

Interactive comment on “Ozone photochemistry in an oil and natural gas extraction region during winter: simulations of a snow-free season in the Uintah Basin, Utah” by P. M. Edwards et al.

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1. The authors state that the inclusion of Criegee Intermediate chemistry only results in a 1% increase in the OH and O₃ formed in the model. Could the authors give more details on the CI scheme used? In particular how are they constraining the fraction of CI from ozonolysis that leads to the formation of HO_x cf. to stabilization. The CIs produced in ozonolysis will be produced with a Boltzmann distribution of vibrational energies. The CIs with enough vibrational energy to overcome the energy barrier to unimolecular decomposition will decompose to produce HO_x. The fraction that produces HO_x depends on the nature of the alkene, indeed, Donahue et al., 2011 (PCCP,

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13, 10848) suggest that for C₂-C₁₅ precursors all CI can be completely stabilised. Given that this fraction will govern the impact of CI on the OH in the model, could the authors give more details on how they treat such chemistry. Furthermore, recent experimental studies (Welz et al., 2012, Science, 335, 204) suggest that CI reactivity is considerably different than had previously been assumed in the MCM. This has been further supported by field studies (e.g. Maudlin et al., 2012 Nature, 488, 193) which suggest a more dominant role of CI chemistry in the troposphere, again more details are required.

Cl in this manuscript refers to chlorine atoms not criegee intermediates, this has been clarified in the text (see below). The role of criegee intermediate chemistry outside of that described in the MCM v3.2 is outside the scope of this work, due to its still highly uncertain nature combined with the low concentrations of alkenes observed during UBWOS, making criegee production small compared to other environments (as shown by the small radical production from O₃ + alkene reactions in Figs. 5 & 6).

“The MCM chemistry scheme has been modified to include the photolysis of ClNO₂ to yield a chlorine radical (Cl).”

2. Only 3 non aromatic alkenes are reported in the Supplementary material. Were other alkenes attempted to be measured? Given that 1,3 butadiene is measured it would seem that there is an influence of combustion sources. This would suggest that there would be the possibility of observing other alkenes. If alkenes were measured but were below the limit of detection this should be stated. This again will have a major impact on the CIs on radical sources

The alkenes used as model constraints (shown in S2 (e)) were the only alkenes with average diurnal concentrations significantly above the instruments limit of detection (~1 pptv). The campaign average ethene was ~600 ppt and propene was 60 ppt. These two compounds were very well correlated ($r^2 = 0.92$) during the campaign indicating a common combustion source without a lot of photochemistry occurring. All of

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the C5 alkenes (pentenes and methylbutenes) were below detection limit in the sample with the maximum alkenes, so they wouldn't expected to be prevalent under "average" conditions. We also looked for biogenics (isoprene and the monoterpenes) but did not see any significant concentrations. Mostly below detection limit for all of these species. The text below has been added to the S2 caption to clarify this. This alkane rich - alkene poor VOC mixture is typical of regions dominated by emissions from oil and gas extraction (Gilman et al. 2013). The below comment has been added to the text in S2 (e).

“(other measured alkenes (C2-C5) were generally below the instruments limit of detection (~1 pptv) throughout the campaign)”

3. Ozone deposition rates vary considerably. Rates vary from 0-9 mms-1 (Wesley and Hicks, 2000, Atmos. Environ, 34, 2261; Emberson et al., Water, Air and Soil Pollution, 2001, 30, 577). How is the variability taken into account the author's model and what impact would heterogeneity have their reported results?

As described in Sect. 2 “The O3 physical loss rate of $4.4 \times 10^{-6} \text{ s}^{-1}$ was chosen based on calculations of nighttime O3 removal and the observed NOx concentrations, assuming the only nocturnal losses of O3 are reaction with NOx and physical removal”. The authors appreciate the considerable variability in observed O3 deposition rates reported in the literature, and realize that the value used in this study is an approximation of what may have been a variable parameter. It is not clear that O3 deposition would have been highly heterogeneous in this environment, however, since it featured rather uniform desert soil and vegetation over a wide area surrounding the measurement site. Furthermore, as the focus of this study is the photochemistry controlling O3 production in this unusual emissions environment, we feel that the approach taken to estimate the average deposition velocity of O3 is valid. Changes in surface loss rates of O3 for this study, although will likely change the overall O3 concentration calculated by the model, will not change the production rates, mechanisms and sensitivities, and thus the conclusions of this paper. In the case of a snow covered “winter O3 event” however, the

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reduction in surface deposition of O3 to the snow surface, compared with the soil surface seen during UBWOS 2012, may have a significant effect on the rate of O3 build up. During the preparation of this manuscript the change in surface deposition rate for O3 was not known, and thus only the chemistry sensitivities were focused on. This parameter was, however, measured during the recent UBWOS 2013 study when snow cover and high O3 episodes were observed, and will be discussed in future work.

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