

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 re-structured 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  $J_{NO_2}$ , 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, CH<sub>4</sub>). 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<sub>3</sub> 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<sub>3</sub> (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<sub>3</sub> (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? GC-FID? 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<sub>1</sub> – C<sub>2</sub> 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).”*

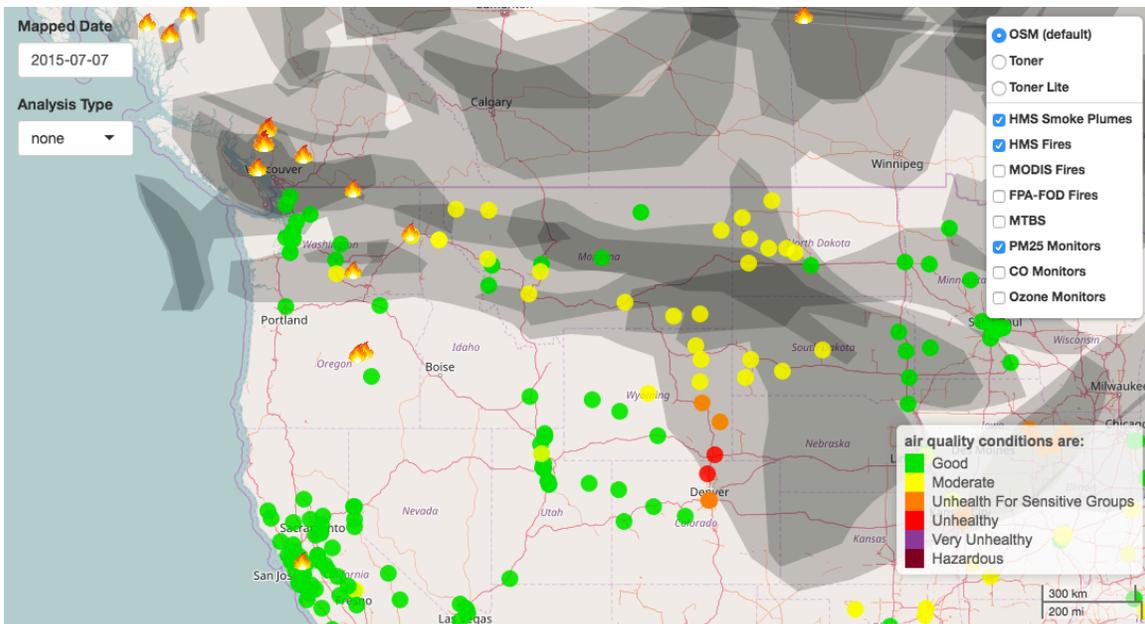
Lines 159-163: By what metric and threshold does the HMS smoke product determine smoke impact? More explanation is needed here given that the field sites are just outside of the grey shaded “smoke-influenced” regions on July 7 (Figure 2), suggesting less relative smoke impact than the August time period where BAO is in the middle of smoke-impacted region; and yet the concentrations of CO and PM<sub>2.5</sub> 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.*

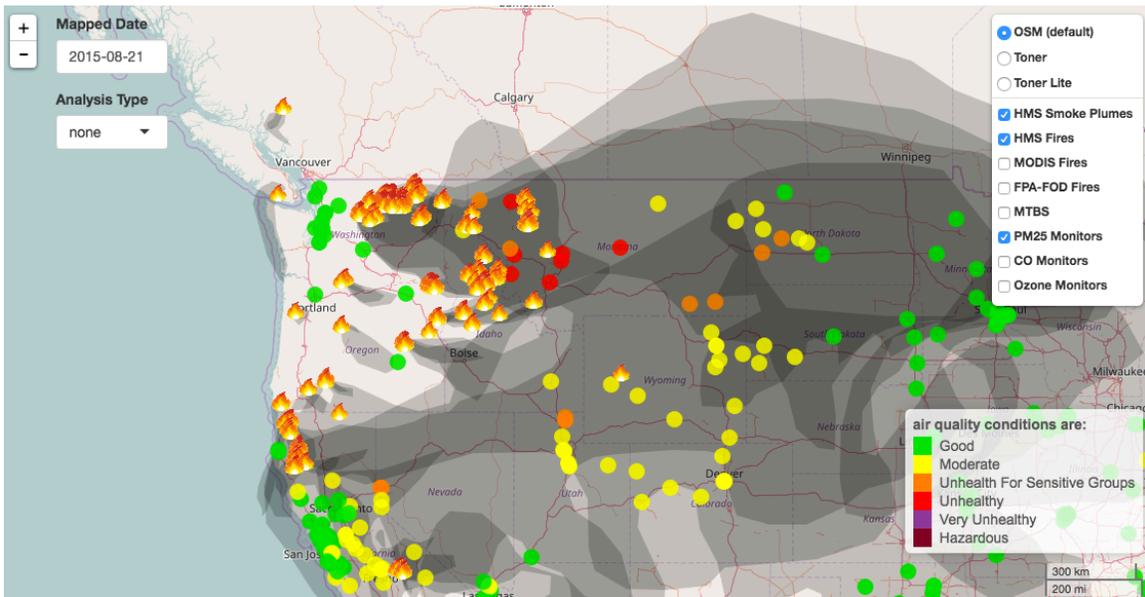
*“The NOAA Hazard Mapping System smoke polygons (grey shading) show that the smoke events observed at BAO were large regional events. The HMS smoke product is produced using multiple NASA and NOAA satellite products (Rolph et al., 2009). Smoke in the atmospheric column is detected using both visible 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 PM<sub>2.5</sub> 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 PM<sub>2.5</sub>, 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 smoke-impacted 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<sub>2.5</sub> measurements in the July smoke period (Figure 1).”*

Lines 198-202: “Average enhancements of CH<sub>4</sub> 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 CH<sub>4</sub> enhancement during the smoke impacted periods, but that is not how the sentence reads. Is the observed CH<sub>4</sub> enhancement of 3% statistically significant given that the stated uncertainty in the CH<sub>4</sub> measurement is 6% (line 99)? Also, the emission factor of CO is generally >10x that of CH<sub>4</sub> from biomass burning (Akagi et al., 2011), thus it is curious that the CH<sub>4</sub> 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 CH<sub>4</sub> 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<sub>4</sub> 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<sub>4</sub> 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<sub>4</sub> and the large local sources of CH<sub>4</sub> in the Front Range served to mute the impact of the August smoke on overall CH<sub>4</sub> abundances. The diurnal cycle of CH<sub>4</sub> 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<sub>4</sub> 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 O<sub>3</sub> 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<sub>3</sub>. 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<sub>2</sub>-C<sub>3</sub> alkenes was small (Abeleira et al...). Thus, while the hypothesis that smoke suppressed biogenic emissions remains feasible, we will consider other potential causes for the observed decrease in alkene abundances.

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

Lastly, we move on to our final hypothesis. Alkenes have much higher rates of reaction with O<sub>3</sub> than the other VOCs we quantified. As we will demonstrate in Section 4.3, the August smoke-impacted period was characterized by higher O<sub>3</sub> abundances than would otherwise be expected. Therefore, the fourth hypothesis regarding decreased alkene abundances is that enhanced alkene oxidation by O<sub>3</sub> decreased the observed mixing ratios. Two factors complicate this hypothesis though. First, we do not observe a negative relationship between O<sub>3</sub> and alkene abundance during the smoke-free time periods (i.e. increased O<sub>3</sub> is not correlated with decreased alkenes when no smoke is present). Second, despite having a higher reaction rate with O<sub>3</sub> compared to propene and ethene, cis-2-butene does not decrease during the August smoke-impacted period.

After careful consideration, there is no strong evidence supporting any of these four hypotheses over the others (suppressed anthropogenic emissions, suppressed biogenic emissions, increased OH, increased O<sub>3</sub>). 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. “

Akagi, S. K., Craven, J. S., Taylor, J. W., McMeeking, G. R., Yokelson, R. J., Burling, I. R., Urbanski, S. P., Wold, C. E., Seinfeld, J. H., Coe, H., Alvarado, M. J., and Weise, D. R.: Evolution of trace gases and particles emitted by a chaparral fire in California, *Atmos. Chem. Phys.*, 12, 1397-1421, 10.5194/acp-12-1397-2012, 2012.

Hobbs, P. V., Sinha, P., Yokelson, R. J., Christian, T. J., Blake, D. R., Gao, S., Kirchstetter, T. W., Novakov, T., and Pilewskie, P.: Evolution of gases and particles from a savanna fire in South Africa, *Journal of Geophysical Research: Atmospheres*, 108, n/a-n/a, 10.1029/2002JD002352, 2003.

Liu, X., Zhang, Y., Huey, L. G., Yokelson, R. J., Wang, Y., Jimenez, J. L., Campuzano-Jost, P., Beyersdorf, A. J., Blake, D. R., Choi, Y., St. Clair, J. M., Crouse, J. D., Day, D. A., Diskin, G. S., Fried, A., Hall, S. R., Hanisco, T. F., King, L. E., Meinardi, S., Mikoviny, T., Palm, B. B., Peischl, J., Perring, A. E., Pollack, I. B., Ryerson, T. B., Sachse, G., Schwarz, J. P., Simpson, I. J., Tanner, D. J., Thornhill, K. L., Ullmann, K., Weber, R. J., Wennberg, P. O., Wisthaler, A., Wolfe, G. M., and Ziemba, L. D.: Agricultural fires in the southeastern U.S. during SEAC4RS: Emissions of trace gases and particles and evolution of ozone, reactive nitrogen, and organic aerosol, *Journal of Geophysical Research: Atmospheres*, n/a-n/a, 10.1002/2016JD025040, 2016.

Yokelson, R. J., Crounse, J. D., DeCarlo, P. F., Karl, T., Urbanski, S., Atlas, E., Campos, T., Shinozuka, Y., Kapustin, V., Clarke, A. D., Weinheimer, A., Knapp, D. J., Montzka, D. D., Holloway, J., Weibring, P., Flocke, F., Zheng, W., Toohey, D., Wennberg, P. O., Wiedinmyer, C., Mauldin, L., Fried, A., Richter, D., Walega, J., Jimenez, J. L., Adachi, K., Buseck, P. R., Hall, S. R., and Shetter, R.: Emissions from biomass burning in the Yucatan, *Atmos. Chem. Phys.*, 9, 5785-5812, 10.5194/acp-9-5785-2009, 2009.

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 NO<sub>2</sub> 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 NO<sub>2</sub> 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<sub>2</sub> was within the range of smoke-free measurements. In contrast NO<sub>2</sub> 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 NO<sub>x</sub>. 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<sub>2</sub>. The thermal decomposition of PAN can be a source of NO<sub>2</sub> (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<sub>2</sub>. PAN abundances were likely higher in the fresher plume, but still not likely sufficient to be the sole source of the additional NO<sub>2</sub>.”*

Lines 368-370: “we found the same enhancement in O<sub>3</sub> for a given temperature when comparing smoke-impacted 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 smoky 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 95<sup>th</sup> 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 95<sup>th</sup> 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 95<sup>th</sup> 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<sub>3</sub> day for two reasons. First, BAO is not an EPA designated O<sub>3</sub> NAAQS site, and the BAO O<sub>3</sub> data are not explicitly calibrated to the EPA O<sub>3</sub> calibration scale. Thus, while we can calculate the MDA8 values for the BAO O<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> mixing ratio greater than the “high O<sub>3</sub> day” 95<sup>th</sup> percentile threshold (71.75 ppbv) in our study period. The average number of high O<sub>3</sub> days within those two months for a given year is 15.7. 2015 was lower than this, with 9 high O<sub>3</sub> 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<sub>3</sub> day” as any day in our study period with at least one hour above the 95<sup>th</sup> percentile (71.75 ppbv) of all 11am – 4pm MDT hourly average O<sub>3</sub> measurements during the campaign. We found 9 individual high O<sub>3</sub> days during our study period, of which 2 occurred during the August smoke-impacted period (Figure 7). The total number of high O<sub>3</sub> days is lower than normal for the same time period in previous years. As we stated above, high O<sub>3</sub> 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<sub>3</sub> is the ozone production efficiency (OPE). OPE is calculated as the slope of the relationship between O<sub>3</sub> and NO<sub>z</sub> (= NO<sub>y</sub> – NO<sub>x</sub>) (Trainer et al., 1993). OPE is a measure of how the number of molecules of O<sub>3</sub> that are produced before a given NO<sub>x</sub> molecule is oxidized. To calculate OPE we used one minute O<sub>3</sub> and NO<sub>z</sub> 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<sup>2</sup> > 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 O<sub>3</sub> 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<sub>3</sub> is the ozone production efficiency (OPE). OPE is calculated as the slope of the relationship between O<sub>3</sub> and NO<sub>z</sub> (= NO<sub>y</sub> - NO<sub>x</sub>) (Trainer et al., 1993). OPE is a measure of how the number of molecules of O<sub>3</sub> that are produced before a given NO<sub>x</sub> molecule is oxidized. To calculate OPE we used one minute O<sub>3</sub> and NO<sub>z</sub> 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<sup>2</sup> > 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). Thus from the OPE perspective it does not appear there were any changes in the local production efficiency of O<sub>3</sub> due to the presence of smoke. On the other hand, we documented many changes to the atmospheric composition of O<sub>3</sub> precursors, particularly with respect to CO, benzene, ethyne, the alkenes, and PANs. Additionally the smoke may added many O<sub>3</sub> precursors that we were not set up to measure (e.g. many OVOCs). Due to the nonlinear nature of O<sub>3</sub> chemistry, the different mix of precursors could have caused enhanced local O<sub>3</sub> production, depressed local O<sub>3</sub> production, or had no effect on local O<sub>3</sub> production. Taken together, the observations do not suggest a single mechanism that describes smoke influence on O<sub>3</sub> 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 μm PTFE filter membrane” Do you mean the pore size, not the filter size, was 1 μm?

*The reviewer is correct, the filter pore size is 1 μm. 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 μm 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.*

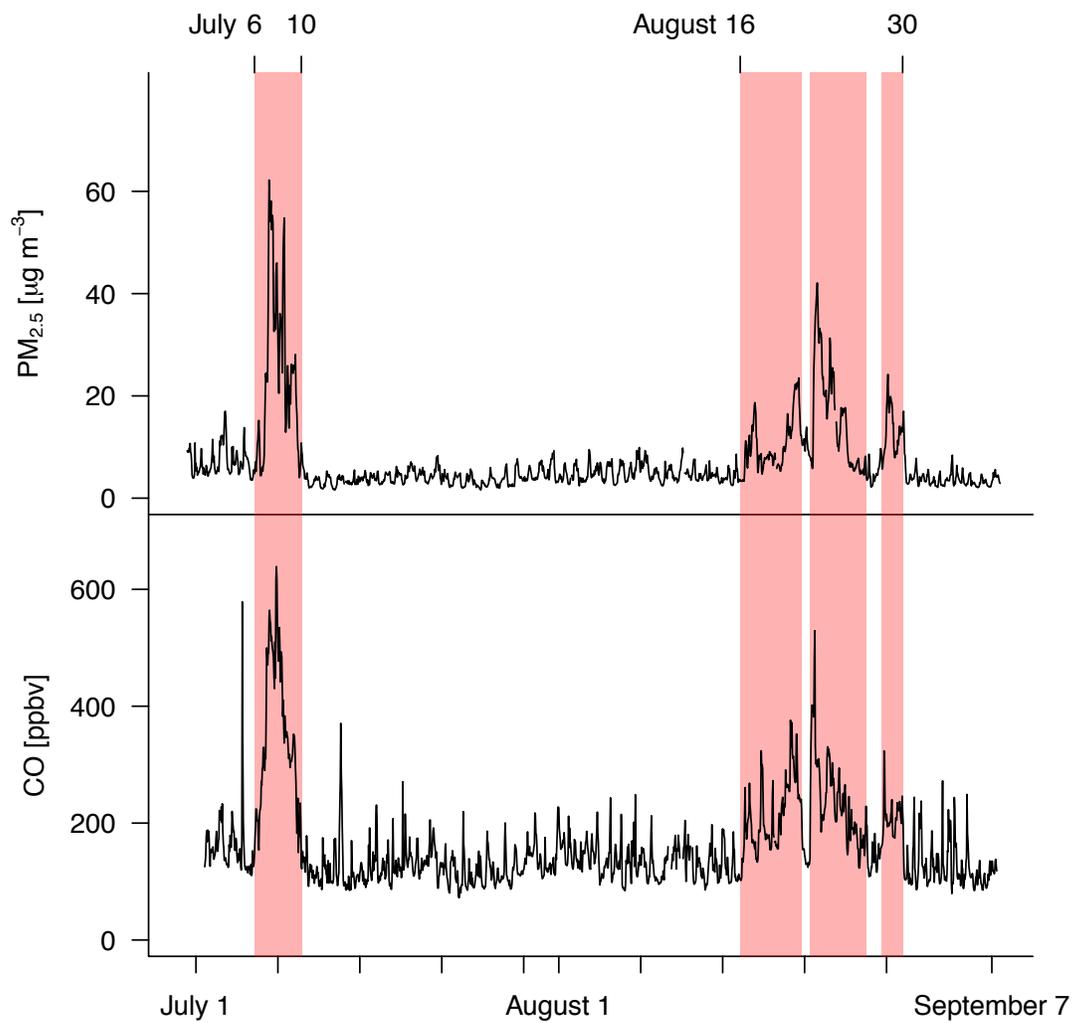
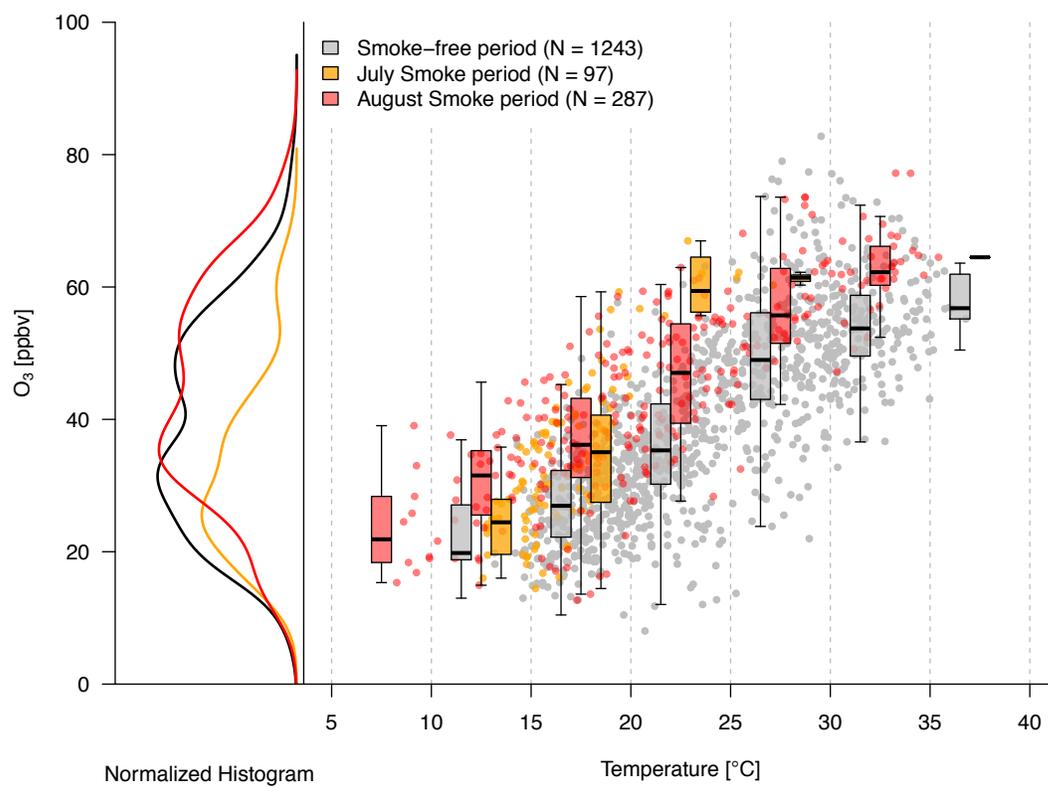


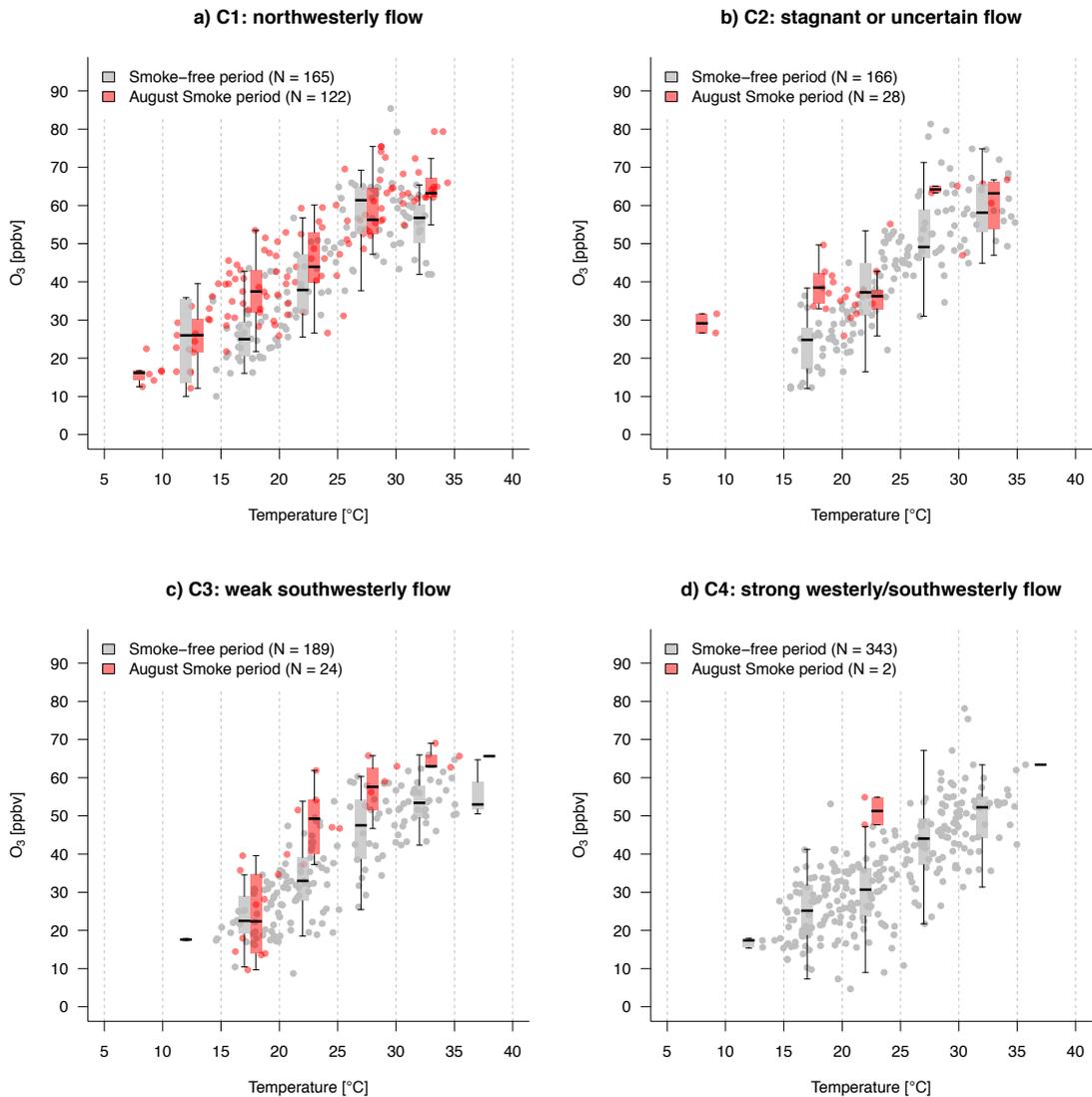
Figure 6: Can Fig. S4 be merged with this one so all of the data is included in a single plot?

*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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