Atmos. Chem. Phys. Discuss., 13, C2551–C2555, 2013
www.atmos-chem-phys-discuss.net/13/C2551/2013/

Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #1

Received and published: 21 May 2013

Previous measurements at this location in the winters of 2009-2010 and 2010-2011 demonstrated high levels of ozone (above the regulated limit) during a period of snow cover and very cold temperatures. The region is associated with high levels of VOCs owing to gas/oil production, and significant levels of NOx. The very high levels of ozone were surprising, and this paper describes a return visit to the site in early 2012 with a wider suite of measurements in order to try to understand the chemical mechanisms responsible for the observed levels of O3 production.

However, conditions were quite different in early 2012 compared to the earlier studies, namely there was no snow cover (so albedo lower and possibly differences in hetero-

geneous processes) and the temperatures were much higher (so the boundary layer height likely higher and rates of OH reactions with VOCs faster). Although O3 production was still observed (with a regular daily cycle), the levels of O3 were much lower and not above the regulated limits. The paper uses the suite of measurements and a detailed box model (MCM v3.2) in order to probe the major O3 production mechanisms, the routes to radical generation, and whether the O3 production is VOC or NOx limited.

There are an impressive set of measurements including HCHO, HONO and ClNO2, which are all difficult to measure and often missing from such studies. The composition has been determined in a very high level of detail for this region which is impacted by significant industrial activities via the oil/gas wells. There were no radical measurements (e.g. OH, HO2, OH reactivity) which would have enabled further model comparisons (and reinforced the accuracy of quantifying the major radical loss or production processes). The model was used to identify the major radical sources – O1D/H2O and O3/alkene were found to be very small, whereas HCHO/HONO/ClNO2 photolysis were significant. However, the model could not reproduce HCHO, HONO or ClNO2. Sensitivity studies were run varying a number of parameters, for example aromatics (setting aromatics to zero reduced the O3 production significantly, not the case for setting other VOCs to zero). Owing to the smaller photoylsis rates the radical production rate was lower than the emission rate of NOx, and so NOx dominated the loss of OH (rather than radical-radical), and the O3 production was very VOC sensitive even though the levels of VOCs were much higher than NOx. This is perhaps the most important conclusion from the paper as it is surprising. This finding was supported by sensitivity studies on the rate of O3 production whilst VOCs and NOx levels were varied, although the impact on radical concentrations (which drive the O3 production) was not studied directly.

Although there was no snow or cold temperatures for the 2012 study, the model was used to simulate these conditions (increased albedo, higher levels of VOCs/NOx/radical precursors owing to lower boundary layer), and found O3 levels were considerably

higher (not surprisingly) but still not as high as the levels observed in the previous years. A future study is needed in this oil/gas region during cold conditions with snow (with HONO, ClNO2, HCHO, and ideally also with radical measurements) is needed to confirm the conclusions.

This is a good paper with a lot of high quality measurements, including those not often measured (ClNO2, HONO) enabling more quantitative calculation of radical production rates in a region characterised by unusual emissions. The chemical mechanism used is highly detailed, and a number of interesting model runs enable the controlling influence of VOC and NOx emissions to be probed. The study is appropriate for ACP, and although further work will be need to confirm the findings (e.g. model runs under snow conditions), the results are interesting and worthy of publication. Some specific points are indicated below:

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?

Page 7512, line 5, “exceptional levels”

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

How is NOx constrained in the model, this was not that clear (and not included in the initial list of model constraints).

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

Page 7515 line 27 “Diurnally averaged”

Page 7516 line 19 “model simulated”

Page 7517 line 28 “near the surface”

Page 7518-9, the model is not able to calculate the mixing ratios of HONO, HCHO and ClNO2. 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.

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

Page 7523 – line 15-20. Will there be species not measured or in the model that contribute to OH reactivity – and so the loss rate of OH will be underestimated in the model? Some comment needed.

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.

Page 7524, line 13, “radical limited”

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 O3 right as the precursors are adjusted for this to occur?

Page 7528 – given that the snow increases the photolysis rates and radical levels considerably, having OH/HO2 measurements for any future study (perhaps with and

without snow) would be beneficial. It is clear that it is essential to have HONO, ClNO2 and HCHO measurements as the model cannot reproduce the observed levels.

Page 7444, figure 6. Line 2 of caption should be figure 5. Would using the term "net" OH production from HONO be a better way of describing the "primary" OH from HONO?

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

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"

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