in meteorological conditions were solely responsible for the significant differences in composition or O_3 that we observed during the smoke-impacted period.”

38) Figure S5-7. The authors should explicitly discuss how the data in these figures supports their argument. This is a good supporting point, but there is need to flush out the discussion and figures better. Devoting 3 figures vague scatter plots to this is excessive. Could they be layered in 3 dimensions on a single plot? Alternatively, make one 3-panel figure or remove entirely and only quote the R^2 .

Viewing these from the lens of a reviewer, we agree this is excessive. We have removed these figures from this version. We now only quote the R^2 as suggested by the reviewer. We have added the following sentence to the manuscript.

“The positive relationships between MDA8 O_3 and 700 mb temperature, 500 mb geopotential height, and surface winds are very weak, $R^2 = 0.04$, and $R^2 = 0.08$, and $R^2 = 0.0009$ respectively.”

39) Line 368. Is this flow discussion where you should refer to Figure 4?

No, this should not be a reference to Figure 4. This is correct that it should reference the original S9 and S10.

40) Figure 7. This figure needs to be put into context. Did the Front Range exceed the NAAQS this year? Was this one of the four maximum values that put the region into non-attainment for the year? Or was it much further down the list? This is valuable context information that should be discussed in the text. One exceedence is generally irrelevant to the overall policy discussion, but if this is not the case, it is certainly worth discussing in more detail.

We have added the following information to this section as suggested above.

“Several Front Range O_3 monitors recorded elevated ozone during the August smoke-impacted period. Specifically, the maximum daily 8-hour average ozone mixing ratio at Aurora East exceeded 75 ppbv on 21 August. This was the first highest maximum for this station for summer 2015. The second highest maximum for summer 2015 coincided with the August smoke-impacted period at Fort Collins West, Greeley, La Casa, Welby and Aurora East. The third highest maximum for summer 2015 coincided with the August smoke-impacted period at Aurora East, South Boulder Creek, Rocky Mountain National Park, and Fort Collins – CSU.”

41) Paragraph lines 373-375. Why did you pick 65 ppbv MDA8, when this is not the standard? This seems arbitrary. Please use the current standard and put into the correct context of this year’s ozone for the entire area as mentioned in a previous comment. Please also adjust your conclusions accordingly.

In response to this concern and the one above, we have now re-framed everything in terms of 95th percentile ozone. This does not change any of our conclusions, the highest ozone days are still apparent regardless of the cutoff used.

42) Figure 8. Same comment as for Figure 6. This needs to include the first fire period. Also, why were these sites chosen? Is it because they are remote? If so, why was an example of a nearby monitor not included? Was your point to show that the smoke was widespread? Pick more, not less sites. Was Colorado Springs impacted? It is not necessary to show all the sites, but just clarify your rationale and pick sites to make your point and then say why you picked them.

To be consistent with the revised version of Figure 6 (which now also includes the data plotted originally in S4), we have also added the July period to these plots. Ozone was not notably high in the July period. We picked the two sites because they are at different altitudes than BAO, and offer different information than additional surface sites within the polluted Front Range urban corridor. The RMNP site is often influenced by Front Range polluted air parcels in the afternoon, but not consistently throughout the day. The Walden site is largely free from Front Range influence – that is why it was chosen. The August smoke-impacted period at Walden also has higher ozone for a given temperature, and this is consistent with the hypothesis that at least a fraction of the ozone production within the August smoke plume occurred upwind of the polluted Front Range. This choice is explained in the following paragraphs which have been expanded to make this choice clearer.

“As mentioned in the Introduction, wildfire smoke can produce O_3 within the plume as it is transported, as well as contribute to O_3 photochemistry by mixing additional precursors into surface air masses. To assess the possibility of O_3 production with the plume, we analyzed hourly O_3 measurements from two National Park Service (NPS) Air Resources Division (<http://ard-request.air-resource.com/data.aspx>) measurement locations that are located outside the polluted Front Range urban corridor. The Rocky Mountain National Park long-term monitoring site (ROMO; 40.2778°N, 105.5453°W, 2743 meters A.S.L.) is located on the east side of the Continental Divide and co-located with the Interagency Monitoring of Protected Visual Environments (IMPROVE) and EPA Clean Air Status and Trends Network (CASTNet) monitoring sites. Front Range air masses frequently reach this site during summer afternoons (Benedict et al., 2013). The Arapahoe National Wildlife Refuge long-term monitoring site (WALD; 40.8822°N, 106.3061°W, 2417 meters A.S.L.) near Walden, Colorado, is a rural mountain valley site with very little influence from anthropogenic emissions. These two sites follow a rough urban to rural gradient; from primarily influenced by anthropogenic emissions (BAO), to sometimes influenced by anthropogenic emissions (ROMO), to very little influence from anthropogenic emissions (WALD). Figure 8 shows that the August smoke-impacted period produced increases in O_3 mixing ratios across all three sites. When comparing all data for a given temperature, there are average weighted enhancements of 10 ± 2 ppbv, 10 ± 2 ppbv, and 6 ± 2 ppbv O_3 at BAO, ROMO and WALD respectively. O_3 enhancements across all three sites, across an approximate urban to rural gradient, suggest that some amount of the O_3 enhancement observed at BAO during the August smoke-impacted period is the result of O_3 production within the plume during transit. O_3 during the July smoke-impacted period in Figure 8 shows a different pattern. As we saw in Figure 6, O_3 is enhanced above the level predicted by the ambient temperature at BAO. But no statistically significant enhancements are observed at ROMO and WALD for the July smoke-impacted period. One possible reason for this nuance is that, based on the HMS smoke product shown in Figure 2, it is less obvious that smoke was present at ROMO and WALD during the July smoke-impacted period.”

43) Lines 414-416. What are you trying to say here? Can you refer to Figure 4? Are you trying to say the smoke was widespread? If so, say that and present evidence.

Yes, we are referring to Figure 4 here. We have changed these sentences to read.

“We did not observe any consistent shifts in wind direction or changes in wind speed that can explain the observed changes in composition (e.g. Figure 4), and the changes in abundances that we observed for a given species were generally present across all directions and speeds. The smoke was ubiquitous across the Front Range as evidenced by enhanced $PM_{2.5}$ at CAMP and 9 other Front Range CDPHE monitoring sites.”

44) Line 424-6. You should state this much more strongly and earlier on. It is a major conclusion of the paper. You have direct evidence of this variability.

We have changed this paragraph to read:

“It is important to note that the presence of smoke does not always result in very high O₃ abundances. Many other factors contribute to the overall level of surface O₃, and smoke can also be associated with relatively low O₃ at times, such as during the July smoke event described above. This case study describes two distinct smoke events where the presence of smoke likely increased O₃ abundances above those expected by coincident temperatures. However, we do not intend to claim that all high O₃ episodes in the Front Range are caused by smoke, nor that smoke will always cause higher than expected O₃. Each smoke event has unique characteristics and thus it is important to study and characterize more events such as these in the future.”

45) Figure S9-S10. Are these figure needed? Could they be combined with Figure 4 and used together as supporting evidence?

These figures show different information than that contained in Figure 4. Figure 4 refers to local wind direction, whereas Figures S9 and S10 display the effect of long range transport and air mass history on the ozone temperature relationship. We have substantially reduced the number of supplemental figures in response to other comments – the original S8, S9, and S10 are the only remaining supplemental figures.

46) Figure S11. Is this figure needed? Could you just state the values in the text? An entire figure for two data points with error bars is excessive.

We have removed this figure, and added the values to the text.

“We do not find any significant differences in average calculated OPE between the smoke-impacted (8 ± 3 ppbv/ppbv) and smoke-free periods (7 ± 3 ppbv/ppbv).”

47) References. Please include reference showing where the public data you used came from (CDPHE, Forest Service, NPS).

We have verified a reference to the data source is in every place where the data are introduced, and added it if it was missing.

Minor Issues/Typos

1) Line 62. The use of the pronoun “they” is vague. Please clarify the wording.
Line 62 has been corrected to be more specific. The edited sentence is below.

“Brey and Fischer (2016) investigated the impacts of smoke on O₃ abundances across the U.S. via an analysis of routine in situ measurements and NOAA satellite products. Their analysis demonstrated that the presence of smoke is correlated with higher O₃ mixing ratios in many areas of the U.S., and that this correlation is not driven by temperature.”

2) Line 76. The term “This region” is vague and should be made more specific and the wording should be clarified.
The sentence has been edited for clarity.

The Northern Colorado Front Range region violates the NAAQS for O₃, and has been the focus of several recent studies (e.g. McDuffie et al., 2016; Abeleira et al., 2017).

3) Line 220. There should be a comma after “however”
Corrected.

4) Line 243. A comma is needed after “Thus”
Corrected.

5) Line 278. A comma is needed after “Thus”
Corrected.

6) Line 286. This is important and should be emphasized more if possible, rather than burying it deep in a paragraph. Perhaps making the PAN and alkyl nitrate discussions separate paragraphs would clarify enough.

This appears to be very confusing for the reviewer and we apologize for this. We do not mean to imply that this ratio suggests that there is Asian influence. We meant to simply acknowledge that there is another example like this, where urban and biomass burning influenced ratios are compared, and this is the Roberts et al. [2004] paper. We have removed this sentence from the paper.

7) Line 300. Phrasing is a bit confusing. Rather than saying “fewer days” which is a little vague here, rephrase saying that period 1 had a shorter duration than period 2, or the equivalent.

This has been rephrased, and it now reads:

“... though the mixing ratios were within the range of smoke-free values and the duration of the July smoke-impacted period was much shorter than the August smoke-impacted period.”

8) Line 302. “more significant changes”. . .than what? NO? Clarify the wording here.

Yes, compared to NO. We have changed this sentence to read:

“Figure 5 shows that NO₂ abundances exhibited more significant changes than NO.”

9) Line 310. The phrase “is one hypothesis” is awkward. I suggest rephrasing this sentence.

The part of the sentence containing this phrase was removed.

10) Line 317. A comma is needed after “In this section”

Corrected.

11) Line 419. “Very high” is not specific enough. Include the value here.

This conclusion has been made specific to the 95th percentile of 11am-4pm hourly ozone following the methodology of Cooper et al. (2012).

Cooper, O. R., R.-S. Gao, D. Tarasick, T. Leblanc, and C. Sweeney (2012), Long-term ozone trends at rural ozone monitoring sites across the United States, 1990–2010, J. Geophys. Res., 117, D22307, doi:10.1029/2012JD018261.

12) P 6, line 161-166. Section 3: Things like red triangles, black lines, etc. should be in the figure caption, but not paper text. Only science/discussion should be in the paper body. Also, what are the blue circles? Not in legend or caption. There should be a space between 1000 and m on line 166.

The authors thank the reviewer for catching these corrections. All suggested changes or clarifications have been made.