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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "The impact of aged wildfire smoke on atmospheric composition and ozone in the Colorado Front Range in summer 2015" *by* Jakob Lindaas et al.

Anonymous Referee #2

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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?

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?

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).

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).

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

Specific comments:

Line 60: State the EPA ozone standard.

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?

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 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?

Lines 177-178: “we did not quantify species with known large âĂÍbiomass burning emission ratios (e.g. hydrogen cyanide, acetonitrile, most oxygenated organic species)”. Were these compounds not quantified or not measured/detected? âĂÍIf 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.

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.

Lines 198-202: “Average enhancements of CH4 were a much smaller percentage of (∼3% or 67 ppbv), but comparable in magnitude to, the âĂÍCO 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.

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.

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.

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

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?

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

Lines 368-370: "we found the same enhancement in O3 for a âĂÍgiven temperature when comparing smoke-impacted observations to smoke-free observations assigned to this cluster as we âĂÍfound 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?

Line 373: Include a citation.

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?

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

Line 397-398: "Fully addressing the question of whether the smoke enhanced local O3 production in the polluted Front Range âĂÍrequires the use of a chemical transport model, and is beyond the scope of this work." âĂÍThere 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.

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?

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

Technical corrections:

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

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

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

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

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.

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