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Title: Photochemical aging of volatile organic compounds associated with oil and natural gas extraction in the Uintah Basin, UT, during a wintertime ozone formation event

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Reply to reviewers

We thank the reviewers for their comments. Below we respond to reviewer comments and describe revisions to the manuscript.

Reviewer 1.

Koss et al. present comprehensive wintertime ground VOC concentration measurements and analysis near oil and natural gas extraction activities in the Uintah Basin, UT. Among others, VOC ratios to benzene are used to characterize and discriminate the sources (gas, oil). From the observed VOC concentrations emission or formation rates are estimated using fits of VOC:benzene ratios as a function of time, relying on different assumptions. These ratios are also used to explain oxygenated VOC production and loss via OH chemistry, photolysis, and primary emission. Basin wide extrapolation of benzene emission rate to basin wide methane emission rate was done and showed similar value observed earlier from aircraft. Based on the carbon budget analysis using two independent approaches the authors conclude that a significant missing source must exist in primary emission which is unaccounted for. The OH rate constants were derived for C8, C9 and C10 aromatics in this study. Calculated daily OH concentrations were constrained from actinic flux and VOC concentrations, and agreed well with those from MCM. The data look consistent and of high quality, and proposed analyses seem particularly advantageous because of their simplicity. In summary, these observations are novel and have an important significance elucidating atmospheric impacts from the oil and gas extraction practices, clearly associated with high VOCs and ozone formation events. I therefore would like to highly recommend this paper for publication in ACP, if the following (relatively minor) comments can be addressed:

1. The authors did an excellent job presenting the useful and extremely comprehensive observations of VOCs. I am further wondering if any sulfur containing hydrocarbons such as sulfides (e.g. DMS, DES) or thiols (e.g. methanethiol, ethanethiol) were observed or if they could deserve some attention, given that a variety of sulfur containing hydrocarbons is expected from sour oil and gas (Hammer et al., 2006) and that substantial concentrations of hydrogen sulfide were earlier reported from the same missions (Li et al., 2014).

Response:

Sulfur-containing species are certainly very interesting from an emissions and air toxics perspective. We have limited observations from a PTR-ToF instrument operated in 2013 (Warneke et al., 2015) that could provide information on sulfur-containing hydrocarbons. However, interpretation of these data would require a great deal of further work and analysis of these species is better suited to a separate manuscript.

We can respond as to whether these species would likely have a significant impact on the carbon budget described in section 4. From Li's work (Li et al., 2014), we know that H₂S was present at an average mixing ratio of 0.6ppbv and was typically under 2 ppbv. These concentrations are significant, especially

considering the toxicity of H₂S, but are small compared to mixing ratios of hydrocarbons. From previous work by other research teams, we know that H₂S is typically the dominant reduced sulfur-containing gas phase species in oil and gas producing regions (Tarver and Dasgupta, 1997). Organic mercaptan species, if present, likely had even smaller concentrations than H₂S. These species could still play important roles in air quality and oxidation chemistry, but it is unlikely they contributed significantly to carbon mass budget.

To recognize the possible presence of sulfur species we have added a reference to Li et al. (2014) at Page 6406 line 8, and have added “Some sulfur-containing species were measured (Li et al., 2014) but are not discussed in this manuscript” at Page 6408 Line 29.

2. Methanol was observed in extremely high mixing ratios (up to 200 ppbv) clearly pointing to its primary emission source dominating the site (p.6420 L3-5). Table 1 shows very high methanol average mixing ratio (44.9 ppbv) but places methanol in secondary rather than in primary sources. This might mislead some readers to think that these high concentrations of methanol are mostly of the photochemical origin. Including the primary term in Eq. 6 did not result in a good fit from the OVOC analysis, so does the upper limit of the photochemical methanol carbon mass not seem exaggerated (Figure 10)?

3. Consequently, could it not be more reasonable to present methanol as mostly primary compound since the beginning of the story? In addition, it could make it more clear, if methanol was included in primary, or both primary and secondary sources (or in a third mixed category) in Table 1.

Response (to 2 and 3):

We have added additional explanation to clarify the possible sources of methanol and formaldehyde.

First, in table 1, we have placed methanol and formaldehyde in a third mixed/undetermined source category as suggested.

Second, we have moved Line 17, Page 6409 (“C6-C10 aromatic VOCs were selected for analysis of primary compounds because they have readily identifiable parent masses, they are sensitively detected by PTR-MS, and have a relatively wide range of reactivity with OH ($k_{OH} = 1.22 \times 10^{-12} \text{ s}^{-1}$ to $56 \times 10^{-12} \text{ s}^{-1}$)”) to Page 6411, Line 19 to clarify which VOCs were included in analysis of primary compounds, and why.

Third, on Page 6418, we have revised paragraph 1 to read, “We also assume that the only source of these species is photochemistry; i.e. they are not emitted directly from primary sources. **Methanol and formaldehyde are included in this section as they are oxygenated species. However, the high observed mixing ratios of methanol and formaldehyde (Table 1), previous modeling work (Edwards et al., 2014), and knowledge of industry practices indicates that these two species also have direct (primary) sources. We first analyzed methanol and formaldehyde assuming solely photochemical sources, to investigate the extent to which secondary formation can explain their behavior. We then modified the analysis to consider primary emission of these species.** Methanol and formaldehyde are discussed separately in the analysis (below).” (New content in bold text.)

Fourth, we have split Figure 9 into two panels, to better provide visual distinction between the two groups of compounds, and have updated the caption to read, “The best fit does not reproduce night time variability or trends in methanol and formaldehyde, which may have substantial primary sources uncorrelated with benzene.”

Finally, we have edited Page 6420 lines 1-5 to clarify that methanol clearly has primary sources. Line 1-2 now reads, “For methanol, this behavior is almost certainly due to large primary sources.” Line 3 now clearly states that methanol is used by industry on wellpads. We have added “It is therefore unsurprising that methanol variation is poorly described by Equation (6)” before line 6. We also briefly describe the relationship between formaldehyde and NO_x at line 9 (see response to Reviewer 2).

These revisions, together with the extant discussion of primary emission of methanol and formaldehyde (Page 6420 paragraph 1), clarify our analysis of the sources of these two compounds

We address the reviewer's concern regarding an exaggerated methanol contribution to photochemical carbon mass in our response to point 4 (below).

4. Further on methanol, how would the inclusion of methanol to primary or secondary (or primary+secondary) compounds affect the total carbon mass balance?

Response: We agree with the reviewer that the classification of methanol and formaldehyde as primary or secondary has an effect on the total carbon mass balance. We have constrained this effect by including some additional calculation in the manuscript. We have inserted the following paragraph on Page 6422, after Line 20:

"Methanol and formaldehyde have substantial primary sources, so including them in this calculation artificially increases the percentage of secondary species accounted for: 0.64×10^{-10} gram C cm^{-3} is an upper bound to the mass of measured secondary species. If we assume methanol is entirely primary, measured secondary species only sum to 0.48×10^{-10} gram C cm^{-3} , or 12.9% of calculated secondary carbon mass. If we assume both methanol and formaldehyde have no photochemical sources, measured secondary species sum to 0.46×10^{-10} gram C cm^{-3} , or 12.5% of calculated secondary carbon mass. Figure 10 shows the upper bound to measured secondary species (including both methanol and formaldehyde)."

5. Figure 10. Could "start of ozone event: measured oxygenates" be also zoomed in to show the carbon mass broken down by individual compounds?

Response: We added an additional inset in Figure 10 to show speciation of oxygenates as suggested.

6. Figure 8, the pie chart shows C2-C5 alkanes and methane but the caption indicates that C1-C5 alkanes contributed significantly to OH reactivity. It may seem a little bit confusing because C1 (methane) is shown to have a relatively small contribution.

Response: The reviewer is correct in understanding that C1 (methane) did not contribute significantly to OH reactivity, compared to other alkanes. We have corrected this error in the caption, and corrected Page 6418 Line 21-24 to read "Despite how slowly these compounds react with OH, the very large concentration of these compounds means that C2-C5 alkanes account for most of the reactions between OH and VOCs, and are the most important precursor compounds (Fig. 8b)."

References:

Li, R., Warneke, C., Graus, M., Field, R., Geiger, F., Veres, P. R., Soltis, J., Li, S.-M., Murphy, S. M., Sweeney, C., Pétron, G., Roberts, J. M., and de Gouw, J.: Measurements of hydrogen sulfide (H₂S) using PTR-MS: calibration, humidity dependence, inter-comparison and results from field studies in an oil and gas production region, *Atmos. Meas. Tech.*, 7, 3597-3610, doi:10.5194/amt-7-3597-2014, 2014.

Tarver, G. A. and Dasgupta, P. K.: Oil Field Hydrogen Sulfide in Texas: Emission Estimates and Fate, *Environ. Sci. Technol.*, 31, 3669-3676, 1997.

Warneke, C., Veres, P., Murphy, S. M., Soltis, J., Field, R. A., Graus, M. G., Koss, A., Li, S.-M., Li, R., Yuan, B., Roberts, J. M., and de Gouw, J. A.: PTR-QMS versus PTR-TOF comparison in a region with oil and natural gas extraction industry in the Uintah Basin in 2013, *Atmos. Meas. Tech.*, 8, 411-420, doi:10.5194/amt-8-411-2015, 2015.

Revised Figures

Figure 09

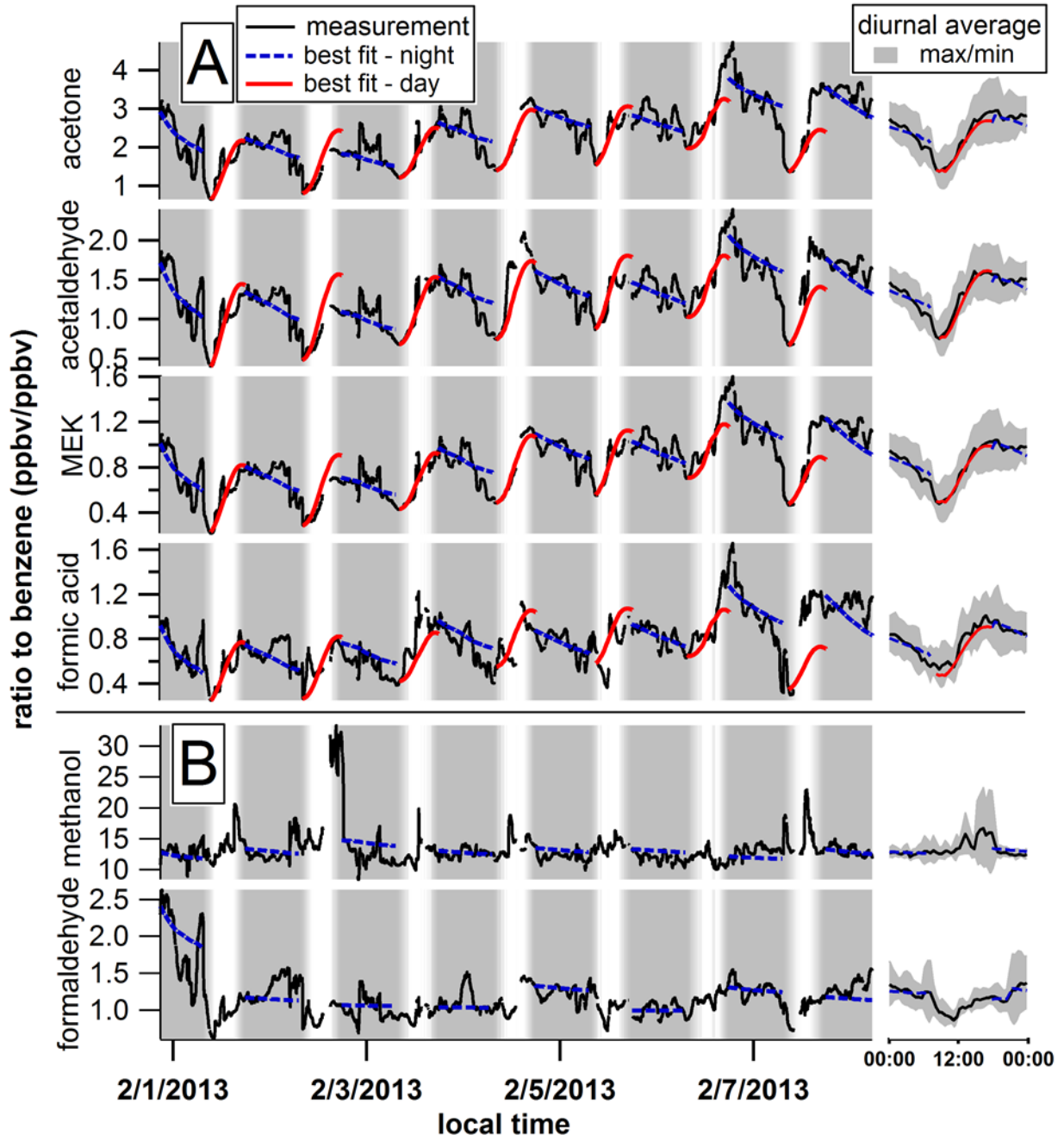


Figure 10

