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Atmospheric Chemistry and Physics Discussions

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 NOx 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 NOx, 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 NOx loss in this particular environment, characterised by high VOC levels (largely alkanes) and low temperatures. The authors may wish to address the following issues.

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 ?

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 NOx losses).

P21398. The authors conclude that nighttime N2O5 processing plays an important role in NOx 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 NOx related processes), and how much is attributable to differences in boundary layer dynamics and entrainment rates.

P21388 L25 "rates" rather than "levels" of NOx oxidation.

P21391 L23 "concentrations" rather than "values"

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