

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_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, characterized 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.

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 O₃ rise at surface level, which suggested chemical production was responsible for 85% of the observed O₃ rise. Second, from comparison of the O₃ 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 O₃ rich air from aloft during morning hours. The text has been clarified to give this range.

“For 2012, when atmospheric conditions were least stable, chemical production was estimated to account for 70-85% of the observed average diel rise in surface O₃. These estimates were derived from comparison of the model to the measured surface level rise and from measurements of the diel average O₃ profile at different heights up to 500 m from a tethered balloon.”

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?

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 N₂O₅ diurnal profile to calculate the derivative.

The figure caption has also been revised accordingly.

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.

Because these data are for a cold environment and dominated by sinks for N₂O₅ rather than NO₃, the N₂O₅ lifetime is the relevant number. Consequently, we prefer not to change Figure 7 to show NO₃ lifetimes, which are very short and not representative of the reactivity of N₂O₅ 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 NO₃-N₂O₅ equilibrium constant, $K_{eq}(T)$, and the NO₂ concentration ($K_{eq}[NO_2]$), equal to the predicted ratio of N₂O₅ to NO₃, was 115 and 440 during nighttime hours in 2012 and 2013, respectively. Late night average NO₃ of 2.2 pptv agreed well with the predicted equilibrium. Average predicted NO₃ of less than 0.5 pptv in 2013 could not be accurately measured. The late night average steady state lifetime of NO₃ in 2012 was approximately 100 s, while in 2013 it was 13 s. Under these cold conditions, the very short NO₃ lifetimes do not represent the reactivity of the NO₃-N₂O₅ system, which is dominated by heterogeneous loss of N₂O₅. We provide them here for reference only.

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.).

We agree with the reviewer that our analysis does not account for potential variability in N₂O₅ 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 N₂O₅ 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 N₂O₅ ...*

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 ?

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 NO₃ reactivity. For example, Crowley et al. (2011) report an important role for reduced sulfur species other than DMS in loss of NO₃ radicals near an oil refinery. Such measurements were unavailable for this UBWOS studies.

P21394 L15 The heterogeneous loss of NO₃ appears to be modeled 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.

The sentence was confusing and has been revised. It was intended to specify how the first order loss rate for NO₃ via VOC reactions should be compared to the first order loss rate for N₂O₅ due to heterogeneous uptake. It now reads.

This first order loss rate coefficient for NO₃ can be compared to the first order loss rate coefficient for uptake of N₂O₅ to aerosol by dividing the former by the equilibrium ratio of N₂O₅/NO₃ (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 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).

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 were 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 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.

We respectfully refer the reviewer to the analysis of Edwards 2013 and Edwards 2014, who explain the NO_x and VOC sensitivities for O₃ 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_y and VOC are significantly more concentrated within the shallow 2013 boundary layer, photochemically active NO_x remained approximately the same. The current manuscript explains the mechanism by which NO_x remains constant while NO_y changed dramatically.

P21388 L25 “rates“ rather than “levels” of NO_x oxidation. P21391 L23 “concentrations” rather than “values”

Changed as suggested

Reviewer #2

Summary and General Comments

Wild and coauthors present a multiyear analysis of measurement of speciated NO_y to determine the role that NO_y partitioning and loss processes has in contributing the elevated ozone mixing ratios observed in mountain valleys in winter. The manuscript primarily highlights the unique set of observations and contrasts the conditions of 2012 and 2014 that displayed varied meteorological conditions and how this translates to difference in (for example) the N₂O₅ lifetime. The manuscript is a nice addition to the literature and should be published following the authors attention to the following points.

Specific Comments:

Page 21385 Line 9: I am stumbling to interpret the first part of this sentence. Perhaps split the sentence in two. Based on the prior sentence, I would expect a comparative statement regarding NO_y partitioning between 2012, 2013, and 2014 in this sentence. This would be helpful. The second part of the sentence (concerning the role of N₂O₅ vs NO₂+OH for P(HNO₃) is critical, however again it would be of interest in the abstract to state how this number changed between years.

The first half of the sentence has been rewritten as “*Nitric acid comprised roughly half of NO_z (=NO_y-NO_x) in 2013, ...*”

The direct comparison of day and night HNO₃ production between 2012 and 2013 is difficult to make because N₂O₅ was much longer lived in 2012 and because N₂O₅ and ClNO₂ were large fractions of nighttime NO_z in 2012, whereas they were not in 2013. Thus, the simplifying assumption of quantitative conversion of NO₂ to HNO₃ via

nighttime chemistry that is applicable to 2013 does not hold for 2012. These details appear in the subsequent analysis of in the paper. In the abstract, we provide the following sentence to clarify this point:

“In 2012, N_2O_5 and $ClNO_2$ were larger components of NO_x relative to HNO_3 .”

Page 21388 Line 5: Consider rephrasing “In this analysis we focus on analysis . . .” Also, shouldn’t this be diel, not diurnal?

The reviewer is correct. “Diurnal” replaced with “diel” throughout.

Page 21390 Reactions: The association reactions (R1, R2, R3, R5) should include M on either side of the equation.

Third bodies have been added to association reactions

Page 21390 Line 26: How different is the average midday OH between the three years?

Calculated OH for 2012 has been added to the text for reference. There was no calculation of OH for 2014.

“During the 2012 study, calculated midday OH was $7 \times 10^5 \text{ cm}^{-3}$ (Edwards 2013)”

Page 21391 Line 5: What does “assume unit efficiency” mean? Please be more specific.

The phrase was intended to mean that the sequence of reactions for nighttime chemistry quantitatively converted NO_2 to HNO_3 . Sentence has been rephrased for clarity.

“The limiting step in reactions (R4) and (R5) is the $NO_2 + O_3$ reaction, and we assume that the sequence of reactions in (R4)-(R7) quantitatively converts NO_2 to stable products, mainly HNO_3 .”

Page 21392 Line 13: Please specify what species are assumed in steady state.

Sentence rewritten to clarify:

“Since Eq. (1) assumes a steady state in NO_3 and N_2O_5 , ...”

Page 21392 Line 13: Please elaborate on the growth factor calculation or provide a reference.

A reference to Bates et al. J. Geophys. Res., 107, 8026, 2002 has been added to the text.

Page 21393 Line 15: There needs to be a better justification for the use of gamma of 0.02. Is this consistent with the composition and RH measurements?

Please see responses above to reviewer #1. The uptake coefficient was chosen because of the similarity of this site to a previous the previous wintertime study of Wagner *et al.*, 2013.

Page 21393 Line 26: Please clarify “the change in aerosol uptake between the two years is in part due to higher relative humidity” Is this due to a change in gamma or a change in surface area?

The sentence is intended to mean a change in aerosol surface area due to greater aerosol hygroscopic growth, with a quantitative measure (factor of 1.3) given at the end of the paragraph. While the reviewer is correct that the RH could also change the uptake coefficient, that effect is much more difficult to predict quantitatively. The sentence has been rewritten.

“The change in aerosol uptake between the two years is in part due to the higher relative humidity measured in 2013, which increases the aerosol surface area through hygroscopic growth. The increased RH in 2013 caused frequent and persistent fog.”

Page 21394 Line 8: What does N₂O₅ hydrolysis in different situations mean? Is this implying a gas-phase hydrolysis? If so, I suggest this be omitted or a citation added that would justify that this occurs.

The sentence has been clarified. It was intended to state that loss of NO₃ and N₂O₅ can be dominated either by NO₃-VOC reactions or by N₂O₅ uptake depending on the characteristics of the sampled air mass.

*“Previous studies in regionally polluted areas have shown that loss of NO₃ and N₂O₅ can be dominated by NO₃-VOC reactions, N₂O₅ uptake or a combination of the two (Aldener *et al.*, 2006; Brown *et al.*, 2011).”*

Page 21394 Line 21: The comparison of the NO₃ loss rates and the N₂O₅ loss rates is for a specific gamma (0.02), which is not known. It should be clearly stated here that this calculation is based on that gamma value, and an assessment of the sensitivity of the NO₃ loss rate to the chosen gamma should be included. For example, if gamma was 0.005 (not unreasonable), I would expect that nocturnal nitrogen loss would be dominated by NO₃ gas phase reactions. Further, is there any evidence from the VOC measurements of NO₃ reactivity at night?

The reviewer is absolutely correct. The phrase “with an N₂O₅ uptake coefficient of 0.02” has been added to the sentence to make it clear that the comparison is for a particular choice of $\gamma(N_2O_5)$. The following sentence has also been added.

“A lower N_2O_5 uptake coefficient would increase the fraction of the NO_3 and N_2O_5 reactivity attributable to NO_3 -VOC chemistry. However, the comparisons of Figure 7 suggest that the average N_2O_5 uptake coefficient is not appreciably smaller than 0.02.”

Page 21395 Line 17: Was the gradient in particle surface area also measured?

No gradient in aerosol surface area was observed. Text now specifies that there was no gradient in NO_2 , O_3 or aerosol surface.

Page 21397 Line 27: Why is $ClNO_2$ production a small effect on NO_x ? Is this because the yield was low? I would have thought the yield of $ClNO_2$ would play an important part here due to NO_x regeneration.

The reviewer is correct, the statement refers to the small yield of $ClNO_2$. The phrase “*due to its low yield*” has been added to the end of the sentence.

Figure 7: I am struggling to understand why the N_2O_5 lifetime increases over the night (as calculated from $P(NO_3)$). Please expand on this point. Is this implying that particle surface area, RH, or particle composition is changing, or is this some sort of bias introduced from the analysis?

The increasing lifetime with time over the course of the night is due to the slow approach to steady state, as described in the text. The inclusion of the McLaren calculation in this figure, in response to reviewer #1, should help to clarify this point, since the McLaren lifetime varies less systematically with time.

Reactive nitrogen partitioning and its relationship to winter ozone events in Utah

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Abstract.

High wintertime ozone levels have been observed in the Uintah Basin, Utah, a sparsely populated rural region with intensive oil and gas operations. The reactive nitrogen budget plays an important role in tropospheric ozone formation. Measurements were taken during three field campaigns in the winters of 2012, 2013, and 2014, which experienced varying climatic conditions. Average concentrations of ozone and total reactive nitrogen were observed to be 2.5 times higher in 2013 than 2012, with 2014 an intermediate year in most respects. However, photochemically active NO_x (NO + NO₂), remained remarkably similar all three years. Roughly half of the more oxidized forms of nitrogen were composed of nitric acid. Nitric acid comprised roughly half of NO_z (\equiv NO_y - NO_x) in 2013, with nighttime nitric acid formation through heterogeneous uptake of N₂O₅ contribut-

ing approximately 6 times more than daytime formation. In 2012, N_2O_5 and $ClNO_2$ were larger components of NO_z relative to HNO_3 . The nighttime N_2O_5 lifetime between the high-ozone year 2013 and the low-ozone year 2012 is lower by a factor of 2.6, and much of this is due to higher aerosol surface area in the high ozone year of 2013. A box-model simulation supports the importance of nighttime chemistry on the reactive nitrogen budget, showing a large sensitivity of NO_x and ozone concentrations to nighttime processes.

1 Introduction

Wintertime ozone air pollution has recently been observed in several North American basins and currently represents one of the most severe air pollution problems in the United States (?????). It has been associated with emissions from oil and gas operations coupled with meteorological conditions that produce high surface albedo and temperature inversions, causing stable stagnation events. As with more conventional summertime urban air pollution, winter ozone production requires photochemistry of NO_x ($=NO + NO_2$) and volatile organic compounds (VOCs). In polluted areas, such as the Uintah Basin, NO_x is emitted mainly from fossil fuel combustion and can further oxidize to form reactive nitrogen species such as HNO_3 , acyl peroxy nitrates (PAN), N_2O_5 , NO_3 , $ClNO_2$, organic nitrates, etc., which, together with NO_x , make up total reactive nitrogen (NO_y). Oxidation of NO_x occurs through different reaction pathways during the day than at night, but both contribute significantly to NO_y speciation. Some of these species tend to be permanent sinks of NO_x , such as HNO_3 , whereas others such as PAN or N_2O_5 can act as temporary sinks (reservoirs) and revert to NO_x via photo- or thermochemistry. Thus, an understanding of the reactive nitrogen budget contributes to understanding ozone formation.

To study the conditions and precursors that cause these anomalous wintertime ozone events, we deployed a suite of ground based chemical, radiation and meteorological measurements as part of the Uintah Basin Winter Ozone Studies (UBWOS) in 2012, 2013 and 2014. The UBWOS studies in 2012 and 2013 experienced very different meteorological conditions and yielded strikingly different results. In 2012, the lack of snow cover and the associated shallow inversions produced ozone with average values that showed distinct photochemistry but did not approach the 75 ppbv 8 hour National Ambient Air Quality Standard (NAAQS), presenting a valuable baseline of chemical concentrations for this oil and gas-producing region (?). In 2013, however, the snow cover resulted in strong temperature inversions, increased precursor concentrations, and increased photochemistry, which brought about elevated ozone levels (?). The ~~Horse Pool~~ Horsepool measurement site in the Basin experienced exceedances of the ozone NAAQS on 20 out of the 28 days of measurement in 2013. In 2014 the conditions were intermediate both meteorologically and chemically. A direct comparison of 2012 with 2013 provides valuable insight into the key elements that cause high wintertime ozone. In this paper we focus on reactive nitrogen and its partitioning during the two years to help explain

the chemical processes that cause high ozone.

2 Field Campaigns and Measurement Techniques

The three successive campaigns were conducted on January 15 - February 27, 2012; January 23 - February 21, 2013; and January 28 - February 14, 2014 at the ~~Horse Pool~~Horsepool site near Vernal, Utah. The site is located at 40.14370°N, 109.46718°W, 35 km south of Vernal, Utah, the largest city
50 in the basin. The basin is mostly rural, with a total population of 50,000 concentrated mainly in three towns (Vernal, Roosevelt, and Duchesne). Approximately 10,000 producing oil/gas wells are spread throughout the basin, and the ~~Horse Pool~~Horsepool measurement site is situated within the predominantly natural gas producing wells in the eastern half of the basin, as seen in Figure ??.

55 The suite of measurements over the three years varied but was very extensive every year, and descriptions can be found in the final reports for the Uintah Basin Ozone Studies on the website of the Utah Department of Environmental Quality (www.deq.utah.gov/locations/U/uintahbasin/ozone/overview.htm). A brief summary of the ambient gas-phase reactive nitrogen measurements is given here. During all three years, NO,
60 NO₂, NO₃, and N₂O₅ were measured using cavity ring-down spectroscopy (CRDS), which was also used in conjunction with thermal dissociation (TD-CRDS) to measure NO_y in 2013 and 2014 (?). In 2012, NO_y was measured using catalytic conversion to NO on a gold tube at 325 °C with subsequent detection using chemiluminescence (CL) via the reaction with O₃. Nitric and nitrous acids were measured with an acetate ion chemical ionization mass spectrometer (acid CIMS) all
65 three years. Alkyl nitrates and peroxy nitrates were only measured in 2012, by thermally dissociating them to NO₂ and subsequently detecting them via laser-induced fluorescence (TD-LIF). Acyl peroxy nitrates (PANs) and nitryl chloride (ClNO₂) were measured all three years using an iodide chemical ionization mass spectrometer (I⁻ CIMS). Finally, there was extra focus on HONO in 2014,
70 which was measured by a long-path differential optical absorption spectrometer (LP-DOAS), a broadband cavity-enhanced spectrometer (ACES), and a long-path absorption photometer (LoPAP), as well as the acid CIMS and the I⁻ CIMS. The measurements and references for the techniques are summarized in Table ??. Due to the overlap or lack of some measurements in different years, not all the data were utilized in this analysis.

3 Results

75 3.1 Ozone and Reactive Nitrogen Levels

In this analysis we focus on analysis of ~~diurnal-diel~~ profiles, averaged over the duration of each field campaign. This method highlights the general differences between the years but does not distinguish between different meteorological conditions within a campaign. In ~~figure~~Figure ??, we show whole-

campaign ~~diurnal diel~~ averages of the ozone levels at the ~~Horse Pool~~ Horsepool ground site for the
80 winters of 2012, 2013, and 2014. The dotted line shows the NAAQS level of 75 ppbv. On average,
ozone levels were 2.5 times higher in 2013 than in 2012. Additionally, ozone production during
midday (between the dotted lines at 09:45 and 14:30 hours) was 2.7 ppbv/hr in 2012 and 6.9 ppbv/hr
in 2013, a factor of 2.6 higher. In 2014, the ozone levels were intermediate, with the daily increase
85 at 4.8 ppbv/hr. Although the ozone increase is affected both by chemical production and dilution
due to the changing boundary layer, chemical ozone production accounts for most of this increase
at this site. For 2012, when atmospheric conditions were least stable, ~~ozone measurements at 500 m~~
~~indicate that ozone production accounted for approximately 70%~~ chemical production was estimated
to account for 70-85% of the ~~daily increase in ozone concentrations~~ observed average diel rise in
surface O₃. These estimates were derived from comparison of the model to the measured surface
90 level rise and from measurements of the diel average O₃ profile at different heights up to 500 m from
a tethered balloon. (?).

The top plot in Figure ?? shows the diurnally averaged total reactive nitrogen (NO_y). The NO_y in
2013 is on average a factor of 2.5 higher than 2012, with 2014 again at intermediate levels. However,
the middle plot of Figure ?? shows that the total NO_x concentrations are consistently similar for all
95 three years, despite significantly different meteorological conditions and ozone production rates. The
bottom plot shows the ratio NO_x/NO_y, a measure of the level rate of oxidation of reactive nitrogen
independent of dilution, whereby a lower ratio implies more oxidation. The large differences in this
ratio (a factor 2.6 on average between 2012 and 2013) instead indicates large differences in levels of
NO_x oxidation caused by changes in ambient chemistry, which caused the similarity of NO_x levels
100 between the measurement years.

3.2 NO_y Partitioning and NO_x Oxidation

We examine the oxidation pathways and products in order to understand the different levels of NO_x
oxidation for the various years. Figure ?? shows the partitioning of NO_z (\equiv NO_y - NO_x) for 2012
and 2013. In 2012, since NO_x makes up approximately 80% of NO_y, the subtraction to calculate
105 NO_z results in a noisy trace with large uncertainty relative to the amount of NO_z present, and we
instead take the sum of components to define total NO_z. This is not the case in 2013, and the
“missing” part of NO_z is likely organic nitrates (RONO₂) for which we do not have a measurement.

Ammonium nitrate might be measured partially in the acid CIMS and the NO_y instrument due
to heated inlets, and its contribution to NO_z has not been included in this analysis. Measurements
110 of aerosol nitrate, which would include coarse mode aerosol whose source might not be exclusively
photochemical, present an average upper limit of 0.4 ppbv in 2012 and 1 ppbv in 2013. Nitrous acid,
HONO, was measured as a small fraction (2.4%) of NO_z in 2012. Its mixing ratio was measured by
both the acid CIMS and DOAS measurements, which both showed maximum values smaller than
120 pptv average at night and smaller during the day, with agreement to within a factor of 2. During

115 2013, the acid CIMS was the only measurement available. It showed very large signals at the mass normally interpreted as HONO with a distinct, daytime maximum. As described in [?](#), HO₂NO₂ mixing ratios were observed to reach an average daytime maximum of approximately 4% of NO_z. Unpublished laboratory results suggest that a large fraction of the HO₂NO₂ is detected as HONO using the acid CIMS, resulting in a positive daytime bias in the 2013 measurements. Based on the
 120 similarity of DOAS HONO measurements in 2012 and 2014, HONO for 2013 was set equal to that from 2012. For further details on comparisons of HONO measurements, please see [?](#).

In 2012, N₂O₅ and ClNO₂ make up about half of the total NO_z budget at night, whereas they form a small percentage in 2013. Nitric acid (HNO₃) and PAN, however, make up about 75% of total NO_z throughout the whole [diurnal-diel](#) cycle in 2013, with the inferred organic nitrates making up most of the remainder. The major oxidation pathways that produce these compounds during the day are:



where PA is the peroxyacetyl radical and includes all acyl peroxy radicals, with CH₃C(O)O₂ being the most important. The RO₂ include all other organic peroxy radicals, and α is the temperature-dependent yield of organic nitrates from the reaction of organic peroxy radical with NO, where the majority of this reaction produces an alkoxy radical and NO₂ ([?](#)). At night, when NO₃ is photochemically stable, the main pathway for NO_x oxidation is



This N₂O₅ can then further react heterogeneously to form nitric acid and nitryl chloride.



Calculating the reaction rates of [R1-4](#)[R1-5](#) allows us to compare NO_x loss rates (rates of conversion to NO_z) through these different pathways. The reaction rate constants are known, and the concentrations of OH and PA are supplied by a box model simulation using the master chemical mechanism (MCM), as is the production rate of organic nitrates. The MCM utilizes greater than
 125 10⁴ reactions, and the base run accurately reproduces an ozone buildup event in 2013 ([?](#)). Additionally, the OH concentrations agree with OH inferred from VOC ratios ([?](#)) with average midday maximum OH levels calculated by the model to be approximately 1 × 10⁶ cm⁻³. [During the 2012 study, calculated midday OH was 7 × 10⁵ cm⁻³ \(\[?\]\(#\)\)](#). Although PAN can thermally dissociate, the
 130 long lifetime at wintertime temperatures (>10 hours below 10°C) means we can effectively consider

only the forward reaction. The limiting step in R4-5 is the $\text{NO}_2 + \text{O}_3$ reaction and we assume ~~unit efficiency for reaction R5-7~~ that the sequence of reactions in R4-7 quantitatively converts NO_2 to stable products, mainly HNO_3 , at night in 2013 (we calculate N_2O_5 lifetimes to be <2 hours, see below). The NO_x loss rate due to R4 is doubled, because the sum of reactions R4 and R5 would
135 lead to NO_x loss at twice the rate of R4. The reaction pathway to make N_2O_5 is negligible during daylight hours due to photodissociation of NO_3 together with the fast reaction of NO_3 with NO , and has been set to zero. The resulting 2013 NO_x loss rates due to reactions ~~R1-4~~ R1-5 are shown in Figure ??.

Separating the daytime and nighttime partitioning in Figure ?? highlights the species that are
140 long-lived at night and short-lived during the day (N_2O_5 and ClNO_2), demonstrating the role of the nighttime species in reactive nitrogen chemistry. Nitric acid, PAN, and organic nitrates, on the other hand, are long-lived compared to a ~~diurnal-diel~~ cycle, and we do not expect the nighttime or daytime average to reflect chemical production that is restricted to these periods. It instead represents an average not just over a ~~diurnal-diel~~ cycle but over the whole campaign.

145 Integrating the diurnally averaged loss rates gives total daily calculated production of the three major components of NO_z , with the simplifying assumption that all N_2O_5 is converted to nitric acid (we estimate the ClNO_2 yield for 2012 and 2013 to be 11% and 2%, respectively). In Figure ?? we compare the partitioning of these integrated production rates with the measured partitioning of HNO_3 , PAN, and inferred organic nitrates for 2013. Production rates and observed ~~values-concentrations~~
150 should not necessarily be proportional, depending on the loss mechanisms. For example, HNO_3 will be lost via dry deposition to the ground or snow surface such that its measured contribution to nitrogen partitioning may be smaller than that inferred from its production rate. However, the agreement between production rates and observations illustrates that our methods of treating the reactive nitrogen in the current analysis and in the MCM box model are self-consistent.

155 The reactions R1 and R4-7 result in formation of HNO_3 , which makes up the bulk of NO_z in 2013. Furthermore, the integrated nighttime loss toward nitric acid is 5.9 times greater than during the day. Therefore much of the difference in NO_z between the low ozone year of 2012 and the high ozone year of 2013 must be due to a large difference in nighttime N_2O_5 reactivity, which we analyze below.

160 3.3 N_2O_5 Lifetimes

When the sinks of NO_3 are small compared to those of N_2O_5 , and assuming an equilibrium state between NO_2 , NO_3 , and N_2O_5 , the ratio of the N_2O_5 concentration to the production rate of NO_3 equals the N_2O_5 lifetime ($\tau_{\text{N}_2\text{O}_5}$),

$$\tau_{\text{N}_2\text{O}_5} = \frac{[\text{N}_2\text{O}_5]}{k \cdot [\text{NO}_2] \cdot [\text{O}_3]} \quad (1)$$

165 where k is the rate coefficient for reaction R4 (?). An analysis of the resulting lifetimes, which can be
 considered a measure of N_2O_5 reactivity, are shown with the solid lines in Figure ???. Since Equation
 ??? assumes a steady state in NO_3 and N_2O_5 , the relevant period when this lifetime interpretation
 will be most valid is at the end of the night. However, a simple five reaction chemical box model
 including NO_3 and N_2O_5 production and first-order loss (?) shows that it would take >20 hours to
 170 reach a steady state in 2012. After the 14 hours of night, we predict that the lifetime calculated using
 Equation ??? gives us 77% of the actual lifetime. In 2013, the model predicts that the system reaches
 90% of steady state in 1.8 hours. The lifetimes in 2012 are a factor of approximately 2 times longer
 than in 2013, or 2.6 times if we use calculated equilibrium values. ? have suggested an alternate
 method for lifetime analysis that explicitly takes the time derivative of N_2O_5 into account to correct
 175 its lifetime for failure to reach steady state. ~~Application of this method gives an increase of the
 apparent lifetime from 0.46 to 0.85 hours at 19:00 and 2.8 to 3.6 hours at 24:00, in better agreement
 with the calculation based on~~ Figure ??? also shows the steady state lifetime calculated using this
 method using a smooth fit function for the N_2O_5 uptake diel profile to calculate the derivative. Since
 the reaction of N_2O_5 occurs heterogeneously via uptake onto surfaces, the difference in lifetime
 180 between the two years could conceivably be due to higher aerosol surface area or faster ground
 deposition. The average value of the product of the NO_3 - N_2O_5 equilibrium constant, $K_{eq}(T)$,
 and the NO_2 concentration ($K_{eq}[\text{NO}_2]$), equal to the predicted ratio of N_2O_5 to NO_3 , was 115 and
 440 during nighttime hours in 2012 and 2013, respectively. Late night average NO_3 of 2.2 pptv
 agreed well with the predicted equilibrium. Average predicted NO_3 of less than 0.5 pptv in 2013
 185 could not be accurately measured. The late night average steady state lifetime of NO_3 in 2012
 was approximately 100 s, while in 2013 it was 13 s. Under these cold conditions, the very short
 NO_3 lifetimes do not represent the reactivity of the NO_3 - N_2O_5 system, which is dominated by
 heterogeneous loss of N_2O_5 , and we provide them here for reference only.

Lifetimes due to aerosol can be calculated separately using measurements of aerosol surface area
 190 and the equation for heterogeneous uptake, assuming no limitation for gas phase diffusion (valid for
 small particle size and small to moderate uptake coefficients, and consistent with conditions from
 both 2012 and 2013):

$$\tau_{\text{N}_2\text{O}_5} = \left(\frac{1}{4} \gamma \bar{c} S_A \right)^{-1}, \quad (2)$$

where γ is the uptake coefficient, \bar{c} the mean molecular speed, and S_A the surface area density of the
 195 aerosol. The aerosol surface area density was calculated from number size distributions measured
 using a Scanning Mobility Particle Sizer for particles between 20 and 500 nm geometric diameter,
 and an Aerodynamic Particle Sizer for particles between 0.7 and 10.37 μm . Size distribution mea-
 surements were taken at relative humidity < 25%, and a hygroscopic growth factor was calculated
 using measurements of ambient humidity and aerosol composition. ~~Using an uptake coefficient~~
 200 appropriate for wintereconditions of (?) . There are few determinations of N_2O_5 uptake coefficients

in winter. During winter measurements in Colorado, ? 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 the lifetimes of N_2O_5 due to aerosol uptake for 2012 and 2013, plotted as dashed lines in Figure ?? . The 2012 lifetime includes a 10% correction from the contribution of losses due to VOCs (see below). On average, lifetimes calculated from aerosol uptake were a factor of 4.1 higher in 2012 than 2013, compared to the factor 2.6 change in lifetime calculated from the N_2O_5 steady state of Equation ?? and the box model. However, an uptake factor of $\gamma = 0.026$ in 2012 would bring the lifetimes calculated using these two methods into agreement. Since we did not perform eddy covariance flux measurements, we do not know the deposition rate, and the γ values derived from comparison to the steady state lifetimes thus represent an upper limit. Additionally, since the lifetime of N_2O_5 is longer in 2012, the influence of deposition to the ground surface might be greater if it were roughly constant relative to other sinks that increased between 2012 and 2013. The change in aerosol uptake between the two years is in part due to the higher relative humidity measured in 2013, causing which increased the aerosol surface area through hygroscopic growth. The increased RH in 2013 caused frequent and persistent fog. Due to the difficulty in extrapolating a hygroscopic growth factor near saturation, data during periods of relative humidity above 95% have been excluded in this analysis. Hygroscopic growth associated with the higher relative humidity contributed a factor of approximately 1.3 to the difference in lifetime between the two years.

One condition of Equation ?? is that the major sink of NO_3 is through aerosol uptake via N_2O_5 instead of reactions with volatile organic compounds (VOCs). Studies of polluted air Previous studies in regionally polluted areas have shown that loss of NO_3 losses and N_2O_5 can be dominated by VOC reactions or NO_3 -VOC reactions, N_2O_5 hydrolysis in different situations uptake or a combination of the two (??). Given the high VOC concentrations in the Uintah Basin (?), we performed an analysis of NO_3 reactivity to quantify the contribution of NO_3 chemistry to the lifetime of N_2O_5 . The loss due to VOC is simply the sum of all the NO_3 -VOC rate constants (k_i) times the measured VOC concentrations, given by-

$$k_{loss}(NO_3) = \sum_i k_i [VOC_i], \quad (3)$$

and the loss due to heterogeneous uptake on aerosol is the first-order This first order loss rate coefficient for NO_3 can be compared to the first order loss rate coefficient for uptake of N_2O_5 weighted by the to aerosol by dividing the former by the equilibrium ratio of N_2O_5/NO_3 (?) (?). VOC measurements by proton transfer reaction mass spectrometry and gas chromatography in 2012 provided measurements of a more extensive VOC suite than the measurements in 2013, so VOC ratios from 2012 were used to estimate some compounds missing from 2013 measurements, as was done by ?. The calculations show that with an N_2O_5 uptake coefficient of 0.02, NO_3 losses due to reactions with VOCs were approximately 10 times less than N_2O_5 uptake to aerosol in 2012, and

approximately 40 times less in 2013. In this case Figure A lower N_2O_5 uptake coefficient would increase the fraction of the NO_3 and N_2O_5 reactivity attributable to NO_3 -VOC chemistry. However, the comparisons of Figure ?? suggest that the average N_2O_5 uptake coefficient is not appreciably smaller than 0.02. Figure ?? shows the relative loss rates, as well as the breakdown of reactivity with different classes of VOCs. During both years, reactivity with alkanes form the major part of NO_3 loss to VOCs (45-51%). To our knowledge, this is the first instance in which alkanes have been determined as the largest single component of NO_3 -VOC reactivity in ambient air. For example, studies in other locations, such as Houston, Texas, show that alkanes contribute approximately 1% to ambient NO_3 reactivity (?). Despite their very slow rate constants for reaction with NO_3 , alkanes make up an overwhelming fraction of the measured VOC composition in the Uintah Basin, leading to an unusually large contribution to NO_3 reactivity. Isoprene and dimethyl sulfide (DMS) are collectively labeled "biogenic" according to convention, but due to winter conditions we anticipate no biogenic source for these compounds. Rather, we assume both to be emissions from oil and gas operations. For example, an anthropogenic source of isoprene may be emitted in small quantities in vehicle exhaust (?), while DMS may be a component of the reduced sulfur emissions from natural gas. In any case, the measured concentrations of both compounds are small (2 pptv and 0.7 pptv, respectively, nighttime average in 2013), and their contribution to NO_3 reactivity represents the fast NO_3 rate constant with these species. It is possible that other highly reactive but unmeasured VOCs contribute to the NO_3 reactivity. For example, ? report an important role for reduced sulfur species other than DMS in loss of NO_3 radicals near an oil refinery. Such measurements were unavailable for the UBWOS studies.

Since N_2O_5 uptake to the ground can also affect lifetimes, one has to consider differences in inlet height and ground composition between different years. In 2012, N_2O_5 was measured from a scaffold tower at a height of 11 meters, whereas in 2013, the lack of such a tower limited us to a sampling height of 4 meters. To investigate a possible N_2O_5 gradient, we alternately sampled from 14 m and 1 m during the final weeks of the 2014 campaign, spanning the sample heights of the 2012 and 2013 inlets. In 2014, the ground was snow-covered, and conditions generally resembled 2013 more than 2012. The resulting lifetime calculations using NO_3 production rates (Equation ??) are shown in Figure ?? with black solid and dotted lines. We measured roughly twice the N_2O_5 lifetime at the high inlet as compared to the low inlet. This difference results solely from differences in N_2O_5 concentrations; measurements of NO_2 and O_3 and aerosol surface area between 4 and 14 meters did not show significant differences at night and were assumed to be equal for the lifetime calculation. Ground deposition of N_2O_5 can form an important contribution to the lifetime (??), but the year-to-year variability is a significantly larger effect than the measured N_2O_5 gradient. This suggests that nighttime aerosol uptake of N_2O_5 could play a major role in NO_x oxidation and contributes to keeping NO_x levels similar between the three years.

4 Sensitivity of NO_x and O_3 to NO_x oxidation pathways

We again used the MCM box model simulation to investigate the relative sensitivities of nitrogen oxide loss and O_3 production rates to some of the different NO_x oxidation pathways discussed above. We increased/decreased the reaction rate constants of reactions R1 ($\text{NO}_2 + \text{OH}$), R2 ($\text{NO}_2 + \text{PA}$), and R4 ($\text{NO}_2 + \text{O}_3$) by a factor of 2, keeping all else equal, and compared the resulting NO_x and ozone levels after the model stabilized to the base simulation results that matched observations. The base simulation included a continuous source of NO_x , tuned to match observed levels (?). In the MCM, the rate of reaction R6 was set empirically to match the observed N_2O_5 concentrations. The resulting rate was fast enough that reaction R4 was the rate-limiting step in the reaction pathway R4-R7, and was therefore used to test the sensitivity of that pathway.

The results are shown in Figure ??, with the left panel showing the final day of the simulation, and the right panel comparing the final day's 24-hour averages. For reactions R1 and R2, an increased/decreased rate has very little effect on NO_x once the model has stabilized. The nighttime heterogeneous-pathway has a much larger effect, however, and an doubled rate leads to a 28% NO_x reduction. Halving the rate causes a 43% increase. During the day, changing the rate of R4 has no effect due to the fast photodissociation of NO_3 . The response of O_3 concentrations is also shown, with the nighttime reactions having the greatest effect. Changing PAN and HNO_3 production have comparable effects on ozone even though the effective NO_x removal rates are approximately 4 times different. This may be because the $\text{OH} + \text{NO}_2$ affects the propagation of the HO_x cycle directly with OH either reacting with NO_2 or a VOC. PAN production, on the other hand, has its effect based on whether PA reacts with NO or NO_2 , which scales as the ratio of PA loss to NO vs loss to NO_2 .

Although organic nitrates are the largest photochemical pathway for nitrogen loss, we did not perform an analogous simulation using reaction R3 ($\text{NO} + \text{RO}_2$). Since a comparable simulation involves changing all the rate coefficients for a large number of reactions, performing these simulations are beyond the scope of this paper. However, if we scale the sensitivity of doubling/halving the reaction rates for organic nitrate production to the sensitivity to daytime production of nitric acid (a factor of 4.6), we get a change in NO_x of approximately 7% and a change in O_3 of approximately 17%. The effect could be larger since NO_x is higher in the morning when the $\text{RO}_2 + \text{NO}$ rate is largest. Scaling it to PAN production (R2) causes a change in NO_x and O_3 of approximately 3% and 6%, respectively. If instead we were to scale α by a factor of two, the effect could be larger since there is no competition for the fate of RO_2 ; every RO_2 reacts with NO. For example, ? found that a 50% increase in α results in a 7 ppb decrease in ozone (at an ozone concentration of ~ 60 ppbv), and they estimate a 25 ppbv effect (at ~ 140 ppbv ozone) for conditions with higher J values and slower mixing. Thus, although organic nitrate production should have the largest influence of the photochemical NO_x loss mechanisms on both NO_x and O_3 , we anticipate that it still has a smaller effect on NO_x loss pathways than the nighttime chemistry in this winter environment.

Winter O_3 should be more sensitive to N_2O_5 chemistry because it is predominant during winter

310 conditions, with low primary radical generation during daytime and longer duration of darkness. The majority of polluted winter conditions do not produce O_3 efficiently due to low photochemical radical production rates. These systems are typically NO_x saturated (??). The result of N_2O_5 chemistry in most of these situations would be to increase O_3 photochemistry during the daytime by reducing the NO_x levels overnight. In summertime urban environments, N_2O_5 chemistry should
315 have an effect, but it would be smaller because it will consume a smaller fraction of reactive nitrogen compared especially to reaction R1 in more typical summertime ozone photochemical systems. Its effect on O_3 will be highly sensitive to the O_3 - NO_x sensitivity in any given region, and would be difficult to generalize.

The influence of $ClNO_2$ production from N_2O_5 is not explicitly considered here, and was deter-
320 mined to be a small effect on NO_x due to its low yield. However, it may be an important effect on O_3 production in other regions during both summer and winter, especially if $ClNO_2$ photolysis is a larger contribution to photochemical radicals than was determined for the UBWOS 2013 study.

5 Conclusions

The measurements at Horsepool in the Uintah Basin, Utah, during the winters of 2012, 2013, and
325 2014 and subsequent modeling provide much insight into the fate of reactive nitrogen and its relationship to ozone production in the basin. Ozone levels were highly elevated in 2013 compared to 2012, with 2.5 times more ozone on average and 20 out of the 28 days of the measurements at ~~Horse~~
~~Pool~~Horsepool experiencing exceedances of the 75 ppbv 8-hour-average daily maximum NAAQS. Total reactive nitrogen, NO_y , was 2.5 times more concentrated in 2013, yet photochemically active
330 NO_x concentrations were approximately equal all three years. This resulted from very different rates of NO_x oxidation leading to much higher concentrations of HNO_3 , PAN, and missing NO_y , presumed to be organic nitrates, with HNO_3 making up the largest part of the NO_z budget. Much of the HNO_3 formed during the night, with integrated NO_2 loss toward HNO_3 approximately 6 times higher at night than during the day. At night, HNO_3 is produced via heterogeneous uptake of N_2O_5
335 onto aerosol, and calculations using measurements of aerosol surface area reproduce the differences in lifetime as calculated using NO_3 production rates. Some of the N_2O_5 is lost to ground deposition, but aerosol uptake forms a major component of HNO_3 formation. A box model simulation confirms that the nighttime N_2O_5 heterogeneous reactions play a significant role in NO_x chemistry and related ozone production.

340 *Acknowledgements.* The Uintah Basin Winter Ozone Studies were a joint project led and coordinated by the Utah Department of Environmental Quality (UDEQ) and supported by the Uintah Impact Mitigation Special Service District (UIMSSD), the Bureau of Land Management (BLM), the Environmental Protection Agency (EPA) and Utah State University. This work was funded in part by the Western Energy Alliance, and NOAA's

Atmospheric Chemistry, Climate and Carbon Cycle program. We thank Questar Energy Products for site preparation and support. This is PMEL contribution number 4353.

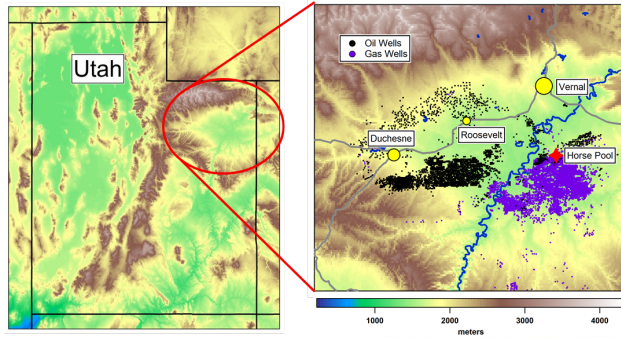


Fig. 1. Map of the Uintah Basin in Utah, showing the [Horse Pool](#) measurement site, active oil and gas wells, and the major population centers. The background is colored by elevation as shown by the color bar.

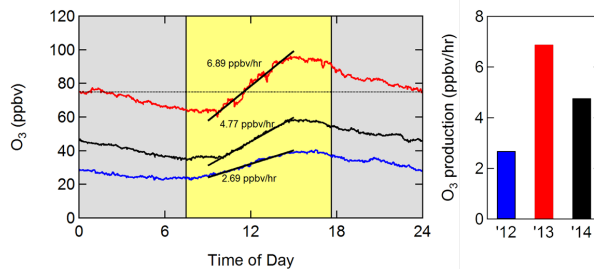


Fig. 2. [Diurnal-Diel](#) averages of ozone mixing ratios during the campaigns in 2012 (45 days), 2013 (28 days), and 2014 (27 days), and the 75 ppbv NAAQS for reference. Average ozone levels were 2.5 times higher in 2013 than 2012. Linear fits to the midday ozone increase illustrates the difference in average daily ozone production, plotted on the right.

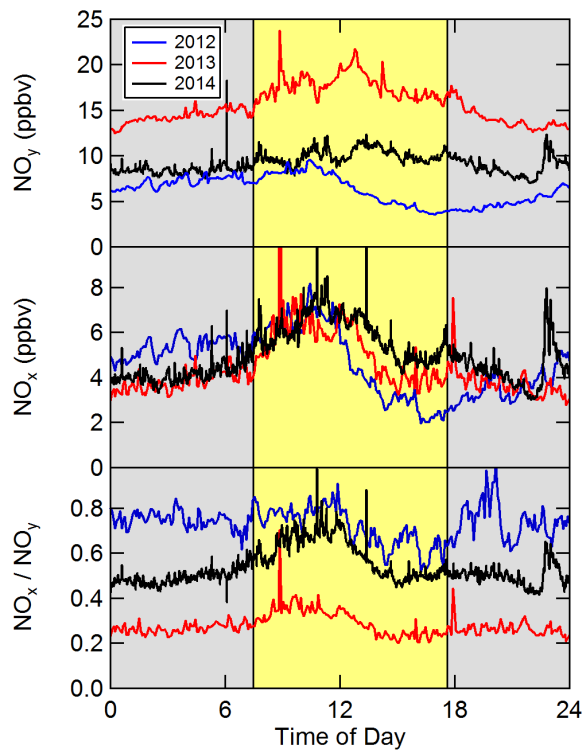


Fig. 3. Diurnal-Diel averages of reactive nitrogen. Top: Total NO_y was a factor of 2.5 times larger in 2013 than in 2012. Middle: The amount of photochemically active NO_x remained at similar levels all three years. Bottom: The ratio of NO_x/NO_y , an inverse measure of the level of oxidation of reactive nitrogen, was a factor of 2.6 smaller in 2013 than 2012.

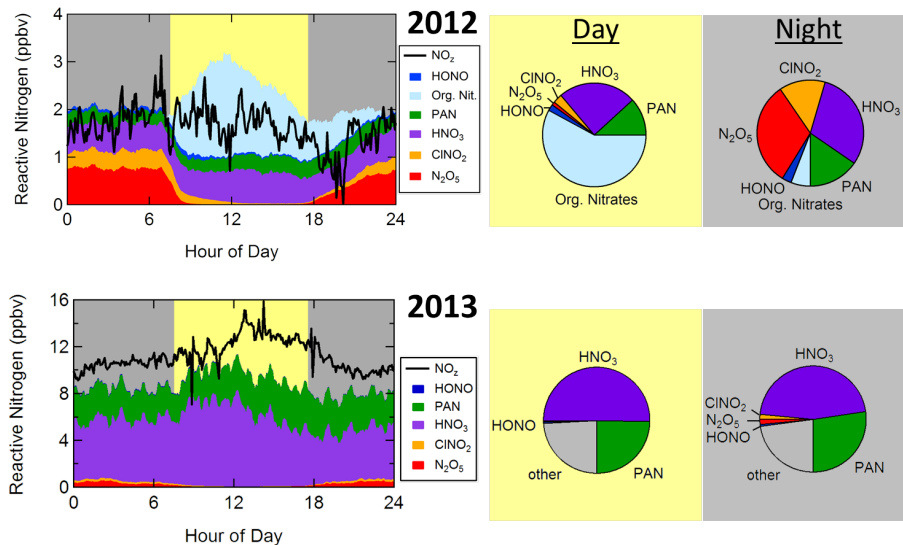


Fig. 4. Partitioning among reactive nitrogen species for 2012 and 2013, shown as diurnal averages (left) as well as daytime and nighttime pie charts (right). We take total NO_z to be the sum of components in 2012, and the difference between NO_y and NO_x in 2013. The missing NO_z in 2013 (labeled “other” in the pie charts) is likely organic nitrates, for which we do not have measurements in 2013. In 2012, daytime organic nitrates and nighttime N₂O₅ and ClNO₂ play an important role compared to 2013, where total PANs and HNO₃ are the largest contributors to NO_z.

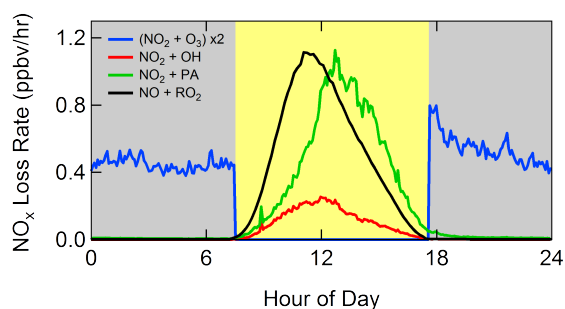


Fig. 5. Daytime and nighttime loss rates of NO_x in 2013 through the major oxidation pathways. Concentrations of OH, PA, and the production rate of organic nitrates (NO + RO₂) were supplied by the Master Chemical Mechanism box model used by ?. The daytime NO₃ production is set to zero because of the fast NO₃ photolysis and reaction with photochemically generated NO, and doubled at night due to reaction R5. The integrated nighttime loss toward HNO₃ is 5.9 times greater than during the day.

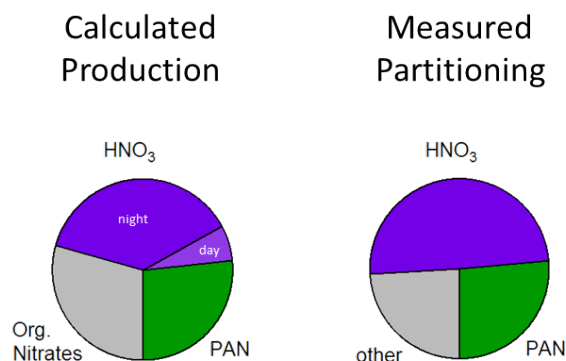


Fig. 6. Comparison of the relative importance in 2013 of calculated oxidized reactive nitrogen production rates to the measured NO_z partitioning for the three largest components of NO_z . On the right chart, "other" refers to the missing NO_z which we attribute to the unmeasured organic nitrates.

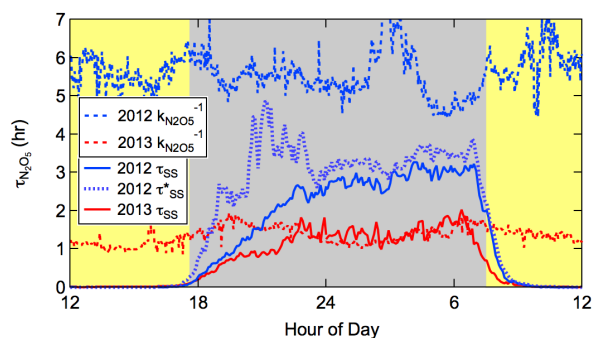


Fig. 7. Lifetimes of N_2O_5 , calculated using the production rate of NO_3 (solid lines), [the lifetime calculated using the method of ? for 2012 \(short dashed line, see text\)](#), and uptake to aerosol using an uptake coefficient of $\gamma = 0.02$ (dashed lines). In 2012 we expect that the calculation gives 77% of the actual lifetime, due to the system not reaching equilibrium at the end of [the night. The McLaren method, based on explicit inclusion of the time derivative for \$\text{N}_2\text{O}_5\$, partially corrects for this effect, especially early in the night.](#) An uptake coefficient of $\gamma = 0.026$ would bring the $\text{P}(\text{NO}_3)$ and aerosol calculations in 2012 into agreement. The observed lifetimes from $\text{P}(\text{NO}_3)$ include deposition, but the calculated curves do not.

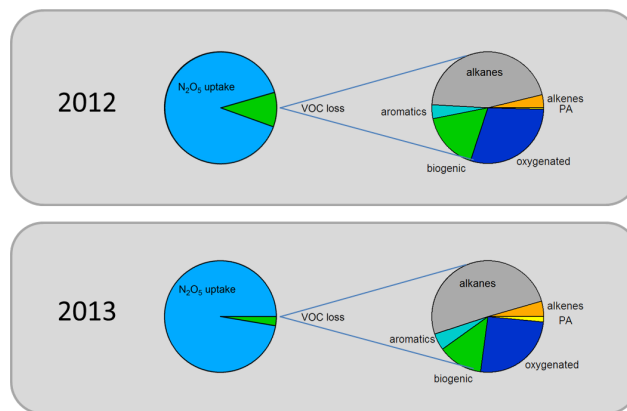


Fig. 8. Contributions to NO_3 reactivity. In both years, formation of N_2O_5 and consequent uptake to aerosol dominate NO_3 loss, and reactions with VOCs are primarily with alkanes. For comparison, the total NO_3 loss rate was 0.016 s^{-1} in 2012 and 0.118 s^{-1} in 2013.

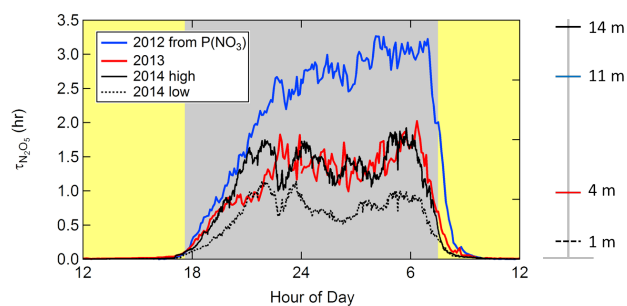


Fig. 9. The effect of inlet height on calculated lifetimes. Red and blue lines are the same as in Figure ?? . Black lines are calculated from 2014 measurements with the solid line from an inlet at 14 meters and the dashed line from an inlet at 1 meter. These inlet heights span the inlets in 2012 at 11 meters and 2013 at 4 meters.

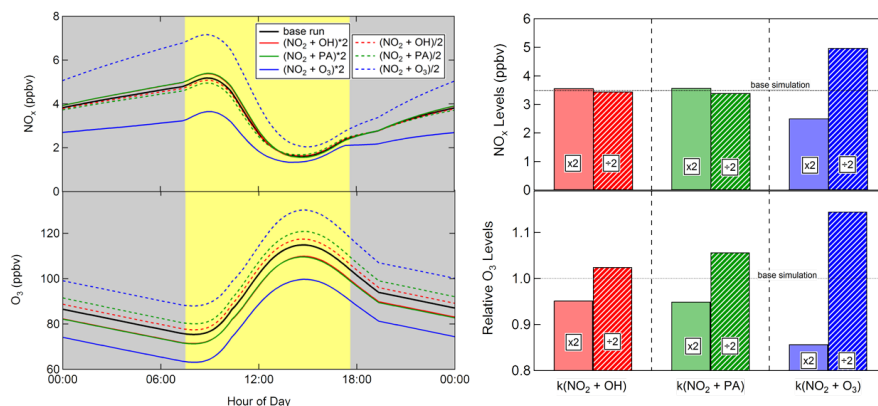


Fig. 10. The effect on NO_x and ozone concentration of changing the rates of select reactions in a box model simulation. The reaction NO₂ + O₃ represents the nighttime reaction pathway to HNO₃.

Table 1. Measurements of ambient gas-phase reactive nitrogen levels during UBWOS 2012-2014. The method abbreviations are described in Section 2, and LOD refers to the Limit of Detection. Not all measurements were used in this analysis.

Species Measured	Campaign Year			Method	Accuracy %	LOD pptv	Reference
	'12	'13	'14				
NO, NO ₂ , NO ₃ , N ₂ O ₅	x	x	x	CRDS	5-10	1-100	?
NO _y	x			CL	20	10-100	?
NO _y		x	x	TD-CRDS	10	20	?
HNO ₃ , HONO	x	x	x	acid CIMS	30	10	?
alkyl & peroxy nitrates	x			TD-LIF	20	24-34	?
acyl peroxy nitrates	x	x	x	I ⁻ CIMS	20	10	?
ClNO ₂	x	x	x	I ⁻ CIMS	20	5	?
HO ₂ NO ₂			x	I ⁻ CIMS	20	5	?
NO ₂ , NO ₃ , HONO	x		x	LP-DOAS	3-8	80, 2, 20	?
NO ₂ , HONO			x	ACES	15	200	?
HONO			x	LoPAP	15	10	?