

First, I apologize for completing this review late.

The manuscript (MS) has been significantly improved compared to the previous version. In several places the authors have greatly clarified arguments which I previously had trouble following (or couldn't follow at all). As stated before, the measurements and analysis described in the MS are very interesting and will contribute to our understanding of pollution events in this region, so this MS should be published.

There are, however, several remaining issues. I first list two issues that need to be addressed, and then one suggestion. *I don't think it's necessary that a revised paper be reviewed again, but perhaps these issues are complicated enough that the Editor will prefer to have the reviewers take another look. (In that case I will be happy to help out and I promise to be much faster!)*

1. In the abstract of the previous version, the MS attributed ~20 ppb O<sub>3</sub> during a couple high ozone events to oil and gas VOC. The abstract of the current version moves away from these statements, attributing the same ~20 ppb O<sub>3</sub> to "Front Range sources." The new formulation in the abstract is a much better description of what the data analysis demonstrates.

Unfortunately, the text of the MS describing the analysis that derives the ~20 ppb O<sub>3</sub> attribution still states, in several places, that the analysis can attribute ozone to more specific source categories such as "light alkanes from oil and gas." I don't agree with that, and the MS is not internally consistent in this way. The whole MS needs to be made consistent with the statement in the abstract. The over-specific attribution statements need to be changed or removed. Furthermore, the four page description of the analysis behind the source attribution - which is reorganized, with a lot of new text - needs to be shortened and substantially edited. More description of the editorial problems with this section is below.

2. In some places, the MS may still oversimplify the source attribution for the upslope events largely ascribed to OG emissions. As I argue below, some of the evidence suggests that these O<sub>3</sub> spikes can be described as mixed source events with a large OG signal, as opposed to "largely associated with VOC from OG," as described in the abstract. Simply put, some of the data presented in the paper suggests to this reader that there could be a significant urban contribution to this O<sub>3</sub>. Other evidence / lines of analysis may complicate the story for those spikes. But on balance, the story seems more complicated than simply saying that the OG signature is "dominant" for those two events.

I suggest that the authors handle this by either a) discussing why the indications of mixed sources (urban, etc.) should be discounted, or b) acknowledging that the evidence is somewhat mixed, and softening some of the statements that oil and gas emissions "dominated" these events.

Below are details on these two issues, followed by the Suggestion I mentioned above.

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**ISSUE 1. Nitrate analysis.** The analysis described on pp 22-26 has substantially more explanation, but the discussion is difficult to follow in various places different conclusions are

attributed to this analysis.

In the abstract, the following statement is made:

"For the high ozone events most associated with emissions from oil and gas activities, we estimate that VOCs and NOx from sources along the Front Range contributed ~20 ppbv of additional ozone."

This is quite different than the statement on p 22, line 16-18:

"Here, we use coincident observations of alkyl nitrates during these elevated O3 periods to estimate the contribution of the light alkanes from oil and gas emissions to O3 production"

The statement in the abstract is an accurate description of what the nitrate analysis shows. The second statement, from p22, is not supported by the discussion in the remainder of this section.

The MS and data establish well that the ozone spikes on 8/8 and 18 are due to upslope events where the O3 spike is nicely correlated with a spike in alkanes and nitrates. This makes sense, since the alkanes are a source of the O3, and as they MS argues, nitrates should be correlated with O3 given the common chemical derivations.

However, NOTHING about this analysis proves that all or even the great majority of the ozone spike comes from alkanes, or from OG! Indeed, this is acknowledged in several places in this discussion.

Because the nitrate signals are very clean spikes from a clean, low background during upslopes, and they are a great fingerprint for upslope ozone generation, the analysis presented here is a great way to quantify the size of the ozone spike that is directly attributable to the upslopes. (Since the ozone trace itself has far more structure, background, variability, local influence, etc., one can't get a clean upslope signal directly from the ozone trace). For this reason, the nitrate analysis well supports the statement in the abstract.

**The authors need to modify or remove the statement above from p 22 and all other statements that state or suggest that the nitrate analysis can ascribe a specific [O3] to light alkanes from OG or emissions from OG. (Statements similar to each of these are currently in the text.)**

In part because there are these variations in the statements about the meaning of the nitrate analysis, this section (p 22 -24) also requires significant reorganization and editing. I believe a lot of it can be cut. Some examples of material that seem extraneous is p 23, lines 13-21 and p 21 line 21 thru p 22 line 3. Moreover, the discussion just needs to be cleaned up. For example, plotting O3 vs nitrate during periods of high O3 is mentioned at the end of p 23, on p 24 lines 18-21, and again on p 25 lines 18-21. This is repetitive. There are other passages which are repetitive or contain extraneous arguments.

P23, line 11 - replace "figure 13" with "figure 12"

P25, line 21 - "and the intercept value was subtracted." Based on the previous discussion of the y-intercept and slope of the O3 vs nitrate plots, I presume this means the intercept value of

ozone. But this (~40 ppb) is not subtracted away from the [nitrate]\*slope product.

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## **ISSUE 2. Description of source attribution for 8.8 and 8.18 events**

This issue is encapsulated by p 21, line 14 - "dominated" by oil and gas. This is a very strong word. What data supports this? The i/n pentane ratio is 0.97, barely below 1, and a good bit higher than values measured at PAO. (the ratio during the 8/2 event is only slightly higher - it does not seem appropriate to draw such a bright line at 1.00...) Fig 3 clearly shows C2Cl4 peaks on those days, and a C2H2 peak on the 18th. Finally, the OHR data shown in Fig 11 shows very large OVOC contribution to OHR. Considering all of this, it does not seem to me that this description is apt. It seems to be an oversimplification to simply describe this as an OG air mass, as it appears to be heavily influenced by OG, but also distinctly influenced by urban pollution, as lines 20-22 (same page) describe.

Later on, the air mass age analysis (pp 29-30) nicely supports the idea that the air masses on the 8th and the 18th rapidly moved thru the OG area, picking up OG emissions and then moving up to ROMO. However, it's conceivable that they did so after being affected by urban emissions - a variation of the 'regional mixing' scenario described on p 21 lines 20-22. If the authors are relying on photochemical age to show that OG "dominates" for the events on the 8th and 18th, that needs to be made more clear. At the same time, the OHR data doesn't support the "dominated" claim, unless OG contributes a large portion of OVOC (*which if true, is not discussed in the MS*).

Simply put, the MS needs to address these 3 issues - especially the peaks in non-OG VOC and the contribution of OVOC to OHR - during these two upslope events. If they are evidence of regional mixing, statements such as p 21 line 14, and the statement in the abstract that these events are "largely associated with OG VOC" should be made less strong. Alternatively, if the 3 factors I mentioned are not indications of substantial regional mixing, that should be explained, since I think other readers will interpret the data similarly to how I have.

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**SUGGESTION** Page 17 / Fig 6... "At their peak values, NMHC mixing ratios observed at ROMO can be of comparable magnitude to urban/industrial regions" Except, that's not true for some of the VOC shown. It would be very helpful to add a brief discussion of why not. I believe that this reflects the influence of OG VOC on ROMO: ethane, propane, n-but, aromatics. That's why i-but and i-pen are low. But why is n-pen so low at ROMO? why is benzene so high???? why is c2h2 so high???

I realize that this is a qualitative, basically contextual result - "can be as high as VOC in urban regions" ... which obviously vary at ton. But still, the different stories for different species are interesting, and rather confusing for readers not familiar with patterns in ambient speciated voc. I suggest adding a couple sentences to tell the reader what's going on here with the various species shown in Fig 6 (at least, some of them).

[Some of this is discussed in the document the authors supplied repsonding to reviewers comments; I believe a few sentences here on the variation between species would be helpful.]