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Comment

Interactive comment on “Reactive nitrogen partitioning and its relationship to winter ozone events in Utah” by R. J. Wild et al.

Anonymous Referee #1

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Wild et al compare the effect of daytime and nighttime losses of NO_x on wintertime O₃ formation in the Uintah Basin. They show that the differences between 2012 (low O₃ levels and production rates) and 2013 (high O₃ levels and production rates) are, to some extent, related to rates of removal of NO_x, with an important contribution from N₂O₅ uptake to aerosol (and perhaps the ground), with longer N₂O₅ lifetimes in 2012 (weaker heterogeneous processing) resulting in higher O₃ production rates. Nighttime formation of HNO₃ dominated over daytime formation.

The manuscript provides insight into the relative importance of the usual routes of NO_x loss in this particular environment, characterised by high VOC levels (largely alkanes) and low temperatures. The authors may wish to address the following issues.

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P21388 L15 Chemical production of O₃ 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 O₃ levels between 2012 and 2013.

P21392 L19 In cases where the losses of NO₃ and N₂O₅ are slow, steady state may not be achieved within the night. The McLaren method of calculating the lifetime of NO₃ or N₂O₅ 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 ?

P21392 L24, Figure7 Replacing [N₂O₅] with [NO₃] in equation (1) would give the NO₃ lifetime for which many values are available for different environments. Comparison of tau-NO₃ with other locations and conditions would be useful. Similarly, comparison of previously reported N₂O₅ lifetimes may indicate to what extent the conclusions from this study are transferable to other (similar) locations.

P21393 L15 The uptake of N₂O₅ 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 N₂O₅ is controlled less by temperature and more by particle composition (nitrate content etc.).

P21394 L10 The calculation of the NO₃ 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 NO₃ loss. Previous reports of NO₃ lifetimes close to oil refinery operations (Crowley et al., Atmos. Chem. Phys., 11, 10863-10870, 2011) indicate an important role for RS. Apart from CH₃SCH₃, were any RS compounds measured ?

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P21394 L15 The heterogeneous loss of NO₃ appears to be modelled by scaling the N₂O₅ loss rate by the NO₂ concentration and the equilibrium ratio. This is not correct. The uptake coefficients of NO₃ are not necessarily the same as for N₂O₅ on the same aerosol (Tang et al Atmos. Chem. Phys., 10, 2965-2974, 2010). What the authors calculate is the indirect loss of NO₃ due to N₂O₅ uptake, which should not be compared to direct losses by reaction with e.g. VOCs.

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 N₂O₅ uptake on and off in the model. Presumably this can be done by modelling the N₂O₅ uptake as a first-order loss process constrained by observed aerosol surface areas. This would then give an idea of the overall effect of N₂O₅ uptake (relative to other NO_x losses).

P21398. The authors conclude that nighttime N₂O₅ processing plays an important role in NO_x chemistry and related O₃ production. However, it remains unclear to which extent the great change (almost factor 3) in O₃ between the years 2012 and 2013 is attributable to this (and other NO_x related processes), and how much is attributable to differences in boundary layer dynamics and entrainment rates.

P21388 L25 “rates” rather than “levels” of NO_x oxidation.

P21391 L23 “concentrations” rather than “values”

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 21383, 2015.

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