Anonymous Referee #1 Received and published: 18 April 2017 Author(s): Jakob Lindaas et al. MS No.: acp-2017-171

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 smokefree 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

(<u>https://raqc.egnyte.com/dl/PwqCfyKZHM/2015%20Ozone%20Season%2010-21.pdf_</u>), 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 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 smokeimpacted 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 exceedences 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 exceedences 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.



Aerosol Subtype UTC: 2015-08-24 09:06:50 Version: 4.1 Nighttime

0 = N/A 1 = marine 2 = dust 3 = polluted continental/smoke 4 = clean continental 5 = polluted dust 6 = elevated smoke

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 PM2.5 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, 125, 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 smokeimpacted 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 PM2.5 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 PM2.5 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, "PM2.5 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 PM2.5 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 smokeimpacted 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 O_3 . 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 C_2 - C_3 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 x 10¹² molec⁻¹ cm³ s) and O_3 (> 0.1 x 10¹⁷ molec⁻¹ cm³ 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 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 airmasses, 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 NOx. 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 was 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 NO_2 peaks observed in the August smoke-impacted period, as well as looked at the correlation of NO_2 with NO. Our assumption was that since I-25 is within 2 miles of the BAO site that large NO_2 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_{NO2}) was most impacted (i.e. reduced) by the smoke near sunrise and sunset."

26) O3 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 NO₂, 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 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 PM2.5. 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 O_3 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 O_3 abundances above those expected by coincident temperatures. However, we do not intend to claim that all high O_3 episodes in the Front Range are caused by smoke, nor that smoke will always cause higher than expected O_3 ."

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.

" 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 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 O_3 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 recirculation 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 (<u>http://mesowest.utah.edu</u>) 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 (<u>http://mesonet.agron.iastate.edu/archive/raob/</u>). 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 R2.

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 O3 and 700 mb temperature, 500 mb geopotenial height, and surface winds are very weak, R2 = 0.04, and R2 = 0.08, and R2 = 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, Greely, La Casa, Welby and Aurora East. The third highest maximum for summer 2015 coincided with the August smokeimpacted 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 rational 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 possibly 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 O_3 abundances. Many other factors contribute to the overall level of surface O_3 , and smoke can also be associated with relatively low O_3 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 O_3 abundances above those expected by coincident temperatures. However, we do not intend to claim that all high O_3 episodes in the Front Range are caused by smoke, nor that smoke will always cause higher than expected O_3 . 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 O_3 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 O_3 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 O_3 , 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:<u>10.1029/2012JD018261</u>.

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.

Anonymous Referee #2 Received and published: 27 April 2017

Thank you to this reviewer for their time and detailed comments. We feel that addressing each of these comments has led to a more precise and improved manuscript. Below our responses and excerpted text to reviewer comments are in italics.

Lindaas et al. measured the influence of transported biomass burning smoke on atmospheric composition in the Colorado Front Range. Their study included measurements for an impressive range of compounds, including VOCs, reactive nitrogen, and ozone; the field work seems to have been carefully performed. The authors assessed several meteorological variables and determined that they were not the cause of the changes observed during the smoke-impacted periods. Unfortunately, however, the manuscript largely reads like a list of observations without clear conclusions, particularly sections 4.1 and 4.2 (a few specific examples are noted below). The authors generally devote a large chunk of the text trying to rule out explanations other than biomass burning for a given observation (which is fine), but they never seem to circle back and discuss clearly how their results contribute new insights into the "impact of aged wildfire smoke on atmospheric composition". What is the significance of the observed changes beyond that they can be attributed to smoke and not meteorology?

We thank the reviewer for their thoughts on how to better focus the paper. We had assumed that most readers would immediately ask if meteorological anomalies could be responsible for the changes observed. However, it seems like we may have provided more information than necessary on this topic. We have restructured the conclusions to better summarize our findings, and we have removed much of the back-up meteorological analysis that supports our conclusion that some of the unique findings must be due to the presence of smoke.

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. 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. This paper demonstrates 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. The paper also shows which ozone precursors also change in the presence of smoke. We do not understand the mechanisms driving all these changes.

Additionally, each species (or class of compounds) is generally discussed independently of the others, with minimum consideration of the overall chemical system. For example, from the Introduction, I expected the measurements of the ozone precursors to inform the observed changes in ozone during the smoke influenced periods, yet section 4.3 focuses solely on the ozone data except for one brief mention of VOCs on line 396. How do the observations all link together?

We agree that it would be ideal to tie this together better, but that would require additional observations in addition to the use of a chemical transport model that represents smoke processes well (which many models struggle with currently). We don't believe that we have the ideal suite of constraints in our measurements. For example we are missing observations of nighttime radical sources and J_{NO2} , both of which would be useful in testing different hypothesized mechanisms for the larger NO_2 during the morning and evening smoke-impacted periods. Additionally, we only observed a limited suite of oxygenated species. We also have no constraints on the gas-phase emissions of this particular fire complex with which to constrain the evolution of the plume. We feel that providing a specific chemical mechanism for the ozone production within the plume during its transport to BAO would be speculative at best.

Further, it is not clear why valid data is omitted from the discussion for the July smoke influence period (i.e., CO, CH4). Also, why was only a small subset of the 40+ measured VOCs included in the manuscript, especially when many of the compounds in that subset have high emissions from other sources in the region and displayed no average change between conditions with and without smoke influence? The

authors should more clearly justify their decisions when focusing on only a fraction of the available data (and ideally include the extra data in the supplement for evaluation).

We actually were as inclusive as possible here. No available data from the field intensive was omitted. We have added a table to the SI that shows the abundance of the VOCs. The only significant changes that we observed in the VOCs were those included in Figure 3. 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) 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 wildfires smoke. However, there are very few measurements of this duration (i.e. aircraft will sample a plume over the course of a few hours) or within a polluted boundary layer.

Lastly, comparison of the observations presented in this manuscript to previous studies of transported/aged biomass burning is needed. There are many more relevant publications than the authors seem to give credit (lines 67-68). A few examples: (Jaffe et al., 2004; Mauzerall et al., 1998; Wotawa and Trainer, 2000; de Gouw et al., 2004) and additional works cited in (Heilman et al., 2014).

We thank the reviewer for noting these papers, and we have added references. All the earlier papers are cited in the Jaffe and Wigder, 2012, review paper that we cite. A key difference here is that these plumes were largely sampled in the free troposphere, and not mixed with polluted boundary layer air. Our study is very unique in the length of time that the smoke was sampled (nearly 14 days). This is a very large number of samples of an aged plume over a long time period. This type of extensive sampling is not possible from an aircraft.

"There are well-documented case studies of within plume O_3 production (see Jaffe and Wigder (2012); Heilman et al. (2014), and references within) and time periods where smoke contributed to exceedances of the U.S. EPA National Ambient Air Quality Standard (NAAQS) for O_3 (Morris et al., 2006; Pfister et al., 2008), currently a maximum daily 8 hour average of 70 ppbv."

For these reasons, I think the paper is in need of substantial revisions before I can recommend publication in ACP.

Thank you for your thorough reading of the manuscript, we feel that we have been able to address all the comments below.

Specific comments: Line 60: State the EPA ozone standard.

This line has been edited. See below for the new text.

"...time periods where smoke contributed to exceedances of the U.S. EPA National Ambient Air Quality Standard (NAAQS) for O_3 (Morris et al., 2006; Pfister et al., 2008), currently a maximum daily 8 hour average of 70 ppbv."

Lines 102-106: Basic details of the GC system are missing. Was it a GC-MS? GCFID? How were air samples trapped and introduced onto the column(s)? Over what time period? Which compounds were included in the calibration mixture? What is the uncertainty associated with the measurement?

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)."

Lines 159-163: By what metric and threshold does the HMS smoke product determine smoke impact? More explanation is needed here given that the field sites are just outside of the grey shaded "smokeinfluenced" regions on July 7 (Figure 2), suggesting less relative smoke impact than the August time period where BAO is in the middle of smoke-impacted region; and yet the concentrations of CO and PM2.5 are significantly higher during the July period compared to the August period (Figure 1). Are data from any additional air monitoring sites available along those air mass trajectories to better establish that the air was indeed originating from regions more strongly influenced by smoke during the July period?

As discussed in response to the other reviewer, 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. The HMS smoke product is a conservative estimate of the smoke because for smoke to be identified, it has to be visible from satellite. A comprehensive description of the HMS smoke product is available in Brey et al. [2017], currently under review in ACPD. There are also additional earlier references within Brey et al. (2017) that also describe this operational product. 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.

There were actually plenty of additional air monitoring sites available along the trajectory of the smoke to establish that the air was indeed originating from regions more strongly influenced by smoke. For example, here is a map showing the location of the fires identified by HMS analysts. We have also plotted the overlapping smoke plumes for that day. HMS does provide contours of concentration, but they are approximate. The colored dots show the locations of PM2.5 monitors throughout the western U.S. You can see that PM was moderate to unhealthy within the plume. When viewing this figure, please keep in mind that the HMS smoke plumes show smoke in the column, not necessarily at the surface. The concentration of PM at the surface will depend on how much of the smoke mixes into the boundary layer. This makes it easy to explore data associated with this even for any region of choice. We have not developed a larger paper on these fires, specifically addressing impacts on composition upwind of Colorado, because we are aware of other groups doing these types of more broad analyses. We decided to focus on our unique set of observations. The figure below was produced using a web-application that we have developed. https://stevenjoelbrey.shinyapps.io/HMSExplorer/



Here is the comparable figure for the August event. You can see that surface PM enhancements were much higher closer to the source fires in this case. You can also see that there were fires in Washington and Idaho, similar to what we already show with the MODIS hotspots in Figure 2. You can see that surface PM was enhanced across the intermountain west during this time.



Lines 177-178: "we did not quantify species with known large biomass burning emission ratios (e.g. hydrogen cyanide, acetonitrile, most oxygenated organic species)". Were these compounds not quantified or not measured/detected? If acetonitrile and HCN were detected (even if not directly calibrated), then it is puzzling that they were omitted from the discussion, as these compounds are more specific biomass burning tracers than CO and PM2.5, with lifetimes much longer than the transport time of the air masses. Could their GC peak areas at least be used to determine relative differences between the periods with and without smoke influence? If no significant changes were observed in the peak areas for these markers, then the implications of that for assessing biomass burning influence need to be discussed. If HCN and acetonitrile were not or could not be observed under the GC operating conditions, please clarify the text. The quoted sentence also needs a citation.

Our GC system was not set up to detect HCN and acetonitrile. Since we did not anticipate sampling wildfire smoke and the focus of the campaign was to assess anthropogenic ozone precursors in the Colorado Front Range, the GC was optimized to be sensitive to the light alkanes, alkenes, and a few OVOCs along with a handful of alkyl nitrates. The chromatograms were checked for HCN and acetonitrile peaks after the campaign but those peaks were not able to be identified.

We have edited these lines to be more specific, see below.

"The focus of the BAO field intensive was to study the photochemistry of local emissions from oil and gas development (e.g. Gilman et al., 2013; Swarthout et al., 2013; Thompson et al., 2014; Abeleira et al., 2017), and the GC system was not set up to quantify species with known large biomass burning emission ratios (e.g. hydrogen cyanide, acetonitrile, most oxygenated organic species) (Akagi et al., 2011). The chromatograms were checked for HCN and acetonitrile peaks after the campaign but those peaks were not able to be identified."

Line 180-181: It's clear why the July period was omitted for the VOCs, but why were the CO and CH4 measurements for the July time period also omitted from the discussion? Those species were not subject to the GC issues. From Figure 1, CO had a much larger enhancement during July vs. August smoke-impacted periods... were the differences between the two periods driven by meteorology, fire size, or other factors? Did methane behave similarly? This seems to be a missed opportunity for an interesting comparison.

The authors appreciate the reviewer catching this oversight. CO was shown in Figure 1, but not specifically discussed. We have added the quantified changes in CO and CH4 during the July smoke period to the discussion, and mention one possible reason for the observed differences in CO and PM between the two smoke periods. The edited text is shown below.

"Mean hourly CO mixing ratios were significantly enhanced by 223 ppbv, or 170% during the July smokeimpacted period and by 92 ppbv, or 70%, during the August smoke-impacted period (Figure 1). This enhancement was present across the diurnal cycle (Figure 3) and a both smoke periods displayed a higher range of CO mixing ratios (July: 127 – 639 ppbv, August: 101 – 529 ppbv, smoke-free: 72 – 578 ppbv). The two smoke periods differed in their sources fires, length, and meteorology, with higher average CO and $PM_{2.5}$ measurements in the July smoke period (Figure 1)."

Lines 198-202: "Average enhancements of CH4 were a much smaller percentage of (~3% or 67 ppbv), but comparable in magnitude to, the CO mixing ratio enhancement." Rephrase this sentence so the meaning is clear. . . I believe the percentage is meant to give the CH4 enhancement during the smoke impacted periods, but that is not how the sentence reads. Is the observed CH4 enhancement of 3% statistically significant given that the stated uncertainty in the CH4 measurement is 6% (line 99)? Also, the emission factor of CO is generally >10x that of CH4 from biomass burning (Akagi et al., 2011), thus it is curious that the CH4 enhancement is "comparable in magnitude to the CO enhancement" and could suggest that the other local sources are dominant. Overall, it is not clear from the discussion if the authors attribute the observed 67ppb CH4 enhancement to biomass burning influence or what conclusions should be drawn from the methane observations.

We agree with the reviewer that this was confusing as originally written. We have re-written this section to read:

"Average enhancements of CH_4 were similar for both periods (July: 52 ppbv, August: 50 ppbv, or ~ 2.5% increase). Methane has a relatively high background at BAO due to large emissions of CH_4 in nearby Weld County from livestock production and oil and gas development (Pétron et al., 2014; Townsend-Small et al., 2016). Taken together, the larger background of CH_4 and the large local sources of CH_4 in the Front Range served to mute the impact of the August smoke on overall CH_4 abundances. The diurnal cycle of CH_4 did not change during the smoke-impacted period as compared to the smoke-free period and we observed a similar range of mixing ratios (~1,840 – 3,360 ppbv) in the both smoke-free and smoke-impacted periods.

We note several large spikes in CH_4 on the order of minutes during the August smoke-impacted period, but we do not believe that these are related to the presence of smoke because they were not correlated with similar excursions in CO and PANs, and exhibited strong correlations with propane and other tracers of oil and gas and other anthropogenic activity."

Lines 215-224: Why is the dampening of the diurnal cycle amplitudes for the alkanes significant if there was no net enhancement of these compounds during the smoke influenced periods (line 210)? Were the changes at certain times of day due to biomass burning influence? What is a possible explanation if not changes in PBL height? The take home message of this discussion regarding the impacts of aged wildfire smoke on the diurnal cycles isn't clear. (Similar questions apply to the discussion of diurnal cycles for the other compounds, as well.) Also, please include the ethane diurnal cycles in Figure 5 or the supplement if they warrant this much discussion. It is difficult to follow the text without seeing the relevant diurnal cycle data.

The discussion on diurnal cycles was meant to be part of the documentation of any and all changes we observed. The authors agree with the reviewer that there is not a clear take home message about the alkane diurnal cycles at this point. Thus, for clarity, this section and associated discussion has been removed for the revised paper.

Lines 236-237: Needs a citation. Also, have the authors considered that decreased alkene abundances locally were due to the increased ozone rather than OH? The abundance of aromatics with similar OH reactivity to ethene (Atkinson and Arey, 2003), but negligible O3 reactivity (toluene, xylene, ethyl benzene) did not change during the smoke-impacted period (lines 257-259). If increased OH oxidation was the cause of the decreased alkene abundances, then shouldn't the aromatics have been similarly influenced? Perhaps a broader discussion of the relative sources and their strengths for the various compounds would also help the discussion.

Thanks to the reviewer for an additional hypothesis that we not consider earlier. The discussion of hypotheses for the decreased alkene abundances has been expanded. See edited section 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 O_3 . 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 C_2 - C_3 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 x 10¹² molec⁻¹ cm³ s) and O_3 (> 0.1 x 10¹⁷ molec⁻¹ cm³ 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 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 airmasses, and what processes might control this phenomenon. "

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Lines 283-287: What is the significance of the PPN/PAN ratio?

In response to Reviewer 1's comments, we have removed these sentences.

Lines 302-304: The NO2 diurnal cycles during the July smoke period and the smoke free period shown in Figure 5c are nearly identical. Are the differences discussed here statistically significant and/or important?

The authors included the discussions of NO2 diurnal cycles during the July smoke period in the spirit of documenting any statistically significant changes in the dataset between smoke-impacted and smoke-free periods. However, since there are no obviously testable hypotheses for the observed changes, the authors have chosen to omit this discussion in the revised paper. The revised section is below.

"During the July smoke-impacted period, NO_2 was within the range of smoke-free measurements. In contrast NO_2 during the August smoke-impacted period followed the same diurnal cycle but had pronounced significant increases in average mixing ratios during the morning and evening hours of ~8 ppbv (17%) following sunrise and 3 ppbv (60%) following sunset. "

Lines 308-309: It has not been explained anywhere that PAN is a reservoir for NOx. Some readers may be confused.

The authors thank the reviewer for pointing this out. This sentence has been edited to make this fact clear.

"Another hypothesis concerns the equilibrium between PAN and NO_2 . The thermal decomposition of PAN can be a source of NO_2 (Singh and Hanst, 1981), but the concurrently observed PAN abundances during the August smoke-impacted period can only account for at most 1 ppbv of additional NO_2 . PAN abundances were likely higher in the fresher plume, but still not likely sufficient to be the sole source of the additional NO_2 ."

Lines 368-370: "we found the same enhancement in O3 for a given temperature when comparing smokeimpacted observations to smoke-free observations assigned to this cluster as we found for the complete dataset (Figures S9 and S10)." First, how can there be fewer datapoints within the "complete dataset" (N=30, Figure S10) than a cluster (N=33, Figure S9a)? Or should the complete dataset instead refer to Figure 6? In which case, the data do not support the claim. There is no discernible difference between smoke-free and smoke-impacted cases in Figure S9, certainly not a 10ppb increase on average for the smoke-influenced periods. Second, why was this cluster analysis limited to just 12:00-17:00? The northwesterly flow cluster was the only one with a meaningful number of data points during the smokey period, so why not use all of the data for a more robust comparison across the trajectory clusters?

The comparison is meant to be between each cluster and the complete dataset in Figure 6. The authors agree with the reviewer that since Figure 6 makes use of all hours, Figures S9 and S10 should plot all hours as well. We have updated the Figures in the SI, and stand by our conclusions.

Line 373: Include a citation.

This section has been revised in light of the change in focus from MDA8 as the definition of high ozone to the 95th percentile of daytime hourly average ozone values. This change is discussed more thoroughly in the response to the next question in this review.

Line 374-377: Is 65 ppbv MDA8 a formal definition of "high" ozone or was it defined by the authors? If the latter, why was this value chosen as a benchmark over the NAAQS value of 70ppb? Also, add more context for how these observations relate to the broader trends in the Colorado Front Range. How many ozone exceedance days are typical in the in this region annually? Is the frequency of high ozone days shown in Figure 7 a departure from "normal" conditions?

In reviewing the decision to choose a definition for "high" ozone the authors have decided to follow the empirical definition outlined by Cooper et al., 2012, in their paper on ozone trends across the U.S. Cooper et al., 2012, define "high" ozone as an hourly average mixing ratio that is greater than the 95th percentile of all hourly average ozone mixing ratios during daytime (11am – 4pm local time) within a given study period. Applying this criteria to our dataset we define a "high ozone day" as any day in our dataset having at least one hourly average ozone mixing ratio above this 95th percentile value, calculated using all available data in our study period. This results in 9 days being defined as "high ozone days" within our study period, with 2 of them falling within the August smoke-impacted period. We have updated Figure 7 accordingly.

We feel this is the correct method for defining a high O_3 day for two reasons. First, BAO is not an EPA designated O_3 NAAQS site, and the BAO O_3 data are not explicitly calibrated to the EPA O_3 calibration scale. Thus, while we can calculate the MDA8 values for the BAO O_3 data, we do not feel comfortable comparing these values to sites designed for regulatory purposes. Second, our definition uses an empirical technique to define a high O_3 day, reducing the subjectivity associated with otherwise choosing a value and aligning our results more evenly with existing literature.

In terms of interannual context, for the months of July and August in each year 2009-2015 we calculated the number of days that had a maximum hourly average O_3 mixing ratio greater than the "high O_3 day" 95th percentile threshold (71.75 ppbv) in our study period. The average number of high O_3 days within those two months for a given year is 15.7. 2015 was lower than this, with 9 high O_3 days, and was the second lowest year after 2009.

The updated section with all this information is copied below.

"Following the definition in (Cooper et al., 2012), we define a "high O_3 day" as any day in our study period with at least one hour above the 95th percentile (71.75 ppbv) of all 11am – 4pm MDT hourly average O_3 measurements during the campaign. We found 9 individual high O_3 days during our study period, of which 2 occurred during the August smoke-impacted period (Figure 7). The total number of high O_3 days is lower than normal for the same time period in previous years. As we stated above, high O_3 during the August smoke period was not a result of abnormal meteorological variables, such as higher than normal temperatures. The lower portion of Figure 7 again shows that maximum daily temperatures during the smoke-impacted periods were the same as or lower than maximum daily temperatures during the smoke-free period."

Line 395: Include a citation and brief description for OPE.

We have updated the discussion of OPE to include the citation of Trainer et al., 1993, and to briefly define the term ozone production efficiency. See edited passage below.

"One measure of local production of O_3 is the ozone production efficiency (OPE). OPE is calculated as the slope of the relationship between O_3 and NO_z (= $NO_y - NO_x$) (Trainer et al., 1993). OPE is a measure of how the number of molecules of O_3 that are produced before a given NO_x molecule is oxidized. To calculate OPE we used one minute O_3 and NO_z data in 30 minute chunks from 12PM - 5PM MDT. The slopes were calculated using a reduced major axis regression (package lmodel2 for R software) and only OPE values corresponding to an $R^2 > 0.3$ were retained. 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)."

Line 397-398: "Fully addressing the question of whether the smoke enhanced local O3 production in the polluted Front Range requires the use of a chemical transport model, and is beyond the scope of this work." There could still be some attempt made to qualitatively link together the observations for the precursors and resulting changes in ozone, which would go a long way toward improving the manuscript. In general, more consideration of chemistry in addition to meteorological variables would help.

We expanded our discussion of OPE and local ozone production in Section 4.3. See below for the added text.

"One measure of local production of O_3 is the ozone production efficiency (OPE). OPE is calculated as the slope of the relationship between O_3 and NO_2 (= $NO_y - NO_y$) (Trainer et al., 1993). OPE is a measure of how the number of molecules of O_3 that are produced before a given NO, molecule is oxidized. To calculate OPE we used one minute O₃ and NO₂ data in 30 minute chunks from 12PM - 5PM MDT. The slopes were calculated using a reduced major axis regression (package lmodel2 for R software) and only OPE values corresponding to an $R^2 > 0.3$ were retained. We do not find any significant differences in average calculated OPE between the smoke-impacted $(8 \pm 3 \text{ ppbv/ppbv})$ and smoke-free periods $(7 \pm 3 \text{ ppbv/ppbv})$. Thus from the OPE perspective it does not appear there were any changes in the local production efficiency of O_3 due to the presence of smoke. On the other hand, we documented many changes to the atmospheric composition of O_3 precursors, particularly with respect to CO, benzene, ethyne, the alkenes, and PANs. Additionally the smoke may added many O_3 precursors that we were not set up to measure (e.g. many OVOCs). Due to the nonlinear nature of O_3 chemistry, the different mix of precursors could have caused enhanced local O_3 production, depressed local O_3 production, or had no effect on local O_3 production. Taken together, the observations do not suggest a single mechanism that describes smoke influence on O_3 in Front Range airmasses during these case studies. Instead, the observations point to the presence of smoke resulting in a complex array of processes that will require more detailed observations and chemical transport modeling to clearly identify and quantify."

Figure 3. Out of the 40+ VOCs measured, why were these compounds chosen when most of them have other large sources in the area? Instead of the binary color scheme, can a colorscale be applied to show the percent change for each species?

These were species that showed significant changes between the August smoke-impacted period and the smoke-free period, which were the two periods during which valid VOC data were collected. The authors feel that a percent change colorscale would make this figure too complex to digest. We have referred readers to the summary of the full VOC dataset in Table S1 for specifics.

Figure 5: Do the color bands represent one standard deviation of each average diurnal cycle?

Yes, the shading represents one standard deviation. The figure caption has been amended to say this.

Technical corrections: Line 94 (and elsewhere): "1 μ m PTFE filter membrane" Do you mean the pore size, not the filter size, was 1 um?

The reviewer is correct, the filter pore size is $1 \mu m$. The text has been corrected. Other sentences that included a reference to filter size were likewise corrected.

The inlet was located 6 m above ground level (a.g.l.), and a PTFE filter membrane with 1 μ m pore size (Savillex) at the inlet was changed weekly.

Figure 1: Please include more tick marks on the date axis so that specific dates can be located on the traces.

Tick marks have been added identifying every 7 days in Figure 1, starting at the first of each month. More tick marks become crowded and distracting to the main point of the figure, which is to identify the smoke-impacted periods. The dates for these periods are labeled at the top of the figure and are specified in the text. The updated figure is below.



Figure 6: Can Fig. S4 be merged with this one so all of the data is included in a single plot? *This can be done. The updated Figure 6 is below.*



Figures S8 and S9: Arrange the panels in the same order.

Arrangement updated so that Figure S9 matches Figure S8. New Figure S9 is shown here.



Figures S9 and S10: Note more clearly in the caption which data are shown (e.g., afternoon only?). Also include labels for the data in the legend, not just the number of points.

We have updated the caption and made the requested changes to the original Figures S9 and S10.

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Changes in ozone and precursors during two aged wildfire smoke

2 events in the Colorado Front Range in summer 2015

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11 Abstract. The relative importance of wildfire smoke for air quality over the western U.S. is expected to increase as the

12 climate warms and anthropogenic emissions decline. We report on *in situ* measurements of ozone (O₃), a suite of volatile

13 organic compounds (VOCs), and reactive oxidized nitrogen species collected during summer 2015 at the Boulder

14 Atmospheric Observatory (BAO) in Erie, CO. Aged wildfire smoke impacted BAO during two distinct time periods during

15 summer 2015: 6 – 10 July and 16 – 30 August. The smoke was transported from the Pacific Northwest and Canada across

16 much of the continental U.S. Carbon monoxide and particulate matter increased during the smoke-impacted periods, along

17 with peroxyacyl nitrates and several VOCs that have atmospheric lifetimes longer than the transport timescale of the smoke.

18 During the August smoke-impacted period, nitrogen dioxide was also elevated during the morning and evening compared to

19 the smoke-free periods. There were <u>nine, empirically defined high O_3 days during our study period, at BAQ</u>, and two of these

20 days were smoke-impacted. We examined the relationship between O_3 and temperature at BAO and found that for a given

21 temperature, O₃ mixing ratios were greater (~10 ppbv) during the smoke-impacted periods. Enhancements in O₃ during the

August smoke-impacted period were also observed at two long-term monitoring sites in Colorado: Rocky Mountain National
 Park and the Arapahoe National Wildlife Refuge near Walden, CO. Our data provide a new case study of how aged wildfire

24 smoke can influence atmospheric composition at an urban site, and how smoke can contribute to increased O_3 abundances

25 across an urban-rural gradient.

26

5

27 Keywords. wildfire smoke, air quality, ozone, in situ observations, biomass burning

28 1 Introduction

29 Over the past 30 years, wildfires in the western U.S. have increased in both frequency and intensity, and this trend will likely

30 continue under future climate change (Westerling, 2016). Wildfire smoke can be transported over thousands of kilometers,

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Jakob Lindaas 6/23/2017 11:00 PM Deleted: six Jakob Lindaas 6/23/2017 11:02 PM Deleted: Jakob Lindaas 6/23/2017 11:02 PM Deleted: where the maximum 8-hour average O₃ at

BAO was greater than 65 ppbv

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37 and exposure to wildfire smoke has significant impacts on human health (Künzli et al., 2006; Rappold et al., 2011; Elliott et

38 al., 2013). While U.S. emissions of most major air pollutants are declining (Pinder et al., 2008), increasing fire activity

39 suggests that wildfires may have a greater relative impact on U.S. air quality in the future (Val Martin et al., 2015).

40

41 Ozone (O₃) is formed when hydrocarbons are oxidized in the presence of nitrogen oxides ($NO_x = NO + NO_2$) and sunlight (Sillman, 1999). Wildfires emit many trace gas species that contribute to tropospheric O₃ production. Along with carbon 42 monoxide (CO), methane (CH₄), and carbon dioxide (CO₂), hundreds of different non-methane volatile organic compounds 43 44 (NMVOCs) with lifetimes ranging from minutes to months (Atkinson and Arey, 2003) are emitted during biomass burning (Akagi et al., 2011; Gilman et al., 2015). Due to relatively large emissions of CO₂, CO, CH₄ and NO_x, the contribution of 45 46 VOCs to the total emissions from fires on a molar basis is small (<1%). However, VOCs dominate the OH reactivity in smoke plumes (Gilman et al., 2015). Recent observations of the evolution of VOCs within aging smoke plumes indicate that 47 OH can be elevated in young biomass burning plumes (Hobbs et al., 2003; Yokelson et al., 2009; Akagi et al., 2012; Liu et 48 al., 2016) in part due to the photolysis of oxygenated VOCs (Mason et al., 2001), which make a large contribution to the 49 total emitted VOC mass (Stockwell et al., 2015). Elevated OH may reduce the lifetime of emitted VOCs and increase 50 oxidation rates and potential O3 production. 51

52

53 Fires are also a major source of oxidized nitrogen; emissions from biomass and biofuel burning represent approximately 54 15% of total global NOx emissions (Jaegle et al., 2005). However, there are major uncertainties in NOx emission estimates 55 from biomass burning, particularly at a regional scale (Schreier et al., 2015). NO_x emissions depend on the nitrogen content of the fuel (Lacaux et al., 1996; Giordano et al., 2016) as well as the combustion efficiency (Goode et al., 2000; McMeeking 56 et al., 2009; Yokelson et al., 2009). Emitted NOx is quickly lost in the plume, either by conversion to HNO3 (Mason et al., 57 2001) or via PAN formation (Alvarado et al., 2010; Yates et al., 2016). HNO3 is not often observed in plumes because it 58 59 either rapidly forms ammonium nitrate or is efficiently scavenged by other aerosols (Tabazadeh et al., 1998; Trentmann et al., 2005). 60

61

62 There are multiple lines of observational evidence indicating that wildfires in the western U.S. increase the abundance of 63 ground level O3. Background O3 mixing ratios across the western U.S. are positively correlated with wildfire burned area (Jaffe et al., 2008), and daily episodic enhancements in O_3 at ground sites can be > 10 ppbv (Lu et al., 2016). There are well-64 65 documented case studies of within plume O₃ production (see Jaffe and Wigder (2012); Heilman et al. (2014), and references within) and time periods where smoke contributed to exceedances of the U.S. EPA National Ambient Air Quality Standard 66 67 (NAAQS) for O₃ (Morris et al., 2006; Pfister et al., 2008), currently a maximum daily 8 hour average of 70 ppby. Brey and Fischer (2016) investigated the impacts of smoke on O₃ abundances across the U.S. via an analysis of routine in situ 68 69 measurements and NOAA satellite products. Their analysis demonstrated that the presence of smoke is correlated with 70 higher O3 mixing ratios in many areas of the U.S., and that this correlation is not driven by temperature. Regions with the

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72 largest smoke-induced O3 enhancements (e.g. the southeast and Gulf coast) can be located substantially downwind of the

- 73 wildfires producing the most smoke.
- 74

75 Despite several recent studies showing that smoke contributes to elevated O₃, there have been relatively few detailed studies

76 of wildfire smoke mixing with anthropogenic air masses near the surface. Morris et al. (2006) demonstrated that smoke from

77 wildfires in Alaska and Canada exacerbated ozone pollution in Houston during two days in July 2004, but did not have in

78 <u>situ measurements of other chemical species apart from O₃</u>. Singh et al. (2012) used aircraft measurements from summer

79 2008 over California to document significant O₃ enhancements in nitrogen-rich urban air masses mixed with smoke plumes.

80 Accompanying air quality simulations were not successful in capturing the mechanisms responsible for these enhancements.

81 In general, measurements of O_3 precursors are hard to make routinely. Instrumentation and calibration methods tend to be

82 time and labor intensive, and thus unpredictable wildfire smoke plumes and their effects on surface O₃ are sparsely sampled.
83

84 Here we present a case study of aged wildfire smoke mixed with anthropogenic pollution in the Colorado Front Range and

85 show its impact on atmospheric composition and O₃. The Northern Colorado Front Range region, violates the NAAQS for

86 O₃, and has been the focus of several recent studies (e.g. McDuffie et al., 2016; Abeleira et al., 2017). First we describe the

87 research location and measurements. Next, we identify the smoke-impacted time periods and show the origin, approximate

88 age, and wide horizontal extent of the smoke plumes. We characterize significant changes in atmospheric composition with

89 respect to the two major classes of O₃ precursors, VOCs and oxidized reactive nitrogen (NO_y). Finally, we present the impact

90 of smoke on O_3 abundances during this period and discuss the underlying causes of this impact.

91 2 Measurements and Research Site

During summer 2015, we made measurements of a suite of trace gases at the Boulder Atmospheric Observatory (BAO), 92 93 located north of Denver, CO, in the middle of the rapidly developing northern Colorado Front Range [40.05°N, 105.01°W, 1584m ASL]. BAO has a history of atmospheric trace gas and meteorological measurements stretching back nearly four 94 95 decades (Kelly et al., 1979; Gilman et al., 2013). Our research campaign from 1 July - 7 September 2015 measured a suite 96 of O₃ precursor species as well as several NO_x oxidation products and greenhouse gases. The intended goal of the field 97 campaign was to improve our understanding of the complex O₃ photochemistry in the Colorado Front Range and the 98 contributions of oil and natural gas activities as well as other anthropogenic emissions to O₃ production. All measurements 99 were made by instruments housed in two trailers located at the base of the BAO tower. Here we briefly describe the 100 measurements used in this paper. Data are available at https://esrl.noaa.gov/csd/groups/csd7/measurements/2015songnex/. 101

We measured CO and CH_4 at ~3 second time resolution with a commercial cavity ring-down spectrometer (Picarro, model G2401) (Crosson, 2008). The inlet was located 6 m above ground level (a.g.l.), and a PTFE filter membrane with 1 μ m pore

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107size(Savillex) at the inlet was changed weekly. Laboratory instrument calibrations were performed pre- and post-campaign108using three NOAA standard reference gases (http://www.esrl.noaa.gov/gmd/ccl/refgas.htmls; CA06969, CB10166, and109CA08244). Field calibration was performed every 3 hours using high, low and middle reference gas mixtures (Scott Marin110Cylinder IDs CB10808, CB10897, CB10881). Mixing ratios were calculated using the WMO-CH4-X2004 and WMO-CO-111X2014 scales. The uncertainty associated with the CH4 and CO data is estimated to be 6% and 12% respectively, and it was112estimated as the quadrature sum of measurement precision, calibration uncertainty and uncertainty in the water vapor113correction.114

- A custom 4-channel cryogen-free gas chromatography (GC) system (Sive et al., 2005) was used to measure selected non-
- 116 methane hydrocarbons (NMHCs), $C_1 C_2$ halocarbons, alkyl nitrates (ANs), and oxygenated volatile organic compounds

117 (OVOCs) at sub-hourly time resolution; approximately one sample every 45 minutes. The inlet was located at 6 m a.g.l. with 118 a 1 um pore size teflon filter. Ambient air for each sample was collected and pre-concentrated over 5 minutes, with a one

118 a 1 µm pore size teflon filter. Ambient air for each sample was collected and pre-concentrated over 5 minutes, with a one

119 Jitre total sample volume. A calibrated whole air mixture was sampled in the field after every ten ambient samples to monitor 120 sensitivity changes and measurement precision. A full description of this instrument and the associated uncertainties for

- 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).
- 122

123 Ozone data at BAO for this time period were provided by the NOAA Global Monitoring Division surface ozone network 124 (McClure-Begley et al., 2014; data available at aftp.cmdl.noaa.gov/data/ozwv/SurfaceOzone/BAO/). Ozone was measured 125 via UV-absorption using a commercial analyzer (Thermo-Scientific Inc., model 49), which is calibrated to the NIST standard 126 over the range 0 - 200 ppbv and routinely challenged at the site. The inlet height was 6m a.g.l. on the BAO tower, located 127 about 50 feet from the two trailers, and measurements were reported at a 1 minute averaging interval with an estimated error 128 of 1%.

129

Nitrogen oxides (NOx=NO+NO2) and total reactive nitrogen (NOy) were measured via NO-O3 chemiluminescence detection 130 (Kley and McFarland, 1980) using a commercial analyzer (Teledyne, model 200EU). Two commercial converters, a 395 nm 131 132 -LED converter (Air Quality Designs, Inc., model BLC) for chemically-selective photolysis of NO2 to NO and a molybdenum in stainless steel converter (Thermo Scientific Inc.) heated to 320 °C for reduction of NO_y to NO, were 133 134 positioned as close to the inlet tip as possible (<10 cm). A 7 µm stainless steel particulate filter was affixed to the upstream end of the molybdenum converter; otherwise no other filters were used. The analyzer switched between sampling from the 135 LED (NO_x) converter and the molybdenum (NOy) converter every 10 seconds, and the LEDs were turned on (to measure 136 137 NO+NO2) and off (to measure NO only) every minute. NO2 was determined by subtraction of measured NO from measured NO+NO2 divided by the efficiency of the LED converter. All three species are reported on a consistent two-minute average 138 139 timescale. The detector was calibrated daily by standard addition of a known concentration of NO, NIST-traceable (Scott-Marrin Cylinder ID CB098J6), to synthetic ultrapure air. Both converters were calibrated with a known concentration of NO₂ 140

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144 nitric acid (HNO₃) generated using a permeation tube (Kintech, 30.5 ± 0.8 ng/min at 40 °C), which was used to confirm

145 >90% conversion efficiency of HNO₃ by the molybdenum converter. Uncertainties of \pm 5% for NO, \pm 7% for NO₂, and \pm 20%

146 for NO_v are determined from a quadrature sum of the individual uncertainties associated with the detector, converters, and

147 calibration mixtures; an LOD of 0.4 ppbv for all species is dictated by the specifications of the commercial detector.

148

149 Peroxyacyl nitrates (PANs) were measured using the National Center for Atmospheric Research gas chromatograph with an

150 electron capture detector (NCAR GC-ECD) (Flocke et al., 2005). The instrument configuration was the same as was used

during the summer 2014 FRAPPE field campaign (Zaragoza, 2016). The NCAR GC-ECD analyzed a sample every five

152 minutes from a 6 m a.g.l. inlet with 1µm pore size teflon filter. A continuous-flow acetone photolysis cell generated a known

153 quantity of PAN used to calibrate the system at 4-hour intervals.

154

An Aerodyne dual quantum cascade laser spectrometer was used to measure HNO₃ (McManus et al., 2011). The instrument employed a prototype 400 m absorption cell for increased sensitivity during the first month of the campaign, after which it was replaced by a 157 m absorption cell. An active passivation inlet (Roscioli et al., 2016) was used to improve the time response of the measurement to ~0.75 s. This technique utilized a continuous injection of 10-100 ppb of a passivating agent vapor, nonafluorobutane sulfonic acid, into the inlet tip. The inlet tip was made of extruded perfluoroalkoxy Teflon (PFA), followed by a heated, fused silica inertial separator to remove particles larger than 300 nm from the sample stream. The inlet was located 8 m a.g.l. with a 18 m heated sampling line (PFA, 1/2" diameter OD) to the instrument. The system was

162 calibrated every hour by using a permeation tube that was quantified immediately prior to the measurement period.

163 3 Smoke Events

We observed two distinct smoke-impacted periods at BAO, identified by large enhancements in CO and fine aerosol (PM25). 164 Figure 1 presents CO observations from BAO and fine particulate matter (PM2.5) observations from the Colorado 165 Department of Public Health and Environment (CDPHE) CAMP air quality monitoring site (www.epa.gov/airdata), located 166 in downtown Denver, approximately 35km south of BAO. PM2.5 was similarly elevated during the smoke-impacted periods 167 at nine other_CDPHE monitoring sites across the Colorado Front Range: BOU, CASA, CHAT, COMM, FTCF, GREH, 125, 168 169 LNGM, NJH (not shown). For our analysis, we defined a July smoke-impacted period and an August smoke-impacted period. The July smoke-impacted period lasted for 4 days from 00 MDT 6 July 2015 to 00 MDT 10 July 2015. The August 170 171 smoke-impacted period was significantly longer (~14 days). For the subsequent analysis, we combined three distinct waves of smoke-impact in this 14 day period into one August smoke-impacted period: 00 MDT 16 August 2015 - 18 MDT 21 172 August 2015, 12 MDT 22 August 2015 - 18 MDT 27 August 2015, and 14 MDT 28 August 2015 - 09 MDT 30 August 173

- 2015. We omitted the brief periods between these times from the analysis due to uncertainty on the influence of smoke 174
- 175 during them. All other valid measurements were considered part of the smoke-free data.
- 176

- 177 Figure 2 presents the extent of the presence of smoke in the atmospheric column during representative smoke-impacted days, 178 7 July and 21 August 2015. The NOAA Hazard Mapping System smoke polygons show that the smoke events observed at 179 BAO were large regional events. The HMS smoke product is produced using multiple NASA and NOAA satellite products, 180 (Rolph et al., 2009). Smoke in the atmospheric column is detected using both visible and infrared imagery and is fully 181 described in Brey et al. (2017). The extent of smoke plumes within the HMS dataset represents a conservative estimate, and 182 no information is provided on the vertical extent or vertical placement of the plumes. Figure 2 also shows active MODIS fire 183 locations for the previous day (Giglio et al., 2003; Giglio et al., 2006) and 5 day NOAA Air Resources Laboratory, Hybrid 184 Single Particle Lagrangian Integrated Trajectory (HYSPLIT) back trajectories initialized each hour of the day from BAO at 185 1000m above ground level (Stein et al., 2015). Trajectories were run using the EDAS (Eta Data Assimilation System) 40 km 186 x 40 km horizontal resolution reanalysis product (Kalnay et al., 1996). In total, Figure 2 demonstrates that the smoke that 187 impacted BAO during both periods was transported from large extreme fire complexes in the Pacific Northwest and Canada, 188 with approximate transport timescales on the order of two to three days. Front Range surface temperatures were not 189 anomalously high in July and August 2015 based on a comparison of reanalysis data for this period to the 1981 - 2010 190 climatology. Surface precipitation, surface relative humidity, and soil moisture in the Front Range were all lower than this
- 191 referent period. The extreme fires in Washington and Idaho were associated with warmer and dryer than average summer
- 192 temperatures in the Pacific Northwest (Kalnay et al., 1996). Creamean et al. (2016) provide a more detailed description of
- 193 smoke transport and the sources of the aerosols associated with the August smoke-impacted period. Summer 2015 was the
- 194 largest wildfire season in Washington, and the Okanogan Complex fire, which likely contributed to the smoke observed at
- 195 BAO, was the largest fire complex in state history. Summer 2015 was also one of the largest fire seasons for northern Idaho,
- 196 with approximately 740,000 acres burned.

197 4 Observed Changes in Ozone and its Precursors

198 4.1 CO, CH₄, and VOC Abundances

199 We quantified CO, CH₄, and 40+ VOC species including C₂-C₁₀ non-methane hydrocarbons (NMHCs), C₁-C₂ halocarbons,

and several oxygenated species (methyl ethyl ketone, acetone, and acetaldehyde) at BAO. The focus of the BAO field 200

- 201 intensive was to study the photochemistry of local emissions from oil and gas development (e.g. Gilman et al., 2013;
- 202 Swarthout et al., 2013; Thompson et al., 2014; Abeleira et al., 2017), and the GC system was not set up to quantify species
- 203 with known large biomass burning emission ratios (e.g. hydrogen cyanide, acetonitrile, most oxygenated organic species) 204
- (Akagi et al., 2011). The chromatograms were checked for HCN and acetonitrile peaks after the campaign but those peaks
- 205 were not able to be identified. In addition, early campaign issues with the online multichannel gas chromatography system

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compromised the data for the July smoke period and thus we restrict our comparison of VOCs in smoke-free versus smokeimpacted periods to a comparison between 16 – 30 August, the *August smoke-impacted period*, and 24 July – 16 August, the *smoke-free period*. The brief smoke-free times during 16 – 30 August (denoted by white between the red shading in Figure 1) were not included in either period since it is difficult to determine whether they were smoke-impacted. GC measurements were made approximately every <u>45 minutes and we compared 251 measurements of VOCs during the August smoke-period</u> to 583 measurements during the smoke-free period. A statistical summary of all VOC measurements for each period is available in Table S1 in the supplement.

In this section, we describe significant changes in VOC abundances and notable exceptions. The HYSPLIT trajectories (Figure 2) suggest that the age of the smoke impacting the Front Range during the August smoke-period was 2-3 days. We

231 observed enhancements in the abundances of CO, CH₄, and VOCs with lifetimes longer than the transport time of the smoke, 232 with the exception of some alkanes that have a large background concentration in the Front Range due to emissions from oil

and gas production. Three of the alkenes we quantified (isoprene, ethene, and propene) were generally near the limit of

234 detection during the August smoke-impacted period, although notably cis-2-butene abundances were not changed.

235 Significant differences were not observed in the four oxygenated VOCs quantified between smoke-impacted and smoke-free 236 periods.

237

238 Mean hourly CO mixing ratios were significantly enhanced by 223 ppbv, or 170% during the July smoke-impacted period 239 and by <u>92</u> ppbv, or <u>70</u>%, during the August smoke-impacted period (Figure 1). This enhancement was present across the 240 diurnal cycle (Figure 3) and a both smoke periods displayed a higher range of CO mixing ratios (July: 127 - 639 ppby, 241 August: <u>J01 – 529 ppbv, smoke-free: J2 – 578 ppbv). The two smoke periods differed in their sources fires, length, and</u> 242 meteorology, with higher average CO and PM2.5 measurements in the July smoke period (Figure 1). Average enhancements 243 of CH₄ were similar for both periods (July: 52 ppbv, August: 50 ppbv, or ~ 2.5% increase). Methane has a relatively high background at BAO due to large emissions of CH4 in nearby Weld County from livestock production and oil and gas 244 development (Pétron et al., 2014; Townsend-Small et al., 2016). Taken together, the larger background of CH₄ and the large 245 246 local sources of CH₄ in the Front Range served to mute the impact of the August smoke on overall CH₄ abundances. The 247 diurnal cycle of CH4 did not change during the smoke-impacted period as compared to the smoke-free period and we observed a similar range of mixing ratios (\sim 1,840 – 3,360 ppbv) in the both smoke-free and smoke-impacted periods. We 248 249 note several large spikes in CH₄ on the order of minutes during the August smoke-impacted period, but we do not believe 250 that these are related to the presence of smoke because they were not correlated with similar excursions in CO and PANs, 251 and exhibited strong correlations with propane and other tracers of oil and gas and other anthropogenic activity. Due to the 252 availability of valid data, the rest of the discussion on VOC composition will focus on changes during the August smoke-253 impacted period. 254

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271 Similar to CO, ethane has an atmospheric lifetime on the order of a month during summertime at mid-latitudes (Rudolph and 272 Ehhalt, 1981) and is emitted by wildfires (Akagi et al., 2011). However, average ethane mixing ratios were not higher during 273 the August smoke-impacted period compared to the smoke-free period. One potential reason for this may be the large local sources of alkanes from oil and natural gas activities within the Denver-Julesberg Basin which contribute to relatively high 274 275 local mixing ratios of these species (Gilman et al., 2013; Swarthout et al., 2013; Thompson et al., 2014; Abeleira et al., 2017). The range of ethane mixing ratios observed at BAO was also not different between smoke-free (0.3 - 337 ppbv) and 276 277 smoke-impacted periods $(1 - 362 \text{ ppbv})_{\pm}$ Similarly, we did not observe significant changes in most of the C₃-C₉ alkanes we 278 measured. Figure 3 shows there were two exceptions to the general alkane observations: 2-methylhexane showed a 279 significant decrease in average abundances (-39 pptv or -45%) and 3-methylhexane showed a significant increase (63 pptv or 280 75%) during the smoke-impacted period, despite both having similar smoke-free abundances and similar rate constants for reaction with the hydroxyl radical (OH; $k_{OH} \sim 7 \times 10^{12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$). 281 282 283 The atmospheric lifetimes of the four alkenes we quantified (isoprene, propene, ethene, and cis-2-butene) range from tens of 284 minutes to hours. Surprisingly, we observed significant decreases in the abundance of isoprene, propene and ethene during 285 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 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.

292 293 Our first hypothesis is that fewer anthropogenic emissions of these alkenes drove the observed decreases in alkene 294 abundances. However, there is no evidence that anthropogenic emissions were different during the August smoke-impacted 295 period. Specifically, the August smoke-impacted period encompassed both weekdays and weekends and did not contain any 296 state or federal holidays. Therefore we move to our second hypothesis, that changes in the biogenic emissions of alkenes 297 accounted for the decreased alkene mixing ratios. Isoprene is widely known to be emitted by broad leaf vegetation, and 298 emission rates are positively correlated with light and temperature, (Guenther et al., 2006). Recent measurements quantified 299 ethene and propene emissions from a ponderosa pine forest near Colorado Springs, CO, with an inter-daily light and 300 temperature dependence similar to isoprene (Rhew et al., 2017). Interestingly, emissions and mixing ratios of ethene and 301 propene were not closely correlated with isoprene within the diurnal cycle, indicating they have different vegetative/soil 302 sources than isoprene at that site. Ponderosa pine stands are present in the foothills on the western edge of the plains in the 303 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 8

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Deleted: but the amplitude of the median diurnal cycle was dampened during the August smoke impacted period (not shown). Median morning ethane mixing ratios were $\sim 10 - 20$ ppbv less during smoke-impacted than smoke-free periods, while afternoon and evening median mixing ratios were ~5 10 ppbv larger. Most of the C₃ – C₉ alkanes we quantified showed similarly dampened amplitudes in their median smoke-period diurnal cycles. A consistently lower planetary boundary layer (PBL) height during the day and a consistently higher boundary layer at night is one potential explanation for these observations; however an estimate of the PBL height in the grid box surrounding BAO from the North American Regional Reanalysis product (Mesinger et al., 2006) did not show any significant changes in PBL height between the smoke-impacted and smoke-free periods. Likewise estimated PBL heights following methods from Coniglio et al. (2013) and using atmospheric soundings at 0Z and 12Z in Denver

(http://mesonet.agron.iastate.edu/archive/raob/) did not show any differences between smoke-impacted and smoke-free periods (Figures S1 and S2).

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338 smoke-impacted period was on average colder than the smoke-free period, and potentially saw a reduction in photosynthetic 339 active radiation (PAR) at the surface due to the increased number of aerosols, it is possible that biogenic emissions of 340 isoprene, ethane, and propene were suppressed. However, biogenic fluxes of these compounds are unavailable for the region 341 around BAO during summer 2015, and extrapolating emissions from one ponderosa pine stand to the rest of the Front Range 342 may be overly ambitious. Further, we note that a PMF analysis of the VOC data from this site did produce a 'biogenic factor' 343 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., 2017). Thus, while the hypothesis that smoke suppressed biogenic emissions 344 345 remains feasible, we will consider other potential causes for the observed decrease in alkene abundances. 346

The alkenes we measured all have high reactivities with respect to OH (> 8 x 10^{12} molec⁻¹ cm³ s) and O₃ (> 0.1 x 10^{17} 347 348 molec⁻¹ cm³ 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-349 impacted period was characterized by higher than normal OH mixing ratios, then a third hypothesis is that the observed 350 351 decreases in alkene abundances could be due to a higher oxidation rate by OH due to higher OH concentrations. However, 352 other measured VOCs such as o-xylene or methylcyclohexane have similar OH reactivities to ethene (Atkinson and Arey, 353 2003), and we do not see associated decreases in abundances of these other VOCs. Thus, the hypothesis of increased 354 oxidation by OH causing decreased alkene abundances in the August smoke period is not supported by the full suite of 355 measurements at BAO.

357 Lastly, we move on to our final hypothesis. Alkenes have much higher rates of reaction with O₃ than the other VOCs we 358 quantified. As we will demonstrate in Section 4.3, the August smoke-impacted period was characterized by higher O3 359 abundances than would otherwise be expected. Therefore, the fourth hypothesis regarding decreased alkene abundances is 360 that enhanced alkene oxidation by O3 decreased the observed mixing ratios. Two factors complicate this hypothesis though. 361 First, we do not observe a negative relationship between O3 and alkene abundance during the smoke-free time periods (i.e. 362 increased O₃ is not correlated with decreased alkenes when no smoke is present). Second, despite having a higher reaction 363 rate with O3 compared to propene and ethene, cis-2-butene does not decrease during the August smoke-impacted periody 364 365 After careful consideration, there is no strong evidence supporting any of these four hypotheses over the others (suppressed 366 anthropogenic emissions, suppressed biogenic emissions, increased OH, increased O₃). It is possible that more than one of 367 these processes could have contributed to the observation of decreased alkene abundances during the 2 week-long August 368 smoke-influenced period. Future field campaigns and modeling work are necessary to understand how common suppressed

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alkene abundances may be in smoke-impacted airmasses, and what processes might control this phenomenon.

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Deleted: These alkenes were among the most reactive species quantified, and one potential explanation for the reduced abundance of these species during the smoke-impacted period is enhanced oxidation capacity linked to the presence of smoke. However, we do not observe decreased abundances of cis-2-butene, which has a comparable OH-reactivity to propene(Atkinson and Arey, 2003) and lower average abundance. An alternative hypothesis for the reductions in the other three alkene species may be reductions in local biogenic emissions during the smoke-impacted period either due to lower air temperatures or due to a reduction in photosynthetic active radiation (PAR) at the surface during the August smoke-impacted period. Isoprene is emitted by However, while we did observe lower average daytime temperatures at BAO during the August smoke-impacted period compared to the rest of the dataset (-2.3°C), the majority of Front Range emissions of propene and ethene are likely from anthropogenic sources. Thus this hypothesis could possibly help explain reduction in isoprene but not likely explain reductions in ethene and propene Shifts in local transport could also help explain differences but we did not observe any consistent shifts in wind direction or changes in wind speed that would indicate consistently different local transport during the August smoke-impacted period

The only alkyne measured was ethyne. Ethyne is emitted by wildfires (Akagi et al., 2011) and has a lifetime of ~1 month during summer. We observed a significant increase in the abundance of ethyne during the August smoke-impacted period.

402 These enhancements were small in absolute mixing ratio (0.163 ppbv), but represented a large percentage increase (67%)

403 and were consistently present throughout the day.

404

It is well known that wildfires produce carcinogenic aromatic hydrocarbons including benzene (Fent et al., 2014). During the smoke-impacted periods, we observed significantly enhanced benzene throughout the day with an average increase of 0.117 ppbv and a percentage increase of 67%. These enhancements followed the pattern of CO and ethyne; there were consistent increases throughout the day and the diurnal cycle retained its shape. Wildfires also produce toluene (Fent et al., 2014); however, it has a substantially shorter lifetime (< 2 days) than benzene (~12 days). Toluene showed no significant changes in its mean mixing ratio, diurnal cycle, or range of values measured at BAO during the smoke-impacted periods. The other aromatic hydrocarbons we quantified (o-xylene and ethyl-benzene) also did not change significantly.</p>

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413 As mentioned in Section 1, oxygenated VOCs are emitted by wildfires and make a large contribution to the total emitted

- 414 VOC mass in wildfire smoke (Stockwell et al., 2015). Additionally they are produced as oxidation intermediates (Atkinson 415 and Arey, 2003). Acetaldehyde, acetone, and methyl ethyl ketone (MEK) showed no consistent changes in their abundances, 416 diurnal cycles, or range during the smoke-impacted period compared to the smoke-free period. Small increases in average
- 417 acetone (~350 pptv) and MEK (~150 pptv) mixing ratios during late afternoon and evening hours were not statistically
 418 significant.
- 419

Given the diversity of emission sources across the northern Colorado Front Range, previous studies of atmospheric composition at BAO have noted a strong dependence of VOC composition on wind direction (Pétron et al., 2012; Gilman et al., 2013). Recent housing development and oil and gas production surrounding the BAO site have made analyses based on wind direction more challenging in recent years (McDuffie et al., 2016). Importantly for our analysis, we found that the statistically significant changes in all species during the smoke-impacted periods occurred across all wind directions. Figure 425 4 shows this for two representative species: benzene and NO₂. We also did not find statistically significant changes in wind direction or wind speed patterns between smoke-free and smoke-impacted periods. Thus, we attribute the changes in

427 atmospheric composition during the August smoke-impacted period to the presence of smoke.

428 4.2 Reactive Oxidized Nitrogen (NO_y) Species

429 Peroxyacyl nitrates and HNO₃ were successfully measured from 10 July - 7 September and alkyl nitrates were measured

430 from 24 July – 30 August. Thus we report significant changes in these species for the August smoke-impacted period only.

431 We observed significant enhancements in both peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) during the

432 August smoke-impacted period. PAN and PPN abundances were consistently elevated across the day by an average of 183

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NO and NO₂ measurements were made during the entire campaign, 1 July – 7 September 2015, so both the July and August smoke-impacted periods were analyzed with respect to potential changes in NO_x. NO was present in the same abundances between the two periods and showed the same diurnal cycle during the August smoke-impacted period as compared to the smoke-free period (Figure 5). During the July smoke-impacted period the morning build_up of NO was slower than the smoke-free period, though the mixing ratios were within the range of smoke-free values and <u>the duration of the July smoke-</u> <u>impacted period was much shorter than the</u> August smoke-impacted period.

450

451 Figure 5 shows that NO₂ abundances exhibited more significant changes than NO. During the July smoke-impacted period, 452 NO₂ was within the range of smoke-free measurements. In contrast NO₂ during the August smoke-impacted period followed 453 the same diurnal cycle but had pronounced significant increases in average mixing ratios during the morning and evening 454 hours of ~8 ppbv (17%) following sunrise and 3 ppbv (60%) following sunset. These enhanced peak abundances appeared 455 during multiple days during the August smoke-impacted period. Out of 7 morning peaks in NO2 during the August smoke-456 impacted period, 3 had concurrent toluene and ethyne peaks. One of these days occurred on a weekend, and the others 457 occurred on weekdays. Toluene and ethyne are common tracers of traffic/industrial emissions. However, 4 of the days did 458 not have corresponding ethyne and toluene peaks. Thus, we can't rule out that traffic did not impact some of the NO2 459 enhancements we observed, however there is also likely another contributing mechanism. There are a few potential 460 hypotheses for a non-traffic related NO₂ enhancement during the August smoke period. One hypothesis is that the photolysis 461 frequency (J_{NO2}) was most impacted (i.e. reduced) by the smoke near sunrise and sunset. Another hypothesis concerns the 462 equilibrium between PAN and NO2, The thermal decomposition of PAN can be a source of NO2 (Singh and Hanst, 1981), 463 but the concurrently observed PAN abundances during the August smoke-impacted period can only account for at most 1 ppbv of additional NO2. However, there could have been significantly higher PAN abundances in the smoke plume prior to 464 465 reaching BAO so this hypothesis for the NO2 enhancements cannot be fully ruled out. We do not have measurements of

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other reactive nitrogen species (e.g. HONO, CINO₂, NO₃, and N₂O₅) to test <u>other potential hypotheses for a different</u>
 chemical mechanism to explain the observed NO₂ enhancements.

490 4.3 Ozone

within the smoke plume.

As discussed in the introduction, wildfire smoke has been found to produce O_3 within plumes and to be correlated with enhanced surface O_3 in areas to which it is advected. The total amount of O_3 at a location is a complex combination of the relative abundances of VOCs and NO_x , meteorological conditions supporting local O_3 production, and the amount of O_3 present in the air mass before local production. In this section, we describe the significant increases in O_3 during both smokeimpacted periods, show that these enhancements were most likely not due to changes in meteorological conditions, and discuss evidence pointing to whether these changes may be due to enhanced local production or transport of O_3 produced

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Figure 5d shows that there were significant increases in O_3 mixing ratios during nighttime and midday during the August smoke-impacted period compared to the average smoke-free diurnal cycle. The mean O_3 mixing ratio across all hours of the day was 6 ppbv (14%) larger during the August smoke-impacted period than the smoke-free period (Figure 6), significant at the 99% confidence level based on a two-sample difference of means t-test. There were no significant changes in the average O_3 mixing ratios during the July smoke-impacted period (Figure 5a). The average mixing ratio of O_3 during the July smokeimpacted period was not greater than absolute average during the smoke-free period (Figure 5a). However, as discussed in Section 2, this period in particular was much colder on average than the smoke-free period.

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507 O3 mixing ratios generally increase with temperature, and this relationship has been attributed to several specific processes 508 including 1) warm and often stagnant anti-cyclonic atmospheric conditions that are conducive to O₃ formation, 2) warmer air 509 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, 510 511 Abeleira and Farmer (2017) show that ozone in in this region has a temperature dependence, but it is smaller than other U.S. 512 regions, consistent with the smaller local biogenic VOC emissions compared to many other locations in the eastern U.S. 513 Finally, there is an additional meteorological factor in the Front Range that can impact the temperature dependence of ozone. 514 Gusty westerly winds are often associated with high temperatures, and these winds serve to weaken or eliminate cyclical 515 terrain-driven circulations that normally enhance Osmixing ratios across the Front Range. Figure 6 presents hourly average 516 O₃ and temperature at BAO and shows a positive relationship between O₃ and temperature for both the smoke-free period 517 and August smoke-impacted period. The increase in O₃ mixing ratios during the August smoke-impacted period compared to 518 the smoke-free period is present across the entire range of comparable temperatures. The same result is apparent during the 519 July smoke-period, where, for comparable temperatures, the July smoke-period has higher O3 than would be expected from 520 the O₃-temperature relationship during the smoke-free period. Across both smoke-impacted periods and for a given

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temperature, the magnitude of the increase in average O_3 was 10 ± 2 ppby. This was calculated as the mean difference 529 530 between medians within each temperature bin weighted by the total number of hourly measurements within each bin. The 531 weighted standard deviation was calculated in the same way. The magnitude of this difference is greater than the average difference in means between the smoke-free O3 mixing ratios and the August smoke-impacted period because there were 532 533 several periods during the July and August smoke-impacted period where air temperatures were colder (~ 5°C) than most observations during the smoke-free period. Thus the lower O3 mixing ratios associated with these smoke-impacted periods 534 $(e.g. \sim 20 - 40 \text{ ppbv})$ were not included in the weighted difference in medians since there were not commensurate smoke-free 535 536 O3 measurements at those same temperatures.

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538 In addition to a positive relationship with surface temperature, elevated O_3 in the western U.S. has also been found to be 539 correlated with monthly average 500 hPa geopotential heights, 700 hPa temperatures, and surface wind speeds on an 540 interannual basis (Reddy and Pfister, 2016). We tested the day-to-day variability in the relationship between O₃ and these 541 meteorological variables during our study period using observations from the 0Z and 12Z atmospheric soundings conducted 542 in Denver (http://mesonet.agron.iastate.edu/archive/raob/). The positive relationships between MDA8 O3 and 700 mb temperature, 500 mb geopotential height, and surface winds are very weak, $R^2 = 0.04$, and $R^2 = 0.08$, and $R^2 = 0.0009$ 543 544 respectively. Thus, we did not find any evidence to support the hypothesis that differences in meteorological conditions were 545 solely responsible for the significant differences in composition or O_3 that we observed during the smoke-impacted period. 546

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547 To determine if a change in synoptic scale transport in smoke-impacted versus smoke-free periods could have contributed to different abundances, we performed a k-means cluster analysis on 72-hour HYSPLIT back trajectories. The trajectories were 548 calculated using the methods described above, and initiated each hour at 2000 m a.g.l. from BAO. We chose to initialize the 549 550 trajectories at 2000 m a.g.l so that fewer trajectories intersect the ground in the Rocky Mountains. Trajectories are unlikely 551 to capture the complex circulations (e.g. potential Denver Cyclones or up/down slope winds) characteristic of summertime in the Front Range, but they should capture synoptic scale air mass motions. The k-means analysis clustered each trajectory 552 into a predetermined number of clusters by minimizing the distance between each trajectory and its nearest neighbor; this 553 554 technique has been used to classify air mass history in air quality studies (Moody et al., 1998). We found 4 predominate 555 trajectory clusters during our study period: northwesterly flow, westerly flow, southwesterly flow, and local/indeterminate flow (Figure S2). We then compared afternoon (12PM - 5PM MDT) hourly O3 measurements separated by trajectory cluster 556 557 and binned by temperature between the smoke-free period and the August smoke-impacted period. Most hours during the 558 August smoke-impacted period were associated with northwesterly flow and we found the same enhancement in O₃ for a 559 given temperature when comparing smoke-impacted observations to smoke-free observations assigned to this cluster as we 560 found for the complete dataset (Figures S3, and 6). Thus we conclude that potential changes in O3 driven by synoptic scale 561 transport conditions cannot account for the observed O3 enhancements during the August smoke-impacted period at BAO.

579	Following the definition in (Cooper et al., 2012), we define a "high O ₃ day" as any day in our study period with at least one	Emily Fischer 6/23/2017 9:36 PM
580	hour above the 95 th percentile (71.75 ppbv) of all 11am – 4pm MDT hourly average O ₃ measurements during the campaign.	Deleted: ozone
581	We found 9 individual high O ₃ days during our study period, of which 2 occurred during the August smoke-impacted period	Emily Fischer 6/23/2017 9:36 PM
582	(Figure 7). The total number of high O ₃ days is lower than normal for the same time period in previous years. As we stated	Emily Fischer 6/23/2017 9:36 PM
583	above, high O ₃ during the August smoke period was not a result of abnormal meteorological variables, such as higher than	Deleted: ozone
584	normal temperatures. The lower portion of Figure 7 again shows that maximum daily temperatures during the smoke-	Emily Fischer 6/23/2017 9:36 PM
585	impacted periods were the same as or lower than maximum daily temperatures during the smoke-free period. Denver	Deleted: ozone
505	avalance and in basis wind netterns can also contribute to 0, production and to circulation in the Erent Dance (see Sulliver	Emily Fischer 6/23/2017 9:36 PM
500	cyclones and in-basin which patterns can also contribute to O ₂ production and re-circulation in the Profit Range (see Sunvan	Emily Fischer 6/29/2017 9:51 PM
587	et al. (2016), Vu et al. (2016) and references within). We examined surface wind observations (http://mesowest.utah.edu) on	Deleted: "
588	the 2 high O ₃ days during the smoke impacted period: 20 August and 25 August. There is no evidence of the establishment	Emily Fischer 6/23/2017 9:37 PM
589	of Denver Cyclones on either of these days. Sullivan et al. (2016) point out that thermally driven recirculation can manifest	Deleted: For broader spatial context on high ozone days within the Front Range
590	as a secondary increase in O3 at surface sites. We did observe a secondary maxima at 17:00 MT on 25 August, but this	Emily Fischer 6/23/2017 9:37 PM
591	feature was not present on 20 August	Deleted: s
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593	Several Front Range O ₂ monitors recorded elevated ozone during the August smoke-impacted period. Specifically, the	Deleted: ozone
594	maximum daily 8-hour average O ₂ mixing ratio at Aurora East exceeded 75 ppby on 21 August. This was the first highest	Emily Fischer 6/23/2017 9:37 PM
505	maximum for this station for summer 2015. The second hiskest maximum for summer 2015 coincided with the August	Emily Fischer 6/23/2017 9:37 PM
595	inaximum for uns station for summer 2013. The second nightst maximum for summer 2013 concluded with the August	Deleted: s
596	smoke-impacted period at Fort Collins West, Greely, La Casa, Welby and Aurora East. The third highest maximum for	Emily Fischer 6/23/2017 9:37 PM
597	summer 2015 coincided with the August smoke-impacted period at Aurora East, South Boulder Creek, Rocky Mountain	Deleted: ozone
598	National Park, and Fort Collins – CSU.	Jakob Lindaas 6/23/2017 12:05 AM
599		average (MDA8) O ₃ mixing ratios, following
600	The presence of smoke was not always associated with high absolute abundances of O3 at BAO. The July smoke-impacted	methodology from the U.S. EPA, and found that out of 6 high Q_2 days at BAO (defined as \geq 65 ppby
601	period and most of the days in the August smoke period did not have maximum hourly mixing ratios greater than the 95 th	MDA8) during our study period, 2 occurred during
602	percentile. However, it is important to note that many of these days did have higher O ₃ abundances than would otherwise be	stated above, elevated O ₃ during the smoke period
603	expected given their temperatures (see Figure 6). Therefore we conclude that the presence of wildfire smoke contributed to	was not a result of abnormal meteorological variables such as higher than normal temperatures,
604	higher Ω_2 mixing ratios than would otherwise be expected during the two smoke events we sampled and that during 2 of	and thus these 2 high O_3 days are very likely caused in part due to the presence of wildfire smoke. The
605	these days the smalle contributed to on empirically defined "high O day"	lower portion of Figure 7 again shows that maximum
605	these days the shoke contributed to an empiricanty defined high O_3 day	periods were the same as or lower than maximum
606		daily temperatures during the smoke-free period.
607	As mentioned in the Introduction, wildfire smoke can produce O_3 within the plume as it is transported, as well as contribute	Deleted: the spatial extent of the Q ₂ enhancements
608	to O ₃ photochemistry by mixing additional precursors into surface air masses. To assess the possibility of O ₃ production with	observed at BAO and to investigate the relative
609	the plume, we analysed hourly O3 measurements from two National Park Service (NPS) Air Resources Division (http://ard-	likelihood of O ₃ enhancements due to transport within the smoke versus greater local production,
610	request.air-resource.com/data.aspx) measurement locations that are located outside the polluted Front Range urban corridor.	Emily Fischer 6/29/2017 9:52 PM
611	The Rocky Mountain National Park long-term monitoring site (ROMO; 40.2778°N, 105.5453°W, 2743 meters A.S.L.) is	Deleted: analyzed
612	located on the east side of the Continental Divide and co-located with the Intergency Monitoring of Protected Visual	Jakob Lindaas 6/23/2017 12:41 PM

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647 Environments (IMPROVE) and EPA Clean Air Status and Trends Network (CASTNet) monitoring sites. Front Range air 648 masses frequently reach this site during summer afternoons (Benedict et al., 2013). The Arapahoe National Wildlife Refuge 649 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 650 651 gradient; from primarily influenced by anthropogenic emissions (BAO), to sometimes influenced by anthropogenic 652 emissions (ROMO), to very little influence from anthropogenic emissions (WALD). Figure 8 shows that the August smokeimpacted period produced increases in O₃ mixing ratios across all three sites. When comparing all data for a given 653 654 temperature, there are <u>average weighted</u> enhancements of 10 ± 2 ppbv, 10 ± 2 ppbv, and 6 ± 2 ppbv O₃ at BAO, ROMO and 655 WALD respectively. O3 enhancements across all three sites, across an approximate urban to rural gradient, suggest that some 656 amount of the O₃ enhancement observed at BAO during the August smoke-impacted period is the result of O₃ production 657 within the plume during transit. O3 during the July smoke-impacted period in Figure 8 shows a different pattern. As we saw 658 in Figure 6, O₃ is enhanced above the level predicted by the ambient temperature at BAO. But no statistically significant 659 enhancements are observed at ROMO and WALD for the July smoke-impacted period. One possibly reason for this nuance 660 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. 661 662 663 One measure of local production of O_3 is the ozone production efficiency (OPE). OPE is calculated as the slope of the 664 relationship between O_3 and NO_z (= $NO_y - NO_x$) (Trainer et al., 1993). OPE is a measure of the number of molecules of O_3 665 that are produced before a given NO_x molecule is oxidized. To calculate OPE we used one minute O₃ and NO_x data in 30 minute chunks from 12PM - 5PM MDT. The slopes were calculated using a reduced major axis regression (package Imodel2 666 for R software) and only OPE values corresponding to an $R^2 > 0.3$ were retained. We do not find any significant differences 667 668 in average calculated OPE_{*} between the smoke-impacted (8 ± 3 ppbv/ppbv) and smoke-free periods (7 ± 3 ppbv/ppbv). Thus 669 from the OPE perspective it does not appear there were any changes in the local production efficiency of O₃ due to the 670 presence of smoke. On the other hand, we documented many changes to the atmospheric composition of O₃ precursors, 671 particularly with respect to CO, benzene, ethyne, the alkenes, and PANs. Additionally the smoke may added many O₃ 672 precursors that we were not set up to measure (e.g. many OVOCs). Due to the nonlinear nature of O_3 chemistry, the different 673 mix of precursors could have caused enhanced local O3 production, depressed local O3 production, or had no effect on local 674 O_3 production. Taken together, the observations do not suggest a single mechanism that describes smoke influence on O_3 in 675 Front Range airmasses during these case studies. Instead, the observations point to the presence of smoke resulting in a 676 complex array of processes that will require more detailed observations and chemical transport modelling to clearly identify and quantify. 677

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measurements are not able to pinpoint exactly how.
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713 5 Conclusions

714 Here we report a time series of detailed gas-phase ground measurements in the northern Colorado Front Range during 715 summer 2015. Clear anomalies in CO and PM2.5 showed that aged wildfire smoke was present at ground-level during two distinct periods (6 - 10 July and 16 - 30 August) for a total of nearly three out of the nine weeks sampled. This smoke from 716 wildfires in the Pacific Northwest and Canada impacted a large area across much of the central and western U.S., and was 717 718 several days old when it was sampled in Colorado. This wildfire smoke mixed with anthropogenic emissions in the Front 719 Range, resulting in significant changes in the abundances of O₃ and many of its precursor species. Our measurements are 720 unique because of 1) the length of time we sampled this smoke-impacted anthropogenic air mass, and 2) the detailed composition information that was collected. 721

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723 During the smoke-impacted periods we observed significantly increased abundances of CO, CH₄, and several VOCs with 724 OH oxidation lifetimes longer than the transport time of the smoke. We measured significant decreases in several of the most reactive alkene species, indicating possible enhanced oxidation processes occurring locally. Mixing ratios of peroxyacyl 725 726 nitrates and some alkyl nitrates were enhanced and peak abundances were delayed by 3-4 hours, but there was no significant 727 change in HNO3 mixing ratios or its diurnal cycle. During the longer August smoke-impacted period we observed significant increases in NO2 mixing ratios just after sunrise and sunset. We did not observe any consistent shifts in wind direction or 728 729 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 730 731 across the Front Range as evidenced by enhanced PM25 at CAMP (Figure 1) and 9 other Front Range CDPHE monitoring 732 sites.

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We observed significantly enhanced O_3 abundances at BAO of about 10 ppbv for a given temperature during both smokeimpacted periods. The enhancements during the August smoke-period led to very high surface O_3 levels on several days; out of Q high O_3 days at BAO during our study period, 2 were during the August smoke-impacted period. These enhancements were not due to higher temperatures, nor anomalous meteorological conditions. We found evidence of O_3 produced within the smoke plume during transit, and changes in the observed abundances of many O_3 precursors indicated that the smoke may have impacted local O_3 production as well. Future modelling work and additional observational studies are needed in order to fully address the question of how much O_3 the smoke produced and how it changed local O_3 production.

742 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 <u>relatively low O₃ at times</u>, such as during

the July smoke event described <u>above</u>. This case study describes two distinct smoke events where the presence of smoke

745 likely increased O₃ abundances above those expected by coincident temperatures. However, we do not intend to claim that

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all high O_3 episodes in the Front Range are caused by smoke, nor that smoke will always cause higher than expected O_3 .

755 Each smoke event has unique characteristics and thus it is important to study and characterize more events such as these in 756 the future.

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Wildfire smoke during these time periods in 2015 most likely impacted atmospheric composition and photochemistry across much of the mountain west and great plains regions of the U.S. Given the BAO, Rocky Mountain and Walden research locations span an urban-rural gradient as well as a large altitudinal gradient, it is likely that both rural and urban locations impacted by this smoke could have experienced enhanced O_3 levels. Additionally, the Pacific Northwest wildfires that produced this smoke were among the most extreme in that region's history. We know that wildfires are increasing in both frequency and intensity throughout the western U.S. due to climate change, and thus wildfire smoke events such as this one will likely play an increasingly problematic role in U.S. air quality.

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766 Author Contribution: J. L. compiled and analysed the data, and wrote the manuscript. All authors participated in data 767 collection at BAO and contributed to the writing of $_{a}$ or provided comments on $_{a}$ the manuscript.

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Figure 2. Representative days during each smoke period observed at the Boulder Atmospheric Observatory (BAO: blue square). NOAA Hazard Mapping System (http://www.ssd.noaa.gov/PS/FIRE/) smoke polygons are plotted in <u>dark grey shading</u> with MODIS fire locations (http://modis-fire.umd.edu/index.php) from the previous day plotted as red triangles. The thin black lines show HYSPLIT <u>120 hour</u> back trajectories from the BAO site initiated <u>at</u> 1000 m a.g.l. for each hour of the day plotted. <u>Yellow</u> cross hatches display the location of each trajectory 48 hours back and orange cross hatches indicate the 72 hour location. The green points show the location of the Rocky Mountain National Park and Walden measurement locations.

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1042Figure 3. Significant changes (two sided Student's t-test, 90% confidence interval) in hourly averaged mixing ratios of a subset of1043species measured at BAO between smoke-free periods and the 16 - 30 August smoke period. Significant increases during smoke-1044impacted periods compared to smoke-free periods are shown in red, significant decreases are in blue.





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 Figure 4. 95th percentiles of all hourly average measurements of a) benzene and b) NO2 during the smoke-free period (in black)

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 and the August smoke-impacted period (in red), as a function of wind direction,

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1053 Figure 5. Average diurnal cycles in MDT of O₃ and oxidized reactive nitrogen species at BAO. Panels a), b), and c) compare

1054 average diurnal cycles from smoke-free time periods (black) to average diurnal cycles from the July smoke-impacted period

1055 (orange). Panels d) - h) show average diurnal cycles during the August smoke-impacted period (red) to the same average diurnal

1056 1057 1058 cycles from smoke-free periods (black). <u>Grey shading indicates plus and minus one standard deviation</u>. PAN and HNO₃ measurements were not available during the July smoke-impacted period. <u>Solar noon on 1 July 2015 was at 1:03 PM, solar noon</u>

on 7 September was 2015 was at 12:57 PM,

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Figure 6. Hourly O_3 data from BAO plotted against hourly temperature data show a positive correlation between temperature and O_3 abundances for the smoke-free time periods in grey and both smoke-impacted periods (July in orange and August in red). Overlaid are boxplots (5th, 25th, 50th, 75th, and 95th percentiles) for each 5 °C bin. On the left normalized histograms of the 1062 1063

1064 hourly O3 data are plotted, with all smoke-free measurements in black, and all hourly measurements made during the July smoke-

1065 impacted period in orange and August smoke-impacted period in red.

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Figure 7. Maximum_hourly average O₃ mixing ratios for each day at BAO plotted in black with maximum daily temperature at BAO in blue. Red boxes denote days that exceed the 95th percentile of all hourly average O₃ mixing ratios between 11am - 4pm MDT₂ Black boxes pinpoint these same days in the temperature timeseries.

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1093	Table 1. Summary of alkene statistics at	the Boulder	Atmospheric	Observatory	during	the	smoke-free	period	and tl	he Augus	st
1094	smoke-impacted period in summer 2015.										

1095 ^a Standard deviation in parentheses

1096 Indicates statistically significant change in mean during August smoke-impacted period as compared to the smoke-free
 1097 period

		Smol	ce-free period		August smoke-impacted period						
<u>Compound</u>	min	median	mean ^a	max	min	median	mean ^a	max			
ethene [*]	0.001	<u>0.2</u>	0.253 (0.212)	<u>1.94</u>	0.001	0.001	0.0464 (0.128)	<u>0.918</u>			
propene*	<u>0.002</u>	0.041	0.051 (0.04)	<u>0.41</u>	0.002	<u>0.008</u>	0.011 (0.012)	<u>0.086</u>			
cis-2-butene	0.001	0.018	<u>0.0236 (0.0292)</u>	0.345	0.001	<u>0.014</u>	0.023 (0.07)	1.08			
isoprene [*]	<u>0.003</u>	<u>0.141</u>	0.223 (0.268)	<u>2.02</u>	<u>0.001</u>	<u>0.048</u>	<u>0.0804 (0.114)</u>	<u>1.16</u>			

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