

We thank the reviewers for their comments and their attention to this manuscript. Reviewer comments are in black, responses in blue, and changes to the manuscript in *blue italics*.

**Reviewer #1:**

Wild et al compare the effect of daytime and nighttime losses of NO<sub>x</sub> on wintertime O<sub>3</sub> formation in the Uintah Basin. They show that the differences between 2012 (low O<sub>3</sub> levels and production rates) and 2013 (high O<sub>3</sub> levels and production rates) are, to some extent, related to rates of removal of NO<sub>x</sub>, with an important contribution from N<sub>2</sub>O<sub>5</sub> uptake to aerosol (and perhaps the ground), with longer N<sub>2</sub>O<sub>5</sub> lifetimes in 2012 (weaker heterogeneous processing) resulting in higher O<sub>3</sub> production rates. Nighttime formation of HNO<sub>3</sub> dominated over daytime formation.

The manuscript provides insight into the relative importance of the usual routes of NO<sub>x</sub> loss in this particular environment, characterized by high VOC levels (largely alkanes) and low temperatures. The authors may wish to address the following issues.

P21388 L15 Chemical production of O<sub>3</sub> is said to dominate (70%) its budget at this site. The reader is referred to Edwards 2013. It would be useful (in short form) to see how this has been calculated (what are the major chemical loss terms etc.) and how this varied between 2012 and 2013. What were the differences in the BL dynamics in the two years? In the end, it will be important to assess the differences in rates of entrainment (and not just chemistry) when talking about the different O<sub>3</sub> levels between 2012 and 2013.

The analysis from (Edwards 2013) for the 2012 conditions calculated the contribution of chemical production two ways. First, from comparisons of the modeled to the measure O<sub>3</sub> rise at surface level, which suggested chemical production was responsible for 85% of the observed O<sub>3</sub> rise. Second, from comparison of the O<sub>3</sub> diel profiles at several heights up to 500 m, which gave a less certain estimate that 70% of the surface level rise was due to chemical production and 30% to mixing of O<sub>3</sub> rich air from aloft during morning hours. The text has been clarified to give this range.

*“For 2012, when atmospheric conditions were less stable, chemical production was estimated to account for 70-85% of the observed average diel rise in surface O<sub>3</sub>. These estimates were derived from comparison of the model to the measured surface level rise and from measurements of the diel average O<sub>3</sub> profile at different heights up to 500 m from a tethered balloon.”*

P21392 L19 In cases where the losses of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> are slow, steady state may not be achieved within the night. The McLaren method of calculating the lifetime of NO<sub>3</sub> or N<sub>2</sub>O<sub>5</sub> then delivers more reliable results. Why do the authors stick to using equation (1) in this case and quote only the differences at two times of night. Could Figure 7 be redrawn using the McLaren method?

The McLaren calculation has now been explicitly included in Figure 7. Text has been revised to read:

*Figure 7 also shows the steady state lifetime calculated using this method using a smooth fit function for the N<sub>2</sub>O<sub>5</sub> diurnal profile to calculate the derivative.*

The figure caption has also been revised accordingly.

P21392 L24, Figure7 Replacing [N<sub>2</sub>O<sub>5</sub>] with [NO<sub>3</sub>] in equation (1) would give the NO<sub>3</sub> lifetime for which many values are available for different environments. Comparison of tau-NO<sub>3</sub> with other locations and conditions would be useful. Similarly, comparison of previously reported N<sub>2</sub>O<sub>5</sub> lifetimes may indicate to what extent the conclusions from this study are transferable to other (similar) locations.

Because these data are for a cold environment and dominated by sinks for N<sub>2</sub>O<sub>5</sub> rather than NO<sub>3</sub>, the N<sub>2</sub>O<sub>5</sub> lifetime is the relevant number. Consequently, we prefer not to change Figure 7 to show NO<sub>3</sub> lifetimes, which are very short and not representative of the reactivity of N<sub>2</sub>O<sub>5</sub> that the figure is intended to illustrate. We do, however, quote these lifetimes in the text for references, as the reviewer suggests.

*The average value of the product of the NO<sub>3</sub>-N<sub>2</sub>O<sub>5</sub> equilibrium constant,  $K_{eq}(T)$ , and the NO<sub>2</sub> concentration ( $K_{eq}[NO_2]$ ), equal to the predicted ratio of N<sub>2</sub>O<sub>5</sub> to NO<sub>3</sub>, was 115 and 440 during nighttime hours in 2012 and 2013, respectively. Late night average NO<sub>3</sub> of 2.2 pptv agreed well with the predicted equilibrium. Average predicted NO<sub>3</sub> of less than 0.5 pptv in 2013 could not be accurately measured. The late night average steady state lifetime of NO<sub>3</sub> in 2012 was approximately 100 s, while in 2013 it was 13 s. Under these cold conditions, the very short NO<sub>3</sub> lifetimes do not represent the reactivity of the NO<sub>3</sub>-N<sub>2</sub>O<sub>5</sub> system, which is dominated by heterogeneous loss of N<sub>2</sub>O<sub>5</sub>. We provide them here for reference only.*

P21393 L15 The uptake of N<sub>2</sub>O<sub>5</sub> is highly variable. Why are the uptake coefficients reported by Wagner 2013 considered to be appropriate? Same temperatures? Same location? Same air masses? Uptake of N<sub>2</sub>O<sub>5</sub> is controlled less by temperature and more by particle composition (nitrate content etc.).

We agree with the reviewer that our analysis does not account for potential variability in N<sub>2</sub>O<sub>5</sub> uptake coefficients. To our knowledge, the Wagner *et al.* reference is the only previous winter data available. It also took place in a similar range of temperature and relative humidity, and at nearly identical latitude and elevation. We have added this information to the text.

*There are few determinations of N<sub>2</sub>O<sub>5</sub> uptake coefficients in winter. During winter measurements in Colorado, Wagner *et al.* (2013) determined an average  $\gamma = 0.02$  under similar conditions of temperature and relative humidity, and at a site with nearly identical latitude and elevation. Using  $\gamma = 0.02$ , we calculate lifetimes of N<sub>2</sub>O<sub>5</sub> ...*

P21394 L10 The calculation of the  $\text{NO}_3$  loss rate in equation (3) implies that all the VOCs were measured. As the authors mention on the next page, reduced sulphur (RS) species may also contribute to  $\text{NO}_3$  loss. Previous reports of  $\text{NO}_3$  lifetimes close to oil refinery operations (Crowley et al., Atmos. Chem. Phys., 11, 10863-10870, 2011) indicate an important role for RS. Apart from  $\text{CH}_3\text{SCH}_3$ , were any RS compounds measured ?

We agree this is an important point. No measurements of other RS species were available. The following has been added to the end of this paragraph.

*It is possible that other highly reactive but unmeasured VOCs contribute to the  $\text{NO}_3$  reactivity. For example, Crowley et al. (2011) report an important role for reduced sulfur species other than DMS in loss of  $\text{NO}_3$  radicals near an oil refinery. Such measurements were unavailable for this UBWOS studies.*

P21394 L15 The heterogeneous loss of  $\text{NO}_3$  appears to be modeled by scaling the  $\text{N}_2\text{O}_5$  loss rate by the  $\text{NO}_2$  concentration and the equilibrium ratio. This is not correct. The uptake coefficients of  $\text{NO}_3$  are not necessarily the same as for  $\text{N}_2\text{O}_5$  on the same aerosol (Tang et al Atmos. Chem. Phys., 10, 2965-2974, 2010). What the authors calculate is the indirect loss of  $\text{NO}_3$  due to  $\text{N}_2\text{O}_5$  uptake, which should not be compared to direct losses by reaction with e.g. VOCs.

The sentence was confusing and has been revised. It was intended to specify how the first order loss rate for  $\text{NO}_3$  via VOC reactions should be compared to the first order loss rate for  $\text{N}_2\text{O}_5$  due to heterogeneous uptake. It now reads.

*This first order loss rate coefficient for  $\text{NO}_3$  can be compared to the first order loss rate coefficient for uptake of  $\text{N}_2\text{O}_5$  to aerosol by dividing the former by the equilibrium ratio of  $\text{N}_2\text{O}_5/\text{NO}_3$  (Brown 2003).*

P21396 L16 Does the “the nighttime heterogeneous pathway” refer to (R4). If so, the word heterogeneous is inappropriate. In this context, it would be useful to examine the effect of switching the  $\text{N}_2\text{O}_5$  uptake on and off in the model. Presumably this can be done by modeling the  $\text{N}_2\text{O}_5$  uptake as a first-order loss process constrained by observed aerosol surface areas. This would then give an idea of the overall effect of  $\text{N}_2\text{O}_5$  uptake (relative to other  $\text{NO}_x$  losses).

The “nighttime heterogeneous pathway” refers to the sum of (R4-R6), but the rate that is changed is for (R4) only. We agree with the reviewer and have removed the word heterogeneous. We also agree with the reviewer that simulations in which only the heterogeneous reaction was switched on and off (rather than scaling the source reactions) would be instructive. We feel that such additional simulations are beyond the scope of this paper at this stage, however.

P21398. The authors conclude that nighttime  $\text{N}_2\text{O}_5$  processing plays an important role in  $\text{NO}_x$  chemistry and related  $\text{O}_3$  production. However, it remains unclear to which extent

the great change (almost factor 3) in O<sub>3</sub> between the years 2012 and 2013 is attributable to this (and other NO<sub>x</sub> related processes), and how much is attributable to differences in boundary layer dynamics and entrainment rates.

We respectfully refer the reviewer to the analysis of Edwards 2013 and Edwards 2014, who explain the NO<sub>x</sub> and VOC sensitivities for O<sub>3</sub> production in the 2 years. The principal role of the boundary layer dynamics between the two years is to concentrate surface level emissions in 2013 relative to 2012. Although both NO<sub>y</sub> and VOC are significantly more concentrated within the shallow 2013 boundary layer, photochemically active NO<sub>x</sub> remained approximately the same. The current manuscript explains the mechanism by which NO<sub>x</sub> remains constant while NO<sub>y</sub> changed dramatically.

P21388 L25 “rates“ rather than “levels” of NO<sub>x</sub> oxidation. P21391 L23 “concentrations” rather than “values”

Changed as suggested