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Discussions

Interactive comment on "Photochemical aging of volatile organic compounds associated with oil and natural gas extraction in the Uintah Basin, UT, during a wintertime ozone formation event" *by* A. R. Koss et al.

Anonymous Referee #1

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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:

General

- 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).

Specific

- 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)?

- 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.

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

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

Technical

- 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.

References

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