

## ***Interactive comment on “Volatile Organic Compounds and Ozone in Rocky Mountain National Park during FRAPPÉ” by Katherine B. Benedict et al.***

### **Anonymous Referee #1**

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**Overall:** This paper reports very useful observations and contains a lot of useful analysis. However, certain portions of the discussion (principally in Section 4, but also 1 paragraph in Section 3) are poorly supported at best. The conclusions drawn by those sections may well be correct, but the manuscript (MS) does not demonstrate them.

My hope is that the authors can rewrite the portions of the MS that are not adequately supported and address some other issues I catalog below so that the MS can be published in ACP.

Furthermore, the paper reports that oil and gas (OG) VOC contributes to about 20 ppbv of O<sub>3</sub> in Rocky Mountain (ROMO). This is very hard to reconcile with the modeling

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results of McDuffie (2016), which are reporting that at BAO, peak ozone concentrations would only be 3 ppbv lower if OG VOC were not present. This paper is cited in the MS, but this critical difference is not mentioned. It does not seem likely that both of these results can be correct: OG VOC only adds about 3 ppbv at BAO but 20 ppbv at ROMO. If there is an explanation for this, or if there is some other explanation for this discrepancy, it should be discussed. If the authors are not aware of an explanation for the discrepancy, that should be acknowledged.

**Section 4.2** First, the PAN & PPN discussion in the 3rd paragraph is difficult to follow, seems tendentious, and it's not clear to me that it adds to the analysis. PPN was not measured at ROMO, but the arguments here seem to rely analysis in a paper by Lindaas (submitted) that says that high PPN/PAN ratios indicate substantial contribution to PAN and PPN from OG alkanes. If these arguments are important to the overall analysis, they should be clarified and simplified. It appears to me that the key result is simply that previous work studying the front range has demonstrated that OG alkanes are a key precursor to PAN and PPN in this area; the measurements of PAN and ROMO don't seem to add much to this.

**Page 12-13** – analysis based on alkyl nitrates. These two paragraphs, which lead to a key finding of the MS (20 ppbv O<sub>3</sub> from OG VOC) are at best inadequately supported. The logic of many of the steps in this analysis is not transparent: simply put, I can't see why its true. These paragraphs are also very, very sparse on citations, so more support is certainly needed.

P12 lines 11-14. I'm afraid I am not familiar with using alkyl nitrate formation as a proxy for O<sub>3</sub> production in this way. Please provide citations to papers that explain the logic of this approach, or do so here (ie with Chemical Equations, etc).

Lines 14-16 “For the August 8 and 18 events, the overall air mass composition (Figure 11) and photochemical age (Figure 12) indicate that the source region emissions and processing times in the Front Range were comparable and these assumptions are

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valid.” The assumptions are the three stated on lines 11-14. First, Figs 11 and 12 don't tell us anything about co-location of NO<sub>x</sub> and VOC. Second, Fig 11 does not allow us to compare anything about Aug 8 and 18, because the data for those two days is averaged on Fig 11. Fig 12 does show that the photochemical ages appear to be quite similar for the high ozone hours (Fig 12 is hourly data?) on 8/8 and 8/18, and on the order of 15 hours. But that is not direct support for any of the three assumptions.

In short, this paragraph does not help me understand why this approach makes sense if the 3 assumptions are valid, nor why the data shown in Figs 11 and 12 supports the validity of those 3 assumption.

Page 13 lines 3 – 8. Again, this simple correlation of alkyl nitrates to O<sub>3</sub> as a way of attributing O<sub>3</sub> to alkenes doesn't seem obvious to me, and the MS just does not explain why this is logical.

The agreement in results when this is done for various alkyl nitrates is interesting, but not convincing, since this analysis does not tell us anything about the contribution from other VOC (non-alkanes) that are simultaneously contributing to O<sub>3</sub>.

**In short, this analysis needs to be justified.**

Page 13 lines 8-9 – consistency with Cheadle 2017. **Be careful here.** First, Cheadle is claiming that on the day when Cheadle suggests the highest contribution of OG emissions to measured O<sub>3</sub> (8/13), NO<sub>x</sub> was also attributable to OG. Therefore, Cheadle is attributing up to 30 ppb O<sub>3</sub> to all OG emissions, not just OG VOC. Second, the conditions on the high O<sub>3</sub> days were light winds. In these conditions, emissions can accumulate to very high levels in air over Weld Cty (where Cheadle measured). For example on 8/3 Platteville flasks measured 50 – 150 ppb ethane – far higher than ethane at ROMO on 8/8 or 8/18. Therefore, I don't agree that Cheadle's results are really consistent with what the MS is claiming about O<sub>3</sub> at ROMO attributable to OG VOC.

Page 13 line 16 – again, Fig 11 simply does not show how similar airmasses were on

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Aug 8 and 18 because the data for those two days is avgd. in the figure.

There is no question, based on the results shown in the MS, that OG contributes to O<sub>3</sub> at ROMO. However, the analysis used in the MS to estimate that 20 ppbv of the peak O<sub>3</sub> on these two days is attributable to OG VOC seems very questionable.

**Section 3** Page 8-9, paragraph beginning on p 8 line 19, and Figure 6 This paragraph makes a number of unsupported statements – which may very well be true – and is poorly organized. Figure 6 does not well support the statements and has issues itself.

As it stands now, the statements that NMHC levels at ROMO “can be comparable . . . to other [sic] urban/industrial areas” and “Observed mixing ratios during afternoons with upslope flow can be similar to those observed simultaneously in the Front Range” are not supported.

These statements appear to be the main point of the paragraph, but they are not supported by Fig 6, since Fig 6 clearly shows significantly lower MRs for ROMO than everywhere else. I suspect that this has a lot to do with the averaging, so I don't doubt the statements above, but again, the statements are not supported.

- First and foremost with the figure, what data are being compared. I presume that the transect whole air samples are all collected during the day (I don't think this is stated either way), while the ROMO data are averages / medians for 24-hour data? Since Fig 3 appears to show that at ROMO the spikes in NMHC are all daytime only when upslope is happening, comparing the 24 ROMO average to daytime-only (?) transect data arguably artificially decreases the ROMO data in this sense.

- Then, the figure compares these values to PAO data and BAO data. But, those are probably 24hour averages (???) and may well include high values measured at night with low boundary layers (?). I'm speculating, but there is no discussion of any of this. How comparable are these values?

The simple way to handle this might be to compare values at ROMO during upslope

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events to values at PAO, or during afternoons at ROMO. But right now, the statements are not supported.

There are other issues with the paragraph and figure that need to be addressed.

- BAO is first introduced here, but the acronym is not defined, and no context about the site (ie, “a site in the NFRMA somewhat more removed from OG production than PAO”) is provided.

- The fact that ethyne and benzene are similar at ROMO and during the transects, and they are far more similar to PAO and BAO levels than the alkanes, needs some discussion. It’s just mentioned in passing. ???

- For the figure:

  - o Define the limits of the boxes and whiskers for the data from this study

  - o Define the error bars for the Baker 2008 data

  - o Ideally, draw vertical lines or something like that between each set of symbols (that is, a line between the ethane and propane symbols, a line btwn the propane and i-C4 symbols, a line btwn i- and n-C4 symbols, etc.) As it is now it’s really hard to read the graph.

### Minor Issues

- It’s really helpful for future readers if you put the dates of the observations (months and the year) in the abstract

- P4 line 6 – what time of day were the canisters collected?

- P4, lines 14-16 – this is not very clear or helpful. First, I think it means that the analytical system was calibrated for multiple species with a whole air standard which was run every 10 samples. Second, the precisions listed are very good (1%!) . . . but at what mole fraction? Comparable to the mole fractions measured at ROMO? A specific

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reference here is needed, even if it is one of the 3 papers listed in the pvs sentence.

- P6, lines 16-19. This passage about the contents of propane LPG cylinders is poorly drafted and mildly inaccurate (it appears to carry over an error from Wikipedia about the specifics of the hd-5 standard). The “mild error:” HD-5 must be >90% propane, <5% propene, and <2.5% C4+, according to astm 1835 (those are liquid vol %s). There is no limit of ethane except the 10% upper limit (since the gas must be 90% propane). This passage needs proper references.

- Page 7 – top – headings. Having two headings here is superfluous... I suggest you replace the two headings with “3. Temporal and Spatial Trends in Volatile Organic Compounds”

- Page 7, line 17-18 – significant MeOH from oil and gas has been observed in Utah by NOAA. Is this not the case in the DJ in the summertime? I can believe it since I think it’s main use for OG is inhibition of hydrate formation in cold weather. But I think that would be valuable to note; it should not be assumed that OG is not part of the source mix for MeOH at ROMO.

- Page 7 lines 19-20. It won’t be obvious to some readers what “hourly 2-day ensemble back trajectories” are. (I don’t know in what sense they are “ensembles”). How about “two-day back trajectories were calculated for each hour of the study”

- Figure 4. The units are not clear. Is this the % of trajectories that include (go through) each pixel, or that end in each pixel? Clarify. The term ORT seems to imply the former to this reader, but the units at the top of the color bar says “% ends.” Also the units are cut off on the figure. %ends / g???

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-375>, 2018.

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