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# ***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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Received and published: 24 July 2013

1. Abstract, the phrase “highly radical limited” needs some qualification as it is not entirely clear what this means before it is covered in the text “Primary radical source” needs defining in the abstract, as again the precise meaning of this (which can vary from study to study) is not given until later in the paper. “Radical amplification reactions” again might just need defining in the abstract briefly Does the abstract want to include a sentence on the model run with conditions similar to those under snow-cover/low temperature conditions?

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These phrases have been defined in the abstract, and the following sentence added about the cold pool snow-cover simulations.

“Model simulations attempting to reproduce conditions expected during snow-covered cold pool conditions show a significant increase in O<sub>3</sub> production, although calculated concentrations do not achieve the highest seen during the 2010-2011 O<sub>3</sub> pollution events in the Uintah Basin.”

2. Page 7512, line 5, “exceptional levels”

Corrected

3. Page 7513, line 25, should it be “<” and not “>”? Otherwise some comment is warranted.

Typeset error missed during proof – now corrected

4. How is NO<sub>x</sub> constrained in the model, this was not that clear (and not included in the initial list of model constraints).

This is described in mode detail in Sect. 3, however, the text below has been added to Sect. 2.2 (pg 7513)

“In order for NO<sub>x</sub> concentrations to be consistent with the model chemistry scheme, model NO<sub>x</sub> is constrained by the use of an emission of NO which is tuned to best match the observed NO and NO<sub>2</sub> concentrations.”

5. Page 7515 line 23 “does a reasonable job” is rather subjective - needs rewording

Have added the text below to make this statement more quantitative

“The model does a reasonable job of simulating the observed O<sub>3</sub> profile, with the daily mean calculated O<sub>3</sub> mixing ratio agreeing with the observations to within 10% and accounting for 85% of the observed daily average 16 ppbv rise in O<sub>3</sub> mixing ratio.”

6. Page 7515 line 27 “Diurnally averaged”

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Corrected

7. Page 7516 line 19 “model simulated”

Corrected

8. Page 7517 line 28 “near the surface”

Corrected

9. Page 7518-9, the model is not able to calculate the mixing ratios of HONO, HCHO and CINO<sub>2</sub>. This is left hanging somewhat, can there be some more discussion on the reasons that the model is not able to accurately determine these species (presumably lack of knowledge of their sources which include heterogeneous routes, or deposition rates), and the model runs which use the measured values for these species versus the model calculated values for these species. It seems that the differences are very large (e.g. for Cl atoms) between constraining with measurements or free-running.

The following explanation has been added to the text

“The inability of the chemistry scheme to simulate the concentrations of the radical precursors HCHO, HONO and CINO<sub>2</sub> is due largely to a lack of knowledge about their sources, in particular those of HONO and CINO<sub>2</sub> which are thought to be dominated by heterogeneous process (see Sect. 1) that are not represented in the MCM v3.2 chemistry scheme used in this work. For HCHO it is likely that a primary emission within the Uintah basin that is not described within the model accounts for a significant fraction of the HCHO source (see Sect. 4).”

10. Page 7521. Radical amplification is defined in line 15, but this term is used several times already, it should be defined earlier.

This definition has been moved to the first mention of radical amplification after the abstract (Sect. 4, pg 7517).

11. Page 7523 – line 15-20. Will there be species not measured or in the model that



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contribute to OH reactivity – and so the loss rate of OH will be underestimated in the model? Some comment needed.

Although it is unlikely that there are significant primary emitted OH sinks missing from the observations, due to the comprehensive mix of instrumentation used during UB-WOS 2012 and the single source-type nature of the petrochemical dominated emissions, it is possible that the concentrations of the oxidation products of these primary VOCs are calculated incorrectly within the model. The following statement has been added to this section of the manuscript (also see response to comment 15)

“It is possible that the model calculates unmeasured VOC oxidation products incorrectly, and thus that there is some uncertainty in the OH reactivity. For example, simulations in which measured oxidation products such as acetaldehyde and methyl ethyl ketone were unconstrained calculated the concentrations of these products to within a factor of two of the observations. However, the model calculates a complete set of oxidation products, and even a twofold uncertainty in this calculation would not significantly alter the conclusion that OH reactivity is dominated by VOCs rather than NOx.”

12. Page 7524 line 11, “very few radical-radical collisions “ is an odd phrase here. Although the concentration of radicals will be low, and so radical-radical reactions will not be important, the number of gas kinetic collisions per second between these species will still be quite a high number.

This has been changed to:

“The overwhelming loss of radicals via nitric/nitrate/PAN formation is indicative of the low radical concentrations within the model, resulting in radical-radical reactions being insignificant”

13. Page 7524, line 13, “radical limited”

Corrected

14. Page 7528, line 3, “tuned” is rather an imprecise term. “using an emission”. Should

it be “emission rate”? This sounds the model will get the O<sub>3</sub> right as the precursors are adjusted for this to occur?

The emissions of HCHO, HONO and CINO<sub>2</sub> were not chosen to best match the O<sub>3</sub> concentration, but the observed concentrations of HONO, HCHO and CINO<sub>2</sub>. The text has been changed to:

“For simulation of cold pool conditions, the concentrations of these radical precursors have been constrained using an emission rate, instead of constraining the concentrations themselves.”

15. Page 7528 – given that the snow increases the photolysis rates and radical levels considerably, having OH/HO<sub>2</sub> measurements for any future study (perhaps with and without snow) would be beneficial. It is clear that it is essential to have HONO, CINO<sub>2</sub> and HCHO measurements as the model cannot reproduce the observed levels.

The reviewer makes a good point, and we agree that radical observations would be very useful in this environment. These measurements are, however, difficult to make, and the very high OH sink rates and low radical production during UBWOS 2012 may put OH concentrations close to or below instruments detection limits. As discussed in Sect. 7, radical production rates should increase under snow covered cold pool conditions, and the steady state radical concentrations may increase. In these conditions radical observations, as well as measurements of OH reactivity to better constrain the OH sinks, would be highly useful. The following sentence has been added to the text to this effect.

“Observations of OH and HO<sub>2</sub> radical concentrations, as well as OH reactivity, would also be beneficial during a wintertime O<sub>3</sub> pollution event, as these measurements would provide an excellent test of the models skill in representing the radical sources and sinks.”

16. Page 7444, figure 6. Line 2 of caption should be figure 5 (Corrected). Would using

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the term “net” OH production from HONO be a better way of describing the “primary” OH from HONO?

The reviewer’s recommendation of the term “net” instead of primary is worth considering. However, we feel the use of the word “primary” fits better with the descriptions of the other radical sources within the paper, split into “primary” and “amplification” radical sources.

17. Page 7548, figure 10 (a). There is quite a bit of OH at night, some comment in the text would be useful on this.

In both simulations shown in Figure 10 OH goes to zero at night. HO<sub>2</sub> does persist at sub 106 molecule cm<sup>-3</sup> concentrations throughout the night in the model, due largely to the lack of significant levels of NO during the night.

18. Page 7549, figure 11. “and true radical termination reaction” need something like “see text for details” otherwise this is not clear, or add “i.e. not propagation reactions”

Added “(see text for details)” to figure caption.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 13, 7503, 2013.

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