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# Low temperatures enhance organic nitrate formation: evidence from observations in the 2012 Uintah Basin Winter Ozone Study

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## Abstract

Nitrogen dioxide ( $\text{NO}_2$ ) and total alkyl nitrates ( $\Sigma\text{ANs}$ ) were measured using thermal dissociation laser induced fluorescence during the 2012 Uintah Basin Winter Ozone Study (UBWOS) in Utah, USA. The observed  $\text{NO}_2$  concentration was highest before sunrise and lowest in the late afternoon, suggestive of a persistent local source of  $\text{NO}_2$  coupled with turbulent mixing out of the boundary layer. In contrast,  $\Sigma\text{ANs}$  co-varied with solar radiation with a noontime maximum, indicating that local photochemical production combined with rapid mixing and/or deposition was the dominant factor in determining the  $\Sigma\text{AN}$  concentrations. We calculate that  $\Sigma\text{ANs}$  were a large fraction ( $\sim 60\%$ ) of the  $\text{HO}_x$  free radical chain termination and show that the temperature dependence of the alkyl nitrate yields enhances the role of  $\Sigma\text{ANs}$  in local chemistry during winter by comparison to what would occur at the warmer temperatures of summer.

## 1 Introduction

The Uintah Basin in Utah is a region of concentrated fossil fuel extraction operations using hydraulic fracturing to extract natural gas and oil from shale formations. The basin has experienced high wintertime ozone as has the nearby Upper Green River Basin in Wyoming (Schnell et al., 2009). The observed  $\sim 200$  ppb peak ozone in the basin during the winter of 2011 was associated with elevated concentrations of volatile organic compounds (VOCs) coincident with a shallow boundary layer stabilized by snow cover, which doubled as a solar reflector leading to more rapid photochemistry.

Organic nitrates ( $\text{RONO}_2$ ) are products of atmospheric VOC oxidation in the presence of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ). During daytime, their formation involves the association reaction of alkyl peroxy radicals with  $\text{NO}$ . This reaction terminates ozone formation and suppresses  $\text{OH}$  recycling. The importance of  $\text{RONO}_2$  formation as a  $\text{NO}_x$  sink and chain terminator of ozone production depends on the mixture of VOCs present as a result of variations in  $\text{OH}$  reactivity and organic nitrate yield,  $\alpha$ , among different organic

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molecules (Perring et al., 2013; Farmer et al., 2011). Laboratory studies have shown that the nitrate yield follows standard expectations for 3-body reactions:  $\alpha$  increases with carbon number of the organic peroxy radical and atmospheric pressure, but decreases with temperature (Atkinson et al., 1983; Carter and Atkinson, 1989). Field observations have found RONO<sub>2</sub> compounds to account for 25 % or more of total reactive nitrogen (NO<sub>y</sub>, defined as NO<sub>x</sub> + higher nitrogen oxides). However, none of these prior field experiments (Farmer et al., 2011; Rosen et al., 2004; Perring et al., 2010, 2009) covered a temperature range wide enough to examine the role of the temperature dependence of  $\alpha$  on nitrate formation rates, O<sub>3</sub>, or OH concentrations.

In this paper we present observations of organic nitrates obtained during the UBWOS 2012 experiment (15 January–29 February 2012). We further describe the role of organic nitrates in wintertime ozone production and the associated temperature effect by comparing the  $\alpha$  values either constrained by observed  $\Sigma$ ANs concentration or derived from temperature-dependent yields from VOC composition data. The findings show organic nitrate formation to be one of the primary radical sinks at this site and confirm that the temperature-dependent kinetics are important. However, temperature dependence of organic nitrate yields are not presented in any of the standard photochemical mechanisms used in chemical transport models. Accounting for the temperature dependent yields at 0 °C (the typical daytime temperature during this field campaign) results in a 30 % faster organic nitrate formation rate than what would occur at room temperature (300 K). As a result, we estimate a suppression in OH concentrations by 15 % and ozone formation by 20 % relative to the calculations that do not include the temperature dependence of the RONO<sub>2</sub> yields.

## 2 Instrumentation

The 2012 Uintah Basin Winter Ozone Study occurred from 15 January to the end of February at Horse Pool, Utah, a site approximately 30 miles south of the city of Vernal, Utah. This site was located amid intensive oil and gas extraction operations near the

center of Uintah Basin, with dense gas production wells to the south and oil production wells to the south-west (refer to Fig. 1 of Edwards et al., 2013). A 19 m high tower was on-site for setting up measurements at various heights.

Thermal Dissociation-Laser Induced Fluorescence (TD-LIF) was used to measure  $\text{NO}_2$ , total peroxy nitrates ( $\Sigma\text{PNs} = \Sigma\text{ROONO}_2$ ) and total alkyl nitrates ( $\Sigma\text{ANs} = \Sigma\text{RONO}_2$ ) using methods described previously. (Day et al., 2002; Thornton et al., 2000) Briefly, laser induced fluorescence was used for detection of gas phase  $\text{NO}_2$  using a CW solid-state tunable fiber laser ( $\sim 80$  mW, NovaWave) at 530 nm for excitation with detection of photons at wavelengths longer than 700 nm using a red-sensitive PMT (Hamamatsu H7421) preceded by a dielectric long-pass filter. Quartz tubes with external heating elements were maintained at  $180^\circ\text{C}$  for conversion of  $\Sigma\text{PNs}$  and  $380^\circ\text{C}$  for  $\Sigma\text{ANs}$  to  $\text{NO}_2$  under a residence time of  $\sim 20$  ms. Simultaneous measurements of  $\text{NO}_2$ ,  $\Sigma\text{PNs}$  and  $\Sigma\text{ANs}$  were achieved by operating 3 LIF cells, each measuring the cumulative concentration of  $\text{NO}_2$ -yielding compounds.

Corrections are necessary for the TD channel signals. As a negative interference,  $\text{O}_3$  pyrolysis and subsequent O atom-initiated chemistry in the TD oven reduces the amount of  $\text{NO}_2$  observed for a temperature in excess of  $270^\circ\text{C}$ . This effect is prominent when the contribution of  $\Sigma\text{ANs}$  is small compared to ambient  $\text{NO}_2$ . The correction is an empirical relationship developed in the laboratory by directly observing the loss of the  $380^\circ\text{C}$  signal as a function of both  $\text{O}_3$  and  $\text{NO}_2$  concentrations in the presence of an organic nitrate surrogate (2-ethylhexyl nitrate, Sigma Aldrich). Details of this correction are included in the Appendix A. The factors applied during the daytime hours that are the focus of this study were typically 6–17% of the total  $380^\circ\text{C}$  signal, of which  $\Sigma\text{ANs}$  account for approximately 25%. This amounts to a correction of 24–68% of the final  $\Sigma\text{ANs}$  concentration. Larger corrections were required at night due to higher  $\text{NO}_2$  concentration. There are also additional contributions from inorganic species, including  $\text{N}_2\text{O}_5$  (which decomposes to  $\text{NO}_2$  and  $\text{NO}_3$  at  $\sim 90^\circ\text{C}$ ) in the  $180^\circ\text{C}$  channel and  $\text{ClNO}_2$  (which decomposes to a chlorine atom and  $\text{NO}_2$ , Thaler et al., 2011) in the  $380^\circ\text{C}$  channel. However, accounting for the inorganic signal was straightforward since direct

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measurements of both species were available at the site. (Wagner et al., 2011; Roberts et al., 2009) Overall, the  $\text{ClNO}_2$  contribution to the difference signal between  $380^\circ\text{C}$  and  $180^\circ\text{C}$  was only significant during the night and early morning since, for example, the noontime photolysis lifetime of  $\text{ClNO}_2$  is only 1 h. We note that  $\text{N}_2\text{O}_5$ , present only during nighttime, did not affect daytime  $\Sigma\text{PNs}$  measurements.

In subsequent analyses,  $\Sigma\text{PNs}$  is calculated as the difference in concentrations of the ambient and  $180^\circ\text{C}$  channel minus the  $\text{N}_2\text{O}_5$  contribution, while  $\Sigma\text{ANs}$  is the concentration difference between the  $180^\circ\text{C}$  channel and the  $\text{O}_3$ -corrected  $380^\circ\text{C}$  channel minus the  $\text{ClNO}_2$  contribution.

The TD-LIF instrument was calibrated hourly with a 5 ppm  $\text{NO}_2$  gas standard diluted with zero air to generate 5 different concentration levels at the inlet manifold. In addition, the instrument zero (baseline) was monitored every half-hour by overflowing the inlet with  $\text{NO}_x$ -free zero air. The  $\text{NO}_2$  concentration measured by LIF and nearby chemiluminescence instrument were within 7% of each other on average, giving a linear slope (LIF vs. chemiluminescence) of 0.94, an intercept of 0.02 ppb, and an  $R^2$  value of 0.97.

The inlet was mounted on the southern face of the tower, 16 m above the ground. Other measurements made from similar heights include  $\text{NO}$  and  $\text{NO}_y$  (Kliner et al., 1997), speciated VOCs (Goldan et al., 2004),  $\text{O}_3$  and photolysis rates for  $\text{O}_3$  ( $\text{O}^1\text{D}$ ),  $\text{NO}_2$  and  $\text{NO}_3$ . These measurements are described elsewhere (see description and the Supplement Table S1 in Edwards et al., 2013). Temperature, pressure, relative humidity, wind direction and windspeed were measured from the top of the tower. 3-D wind data were measured using the High Resolution Doppler Lidar (Grund et al., 2001) nearby.

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## 3 Results

### 3.1 Observations

Figure 1 shows the time series (as hourly average) of  $\text{NO}_2$ ,  $\Sigma\text{ANs}$ ,  $\text{O}_3$  and windspeed through the observational period. The time-of-day median values of  $\text{NO}_2$ ,  $\Sigma\text{ANs}$  and  $\text{O}_3$  are plotted in Fig. 2. During periods with windspeed lower than  $5 \text{ m s}^{-1}$ , the chemical species, such as large volatile organic compounds (VOCs) and  $\text{NO}_x$ , accumulate, leading to an increase in concentrations until high wind episodes occur that flush the basin with clean air. The onset of high wind episodes were therefore coincident with a rapid decrease in VOCs and  $\text{NO}_x$  concentrations. During the UBWOS campaign in the year before (2011), up to 200 ppb ozone was observed at the end of accumulation periods with snow cover on the ground. However, during similar period in the 2012 campaign, there was little snow and the ozone concentration did not exceed 51 ppb.

#### 3.1.1 $\text{NO}_2$

$\text{NO}_2$  showed a clear diurnal variation (Fig. 2). Concentrations were highest in the early morning when vehicle traffic as well as oil well machinery emissions became coincident with a stable nocturnal boundary layer. Turbulent mixing in the afternoon diluted the concentration, giving a minimum at 4 p.m. local time. The multi-day effect of high/low wind episodes on  $\text{NO}_2$  concentration is visible for which high windspeed always corresponds to low  $\text{NO}_2$  levels (Fig. 1).

#### 3.1.2 $\Sigma\text{ANs}$

The daily variation in  $\Sigma\text{ANs}$  concentration is less pronounced than for  $\text{NO}_2$  but follows a similar multi-day trend controlled by meteorology. As shown in Fig. 2, the total  $\text{RONO}_2$  concentration increases in the morning to a noon time peak of 1.5 ppb. The contribu-

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tions from C<sub>1</sub>-C<sub>3</sub> alkyl nitrates measured by GC-MS are small and nearly constant at ~ 50 ppt and did not contribute to the diurnal profile observed.

### 3.1.3 O<sub>3</sub>

The observed O<sub>3</sub> concentration ranged from 4 to 50 ppb and was negatively correlated with NO<sub>2</sub>. The diurnal profile has a maximum concentration in the late afternoon, corresponding to a delay of roughly 4 h from the peak of organic nitrates. The increase in O<sub>3</sub> concentration is most rapid (~ 2.4 ppb h<sup>-1</sup>) at noon.

### 3.1.4 VOCs

The VOC composition is influenced heavily by the fossil fuel extraction operations. Alkane oxidation dominates the chemistry in the basin (Table 1), accounting for 67% of total measured VOC reactivity (7.5 s<sup>-1</sup>) at noon. The diurnal profile of VOCs follows NO<sub>2</sub>, reaching a minimum in the late afternoon (see Fig. 3a in Edwards et al., 2012).

## 3.2 The average branching ratio for nitrate formation

The average noontime temperature during the UBWOS experiment was 0 °C. These cold temperatures provide a unique opportunity to examine the role of temperature on the formation of organic nitrates and the associated radical chain termination compared with other field campaigns taking places in summer.

Organic nitrate compounds are formed via OH-initiated oxidation. For the specific mixture of VOCs observed, the dominant reaction starts with hydrogen abstraction from alkanes by OH. The resulting alkyl radical rapidly reacts with O<sub>2</sub> to give alkyl peroxy radical RO<sub>2</sub>, which subsequently reacts with NO to form an energy-rich adduct of the structure ROONO\* (Reaction R1). Under typical atmospheric conditions, a fraction (Reaction R2) of ROONO\* is collisionally stabilized to form the nitrooxy group, RONO<sub>2</sub>, while the unstabilized portion (Reaction R3) dissociates to yield an alkoxy radical and NO<sub>2</sub>. The fate of the alkoxy radical varies depending on the carbon backbone but, in

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general, returns a HO<sub>2</sub> radical.



Given a rate of VOC reaction with OH, the key factor regulating RONO<sub>2</sub> production is the nitrate branching ratio,  $\alpha$ , defined as the overall fraction of the RO<sub>2</sub> + NO reaction that gives an organic nitrate product rather than an alkoxy radical and NO<sub>2</sub> product. The association reaction to form RONO<sub>2</sub> is compound-specific and temperature- and pressure-dependent (Atkinson et al., 1983). In the subsequent sections, we present 2 independent methods for estimating ensemble-averaged  $\alpha$  values (or  $\langle\alpha\rangle$ ) for the specific environment of UBWOS campaign, and demonstrate they agree to within the uncertainty of our observations. The first method (Sect. 3.2.1) is based on parameterizations derived from laboratory experiments and the observed VOC composition data, while the second method (Sect. 3.2.2) uses the observed  $\Sigma$ ANs concentration, photolysis and VOC reactivity.

### 3.2.1 VOC-ensemble method

The averaged  $\alpha$ ,  $\langle\alpha\rangle$ , is defined in equation below as the summation of compound-specific  $\alpha$  values weighted by their relative importance in atmospheric oxidation calculated as the product of OH reaction rate constant and compound concentration (namely, the OH reactivity).

$$\langle\alpha\rangle = \frac{\sum_i k_i [x_i] \alpha_i}{\sum_j k_j [x_j]} \quad (1)$$

Here  $\alpha_i$  denotes the compound-specific nitrate branching ratio,  $k_i$  ( $k_j$ ) the OH reaction rate and  $[x_i]$  ( $[x_j]$ ) the concentration of species  $i$  ( $j$ ). The VOC OH reactivity,  $k_i [x_i]$

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( $k_j[x_j]$ ), in the Uintah basin was dominated by alkanes (see Table 1). We point out here that the net effect of temperature on the OH reaction rate constants was generally small, typically a 5 % reduction in total OH reactivity compared with 298 K values (Atkinson, 1994) and the dominant temperature dependence of organic nitrate production is due to the nitrate branching ratio as detailed below.

For  $\alpha_i$  specific to alkanes, we use temperature- and pressure-dependent, compound-specific  $\alpha_i$  values (Carter and Atkinson, 1989) and include contributions of secondary organic nitrate formation after alkoxy radical isomerization reactions which can be increasingly important for alkanes larger than butane. This increases the individual organic nitrate yield by up to 30 %, generally proportional to the size of the molecule. The compound-specific  $\alpha$  values are summarized in Table 2.

The  $\alpha_i$  value for aldehydes were treated as having the same nitrate yield as the RO<sub>2</sub> having one less carbon, since the major reaction with OH involves aldehydic hydrogen abstraction and decomposition following reaction with NO to give a CO<sub>2</sub> and a C<sub>n-1</sub> alkyl radical.  $\alpha$  for ketones were estimated using the same method as detailed for alkanes. Methanol and ethanol are presumed to have zero nitrate yield, since their reactions with O<sub>2</sub> after hydrogen abstraction to form carbonyls and HO<sub>2</sub> are dominant. Finally, the nitrate yields for aromatics were set to 1 % in this analysis, following the yield of benzyl nitrate from toluene oxidation (Gery et al., 1985; Atkinson and Aschmann, 1989; Atkinson, 1994). The alkyl nitrate yields from aromatics are likely related to the ring-opening products and are still poorly constrained.

The average nitrate formation yield,  $\langle\alpha\rangle$ , as calculated above including all VOC and CO measurements throughout the campaign period, is plotted in Fig. 3 as instantaneous values (gold) and as a daytime (08:00 a.m.–06:00 p.m.) average (red filled symbol). The organic nitrate yield ranged from 3 % to 15 % with low values corresponding to periods of high winds (e.g. 3 February). Variation in VOC concentration and composition is the dominant factor controlling the day to day variation as well as the variation over each day. Daytime averaged values of  $\langle\alpha\rangle$  calculated at a temperature of 300 K are shown in blue. Even at 300 K the  $\langle\alpha\rangle$  is significant, often around 10 %.

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### 3.2.2 Oxidation-production method

Our second approach to estimating  $\alpha$  is based primarily on the  $\Sigma$ AN measurements. In this case,  $\langle\alpha\rangle$  can be expressed as the ratio of the  $\Sigma$ AN production rate over the total VOC consumption rate (Eq. 2a).

$$\langle\alpha\rangle = \frac{\rho(\Sigma\text{ANs})}{[\text{OH}] \cdot \sum_i k_i [x_i]} \quad (2a)$$

$$\rho(\Sigma\text{ANs}) = \frac{d(\Sigma\text{ANs})}{dt} + k_{\text{mix}} \cdot \Sigma\text{ANs} \quad (2b)$$

$$[\text{OH}] = f\left(\sum_i k_i [x_i], J, \langle\alpha'\rangle\right) \quad (2c)$$

The individual terms in Eq. (2a) can be derived from observations, as shown in Eq. (2b) and (2c). The total production rate of  $\Sigma$ ANs ( $\rho(\Sigma\text{ANs})$ ) is expressed, according to mass balance, as the sum of the rate of change of the observed  $\Sigma$ AN concentration and an overall loss term in Eq. (2b). Chemical losses of  $\Sigma$ ANs are found to be negligible compared with turbulent mixing out of the boundary layer. To estimate this effective loss rate constant “ $k_{\text{mix}}$ ”, we employ a tracer method by solving Eq. (2b) using n-propyl nitrate concentrations measured by GC-MS. We chose n-propyl nitrate because its expected loss is also dominated by mixing due to the long chemical lifetime, and its production rate can be calculated independently from measured VOC precursors. Note here that the OH concentration is needed to calculate the production rate of n-propyl nitrate, as well as the VOC consumption rate in the denominator of Eq. (2a). The OH concentration is a function of VOC reactivity and photolysis rates ( $J$  values) as well as the  $\alpha$  value for the radical recycling efficiency. Due to the dependence of the OH concentration on the nitrate yield, it is not possible to represent  $\alpha$  in a closed functional form using all other variables. Therefore, the set of equations must be solved iteratively until a self-consistent  $\alpha$  and OH concentration are obtained ( $\langle\alpha\rangle = \langle\alpha'\rangle$ ).

The calculations proceeds as follows by calculating the following: (1) OH concentration and VOC consumption rate, (2) mixing rate estimates, (3)  $\Sigma$ ANs formation rate and  $\langle\alpha\rangle$ .

### 1. OH concentration and VOC consumption rate:

We used photolysis rates of  $O_3$ ,  $NO_2$ ,  $NO_3$ , HONO,  $CINO_2$ , acetaldehyde, acetone, formaldehyde and  $HNO_3$  to calculate OH and  $HO_2$  production rates. OH formation from alkene ozonolysis reactions was negligible. The medium total radical production of  $2.5 \text{ ppb day}^{-1}$  is similar to the value reported by Edwards et al. (2013). Data for  $NO$ ,  $NO_2$  and VOCs coupled with literature values of OH reaction rate constants corrected for campaign measured temperature and pressure dependence (Atkinson et al., 2004, 2006) were then used for OH and  $HO_2$  calculations including radical recycling. The resulting VOC consumption rate is shown in Fig. 4. Note the VOC consumption rate profile conforms more to the shape of the radical source strength (OH and  $HO_2$  formation rate derived from photolysis, same shape as solar irradiation) than to the OH concentration, consistent with the notion that VOCs are the major reaction partner with OH.

### 2. Mixing rate estimation:

We estimate the dilution loss ( $k_{\text{mix}}$ ) for  $\Sigma$ ANs concentration by substituting [ $\Sigma$ ANs] with n-propyl nitrate concentration in Eq. (2b). The time derivative of n-propyl nitrate concentration was calculated using a finite difference method, followed by application of a 2 h running mean to smooth hourly data. Kinetic studies dictate that  $\sim 24\%$  of the OH reaction with propane at 273 K yielded a primary alkyl radical, (Droege and Tully, 1986) which promptly reacted with  $O_2$  to form the corresponding peroxy radical. Larger alkane molecules can also yield n-propyl alkyl radical as a result of alkoxy radical decomposition from the appropriate structure, and we accounted for all such minor formation channels up to undecane to give a total additional contribution of 14% from sources other than propane. The total formation rate of n-propyl nitrate is presented in Fig. 4 as the red trace spanned

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by the 25 and 75 percentiles in the shaded area. Plotted in blue is the median value of time derivative of n-propyl nitrate concentration showing a diurnal pattern for which peak concentration was reached at noon time when the time derivative crosses the zero line. The initial concentration increase roughly coincides with the start of photochemical reaction, as is also marked by the onset of n-propyl nitrate formation rate. The negative portion of the blue trace in the afternoon then corresponds to faster dilution due both to turbulence and to the elevated concentration. These values are sufficient to solve for the time-varying dilution rate constant,  $k_{\text{mix}}$ , shown in Fig. 5 as green line with dashed traces bounding the interquartile range. Note the slight delay ( $\sim 1$  h) in the daily maximum of the dilution rate constant when compared with the peak of n-propyl nitrate formation rate. As vertical turbulence was promoted by surface heating, this delay is a reasonable consequence of the expected lag in the mixing rate. The median daily maximum mixing rate shows a time constant of 6 h, much more rapid than other loss processes such as the OH oxidative lifetime of n-propyl nitrate of over 150 h under the OH concentration of  $2 \times 10^6 \text{ cm}^{-3}$  (Fig. 4) and a photolysis lifetime of over 200 h, (Luke et al., 1989) consistent with our initial assumption that chemical losses are small.

### 3. $\Sigma$ ANs formation rate and $\langle \alpha \rangle$ :

Using the  $k_{\text{mix}}$  calculated above, the  $\Sigma$ AN formation rate was estimated using Eq. (2b). We then inserted this  $\Sigma$ AN formation rate and VOC consumption rate back into Eq. (2a) to obtain the implied  $\langle \alpha \rangle$  value based on the field observations and also the initial guess of  $\langle \alpha' \rangle$ . For time periods when  $\langle \alpha \rangle$  mismatches  $\langle \alpha' \rangle$ ,  $\langle \alpha' \rangle$  is adjusted toward  $\langle \alpha \rangle$  accordingly and the calculation repeated to achieve consistency. To reduce the number of points needed for calculation, we only estimated one self-consistent  $\langle \alpha \rangle$  value for each day by averaging from 8 a.m. to 6 p.m., the same as the averaging window used for our first method.

Direct comparison of the estimate from Sect. 3.2.2 with the one derived from just the VOC composition (Sect. 3.2.1) is shown in Fig. 6. There were 27 days to

compare and the two methods are nearly identical, yielding a slope of 1.06 and  $R^2 = 0.61$ . The similarity in results of the two methods lends support to the estimates of  $\alpha$  and confirms the importance of a significant temperature dependence to the value of  $\alpha$  affecting the UBWOS chemistry.

## 4 Discussion

The relatively high value observed for the average nitrate yield,  $\langle\alpha\rangle$ , of  $\sim 15\%$ , is a direct consequence of low temperatures and the presence of heavy alkanes, a special condition created by natural gas and oil extraction operations in the basin. In the following sections, we discuss how this elevated nitrate yield affects the fate of  $\text{NO}_x$  emitted into the basin and the rate of local  $\text{O}_3$  production.

### 4.1 Fate of $\text{NO}_x$

Organic nitrate formation was a significant chemical loss for  $\text{NO}_x$  in the Uintah Basin. We calculated that alkyl nitrate formation is 50% faster than  $\text{HNO}_3$  formation during the low wind periods, of  $0.23 \text{ ppb h}^{-1}$  vs.  $0.16 \text{ ppb h}^{-1}$  using the estimated noontime OH concentration. Together, this amounts to a  $\text{NO}_x$  chemical lifetime of 17 h, with relative branching of 59% to alkyl nitrate formation and 41% to  $\text{HNO}_3$  formation. PAN and other peroxyacyl nitrate compounds were not observed to have high production rates based on measured  $\Sigma\text{PNs}$  and PAN concentration and direct calculation of their formation rate from VOC composition including aldehydes. We estimate a lower and upper limit in noontime median net production of 0.01 to  $0.06 \text{ ppb PAN h}^{-1}$ , using bottom-up (VOC speciation) and top-down (observed PAN concentration and dilution rate assuming zero background PAN concentration) methods, respectively. This corresponds to PAN representing a maximum of  $\sim 18\%$  of the  $\text{NO}_x$  sink. Alkyl nitrate formation is therefore the single most important chemical loss pathway for  $\text{NO}_x$  as well as the most important terminator for OH chain propagation. Note that, although  $\Sigma\text{AN}$  formation is

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the largest chemical sink, mixing out of the basin is the dominant overall loss for  $\text{NO}_x$  emitted. We estimate 68 % of  $\text{NO}_x$  loss is to transport out of the basin.

## 4.2 $\text{O}_3$ formation

$\text{O}_3$  formation is closely related to the formation of organic nitrates, since the reaction channels lead from a branching point in a common pathway. Similar to our treatment of VOC-specific  $\alpha$  values, we calculated, for each measured VOC molecule, the average number of  $\text{O}_3$  molecules generated in a single event of OH initiated oxidation, denoted as  $\gamma$  in Table 2. Note that our definition and estimate for  $\gamma$  includes the contribution from multi-generation alkyl nitrate formation, making it slightly different from previous calculations (Rosen et al., 2004; Perring et al., 2013; Farmer et al., 2011) (see Appendix C). The  $\text{O}_3$  production rate is then a product of the ensemble-averaged  $\gamma$  and the VOC consumption rate calculated above, as plotted in Fig. 7. The difference between the  $\text{O}_3$  production rate and the rate of change in  $\text{O}_3$  concentration signifies the contribution of mixing into the background air. When compared with the production characteristics of n-propyl nitrate in Fig. 4, it is apparent that dilution loss is much more important for the case of n-propyl nitrate (> 80 % of the formation rate) than for  $\text{O}_3$  (~ 30 % of formation rate). Using the  $k_{\text{mix}}$  derived from n-propyl nitrate formation, the local  $\text{O}_3$  budget of the whole campaign period can be closed with a background  $\text{O}_3$  concentration in the range of 20–35 ppb, consistent with observations during high wind periods. This also reinforces the notion that our estimate for turbulent mixing is representative. To reproduce the short-term variations in  $\text{O}_3$  production over a 72 h period with a fixed background  $\text{O}_3$  level of 30 ppb, we estimate the expected change in  $\text{O}_x$  ( $\text{O}_3 + \text{NO}_2$ ) concentration using the mass balance equation (Eq. 2b) to find reasonable agreement with the observations (Fig. 8).

Regarding the relative production of  $\text{O}_3$  to  $\Sigma\text{ANs}$ , the average  $\rho(\text{O}_3)/\rho(\Sigma\text{ANs})$  calculated as  $\gamma/\alpha$  for UBWOS is 15. For comparison, a value of 6.2–7.5 was reported for the Deep Water Horizon (DWH) plume study (Neuman et al., 2012). While both plumes were dominated by alkanes, the VOC suite for the DWH study was further enriched in

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heavier organics. By comparison, a typical industrial city plume (Rosen et al., 2004) measured around Houston during Texas Air Quality Study 2000 has a value of 29–41, a direct result from low  $\alpha$  value (6.5–4.7%) caused by high temperature ( $\sim 40^\circ\text{C}$ ) and relatively low contribution from large alkanes.

### 4.3 Temperature

Currently, none of the chemical mechanisms commonly employed in the chemical transport models for regional  $\text{O}_3$  predictions have incorporated the temperature dependence of alkyl nitrate yields. Since alkyl nitrate formation is a radical termination reaction, reduction in temperature decreases the OH recycling probability and shortens the OH radical chain length. For the 2012 UBWOS campaign the effect is to reduce the radical propagation chain length from a noontime median of 3.2 (300 K) to 2.6 (273 K). Since the chain length is directly proportional to the  $\text{O}_3$  production rate, this corresponds to a 20% decrease in the  $\text{O}_3$  formation rate. Table 3 shows the estimated maximum  $\text{O}_x$  concentration in a multi-day low wind accumulation event in the Uintah Basin based on the observed alkyl nitrate yield. We compare a calculation at 300 K to one at 273 K. Note that for a snowless winter condition, such as encountered in UBWOS 2012, the prediction matches well with the observed maximum hourly  $\text{O}_x$  concentration of 51 ppb in the afternoon of 18 February 2012. While estimating the  $\alpha$  value at 300 K always yields a higher predicted  $\text{O}_3$  concentration, the over prediction is greatest for the simulated snow condition (right most column) when persistent snow cover increases the photolysis rate and stabilizes the boundary layer impeding mixing.

## 5 Conclusion

We presented an analysis of field observations obtained in the Uintah Basin during winter 2012 in Utah, USA. We find that the field data can be used to derive the temperature dependence of the ensemble-averaged nitrate yield,  $\langle\alpha\rangle$ , and that this value

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is consistent with a parameterization derived from laboratory experiments. Including the proper temperature dependence based on the dominating VOC species should be considered for models aimed at estimating local O<sub>3</sub> concentrations in order to avoid substantial errors (+15 % at 0 °C from 27 °C values).

## 5 Appendix A: O<sub>3</sub> pyrolysis correction for ΣANs (380 °C) channel

It was necessary to correct for apparent negative signals observed in the ΣANs signal (ΣANs channel showing less signal level than the ΣPNs channel). The cause of this interference was O<sub>3</sub> pyrolysis to yield O atom in the TD oven at elevated temperature. In the absence of organic molecules, the O atom can serve as a promoter for NO and NO<sub>2</sub> interconversion reaction, as illustrated in Reactions (R4)–(R7).



15 NO and NO<sub>2</sub> are interconverted at a cost of one O atom whose steady state concentration is generally controlled by the forward and reverse Reactions (R4) and (R5). If sufficient time is given, NO and NO<sub>2</sub> will ultimately reach an equilibrium ratio which can be calculated from the reaction rate  $k_{1,2}$  and  $k_{1,3}$  (of Reactions R5 and R6, respectively) with pressure dependence. From the O<sub>3</sub> pyrolysis rate and the gas residence time of 0.17 s in our TD oven region, only ΣANs channel at 380 °C should generate sufficient O atom to significantly alter the NO<sub>2</sub> concentration. To confirm this effect, we performed a series of lab experiments under NO<sub>x</sub> and O<sub>3</sub> concentrations covering the range observed during the UBWOS campaign in the presence of ~ 2 ppb of 2-ethylhexyl nitrate, a simple alkyl nitrate standard available from Sigma Aldrich as a surrogate for the collection of ΣANs in Utah. Figure A1 demonstrates the result from

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a temperature scan experiment when the inlet oven temperature of cell 1 was scanned upward from 180 °C to 380 °C, the operating temperature of  $\Sigma$ ANs channel in the field. The red trace represents the NO<sub>2</sub> signal from cell 1, while the black trace is the NO<sub>2</sub> signal from cell 3 whose inlet was unheated. Since there was no peroxy nitrate in the system, at 180 °C cell 3 only detect the same amount of NO<sub>2</sub> as the ambient temperature cell 1. However, starting from ~ 200 °C alkyl nitrate started to thermal dissociate, giving extra NO<sub>2</sub> signal as the red trace increased relative to the black trace. At temperature beyond 280 °C effects due to O<sub>3</sub> pyrolysis started to reduce the excess NO<sub>2</sub> signal, presumably by the interconversion reaction mentioned above and we see the red trace eventually dropped below the black trace at around 320 °C. This interference thus generated substantial negative  $\Sigma$ ANs signal when we subtract the 180 °C channel from 380 °C channel. Indeed, significant portions of uncorrected night time  $\Sigma$ ANs signals throughout the campaign yielded negative values including negative spikes correlated with positive NO<sub>2</sub> spikes from nearby road traffic emissions. This effect was most prominent when high NO<sub>2</sub> concentration existed so that the excess  $\Sigma$ ANs signal was relatively small on the 380 °C channel. Considering that under the same O<sub>3</sub> concentration the fraction of NO<sub>2</sub> converted due to O atom chemistry was a constant, larger overall NO<sub>2</sub> concentration corresponded to a larger overall NO<sub>2</sub> reduction which could easily overwhelm the original  $\Sigma$ ANs signal to introduce negative values when high temperature channel was subtracted from lower temperature ones. For example, we have performed high temperature box model simulations on O<sub>3</sub> pyrolysis reactions inside the TD oven with a residence time of 0.17 s. At an O<sub>3</sub> concentration of 30 ppb the amount of NO<sub>2</sub> loss through 380 °C was around 6 %. This indicates that if the  $\Sigma$ ANs fraction within a sample is less than 6 % of the total concentration from NO<sub>2</sub>,  $\Sigma$ PNs and  $\Sigma$ ANs combined, a negative value will result. The O atom chemistry outlined in Reactions (R4)–(R7) was further complicated by the presence of organics, especially when initial NO<sub>2</sub> concentration was small as signal loss in lab experiments was always more than can be explained in the absence of organics. Since we were uncertain of the effect of possible chain reactions involving organic radicals initiated by O atom, an empirical



in this simple case is the same as the specific branching ratio of the ethylperoxy radical at 0.019.

## B2 $\alpha$ for propane

To calculate the overall nitrate yield for propane, the dominant product channels should be traced, as illustrated in Fig. B2. Two isomers are formed through hydrogen extractions from either the primary or secondary carbon, giving n-propylperoxy and isopropylperoxy radical in a relative yield of 24 % and 76 %, respectively. The overall nitrate branching ratio can then be calculated if the specific  $\alpha$  for each peroxy isomer is known. Starting from n-propylperoxy radical, the direct reaction with NO gives n-propyl nitrate with a relative yield of 2.1 % calculated according to the Carter and Atkinson's method at 273 K and 842 mBar, representative of campaign condition. The remaining portion of the channel proceeding through alkoxy radical reactions has a further branching of decomposition reaction (rather than reacting with O<sub>2</sub>) to form a formaldehyde and an ethyl radical which promptly reacts with O<sub>2</sub> to give ethylperoxy radical. The relative yield of decomposition vs. O<sub>2</sub> reaction can be calculated from the respective reaction rates reported in the literature. We used a decomposition rate of 846 s<sup>-1</sup> (Curran, 2006) and the product of O<sub>2</sub> reaction rate with O<sub>2</sub> concentration giving a first-order rate constant of  $4 \times 10^4$  s<sup>-1</sup> for the O<sub>2</sub> channel. Branching ratios are hence 2 % and 98 % for decomposition and O<sub>2</sub> reaction. The ethylperoxy radical from the decomposition channel can then react further with NO to give organic nitrates with a yield of 0.019, calculated in the previous section. Summing up both yields scaled by the individual channel strength, we have the specific nitrate yield of n-propylperoxy radical as:  $(0.019 \times 0.02 \times 0.979 + 0.021) = 0.021_4$ . Note the correction from the additional ethylperoxy radical nitrate yield is almost negligible, due to the decomposition channel strength of only 2 %. However, for larger molecules, typically starting from n-butane, isomerization reactions can contribute substantially and higher-generation nitrate yield corrections are generally non-negligible. For iso-propylperoxy radical the specific nitrate yield was calculated using the same principle, only that after decom-

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position reaction a methylperoxy radical is formed. Since methylperoxy radical has little yield for methyl nitrate formation, the total specific nitrate yield for iso-propylperoxy radical is just the direct yield of 5.2%. The overall  $\alpha$  for propane-OH reaction is hence the ensemble average of the specific nitrate yield of all peroxy isomers, namely:

$$(0.24 \times 0.021 + 0.76 \times 0.052) = 0.045.$$

### B3 $\alpha$ for higher alkanes and other organics

Using the method detailed above for propane, we carried out an extended estimation for alkanes up to undecane which is the largest alkane reported from GC-MS data. The results are summarized in Table 2. It is noted here that certain simplifications were necessary for this calculation. For example, in estimating  $\alpha$  for more complex RO<sub>2</sub> radicals from higher-generation oxidation products we ignored the possible contribution of other oxygen-containing functional groups toward the estimated yield given by the Carter and Atkinson parameterization so that only carbon number was considered. Further, rate constants used to estimate the relative branching ratios of alkoxy radical reactions were limited to available literature values, generally around 298 K. As carbon chain length becomes longer, experimental data regarding O<sub>2</sub> reaction, isomerization and decomposition rates become scarce and the data available for the most similar structure are used.

### Appendix C: Differences in definition of $\gamma$ used in this work

The  $\gamma$  value, used to denote the amount of O<sub>3</sub> molecule generated from OH-initiated oxidation of an organic molecule in this work, is different from the definition of previous works that focus on only single generation RO<sub>2</sub> chemistry in 2 respects, described as following. First,  $\gamma$  has commonly been given a value of 2 for two O<sub>3</sub> molecules being generated per OH-initiated oxidation of VOCs, from the formation of HO<sub>2</sub> and NO<sub>2</sub> each. This is a good approximation for small alkanes of which isomerization is

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not important, but can be erroneous otherwise. For example, in the absence of organic nitrate formation channel, we estimate  $\gamma$  for n-hexane to be 3.2 due to the efficient isomerization reaction of hydrogen abstraction by the 2-alkoxy or 3-alkoxy radical produced, generating a new alkyl radical and an alcohol group. The presence of large alkanes, up to undecane, necessitates a more careful treatment. Second,  $\gamma$  has been used to calculate the ratio of  $O_3$  production rate over  $\Sigma ANs$  production rate, formulated as  $\gamma(1 - \alpha)/\alpha$ . The factor  $(1 - \alpha)$  in the numerator implies that  $\gamma$  was estimated under the assumption of zero nitrate formation.  $(1 - \alpha)$  therefore accounted for the fraction of reaction that actually proceeded to form  $O_3$ . This is only exact if VOC + OH reaction only forms a single generation of  $RO_2$  molecule, once again a valid assumption for small VOC only. For larger alkanes there exist a non-negligible fraction of higher generation  $RO_2$  reactions from isomerization reactions and we must account for the effective number of  $NO_2$  and  $HO_2$  formed in a cumulative manner over extended generations. This means  $\gamma$  and  $\alpha$  are related by the structure of the molecule under consideration. Our listed  $\gamma$  values in Table 2 is then the better average number of  $O_3$  generated per OH-initiated oxidation with alkyl nitrate formation considered, or in the same spirit, the “ $\gamma(1 - \alpha)$ ” value considered over multi-generation reactions. In Table 2, we observe an increasing trend of  $\gamma$  going from methane to around hexane as larger alkanes are more susceptible to isomerization and further radical reactions, converting more NO to  $NO_2$ . This trend does not continue, however, with further increase of alkane size because of the competing effect of increasing organic nitrate yield, eventually reduces the amount of alkoxy radical formed.

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**Table 1.** Median OH reactivity and associated formation rates at local noon.

Compound Class	OH Reactivity (s <sup>-1</sup> )	$\rho(\Sigma\text{ANs})^*$ (ppt h <sup>-1</sup> )	$\rho(\text{O}_3)^*$ (ppt h <sup>-1</sup> )
Alkane C <sub>1</sub> –C <sub>11</sub>	5.02	172	1760
Alkene C <sub>2</sub> –C <sub>3</sub>	0.15	0.71	44
Alkyne C <sub>2</sub>	0.013	0	2.4
Aromatic C <sub>6</sub> –C <sub>9</sub>	0.58	0.90	120
Alcohol C <sub>1</sub> –C <sub>2</sub>	0.31	0	48
Ketone C <sub>3</sub> –C <sub>4</sub>	0.0084	~ 0	0.37
Aldehyde C <sub>1</sub> –C <sub>4</sub>	0.44	0	130
CO	0.95	0	150
NO	0.61	0	0
NO <sub>2</sub>	0.82	0	0
Total	8.90	174	2250

\* Median noon time [OH] = 1 × 10<sup>6</sup> molecule cm<sup>-3</sup>.

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**Table 2.** Summary of specific organic nitrate and ozone yield calculated at 0 °C.

Compound Class	$\alpha$	$\gamma$	Compound Class	$\alpha$	$\gamma$
<b>Alkane</b>	<b>0.22</b>	<b>2.25</b>	<b>Alkene</b>	<b>0.031</b>	<b>1.94</b>
methane	~ 0	2	ethene	0.025	1.95
ethane	0.019	1.96	propene	0.05	1.9
propane	0.045	1.92			
iso-butane	0.11	2.6	<b>Alkyne</b>	<b>0</b>	<b>1.2</b>
n-butane	0.114	2.17	ethyne	~ 0	1.2
iso-pentane	0.21	2.46			
n-pentane	0.2	2.19	<b>Aromatic</b>	<b>0.01<sup>a</sup></b>	<b>1.3<sup>b</sup></b>
2,2-dimethylpropane	0.25	3.1			
n-hexane	0.42	2.62	<b>Alcohol</b>	<b>0</b>	<b>1</b>
2,2-dimethylbutane	0.36	2.7	methanol	~ 0	1
2-methylpentane	0.29	2.2	ethanol	~ 0	1.05
3-methylpentane	0.33	2.34			
methyl-cyclopentane	0.29	2.9	<b>Ketone</b>	<b>0.077</b>	<b>3.72</b>
Cyclohexane	0.33	2	acetone	0.021	4
methyl-cyclohexane	0.58	2.4	methylethylketone	0.11	3.56
ethyl-cyclohexane	0.5	2.25			
dimethyl-cyclohexane	0.67	1.8	<b>Aldehyde</b>	<b>0</b>	<b>1.96</b>
heptane	0.6	2.2	formaldehyde	0	1
octane	0.6	1.86	acetaldehyde	0	3
nonane	0.62	1.52	propanal	0.019	3
decane	0.74	1.43	butanal	0.045	2.91
undecane	0.81	1.2	methacrolein	0.05	2.45

<sup>a</sup> Previously assumed value of 0.1 is due to contribution of nitrobenzene which we do not detect in  $\Sigma$ ANs channel.

<sup>b</sup> Assumption based on toluene data.

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**Table 3.** Expected maximum  $O_x$  ( $NO_2 + O_3$ ) concentration under UBWOS condition.

Condition <sup>a</sup>	UBWOS 2012 base condition	photolysis $\times 2$ and mixing $\div 2$
$\alpha$ calculated at 273 K <sup>b</sup>	57 ppb	140 ppb
$\alpha$ calculated at 300 K <sup>b</sup>	64 ppb	165 ppb
error	7 ppb	25 ppb

<sup>a</sup> Assuming background  $O_3$  concentration of 30 ppb.

<sup>b</sup> Carter and Atkinson (1989).

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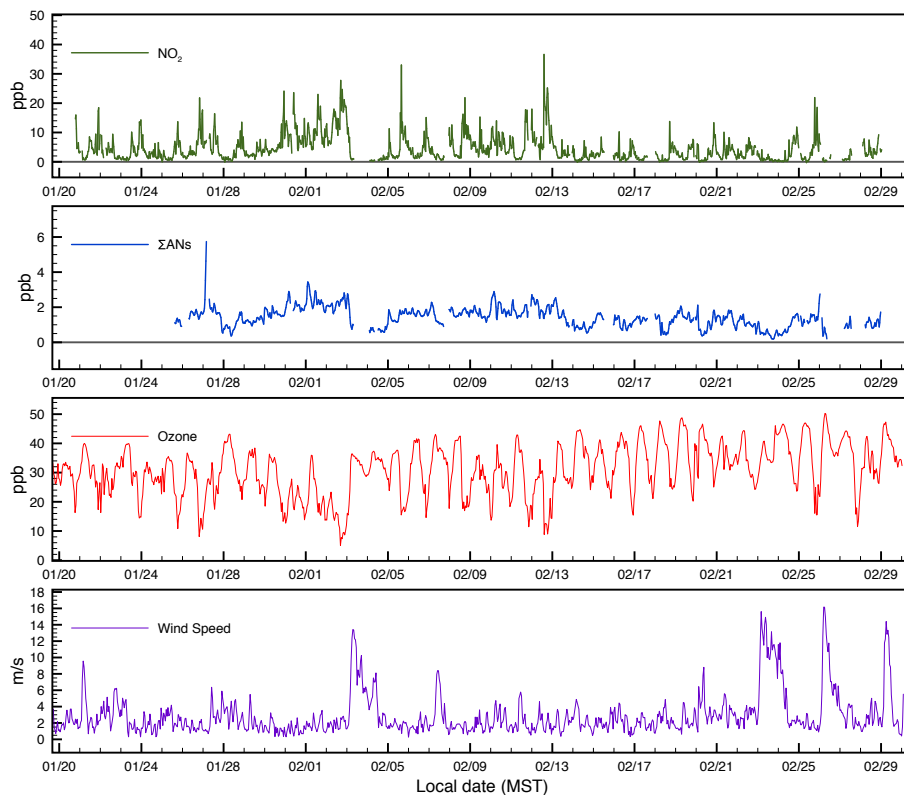
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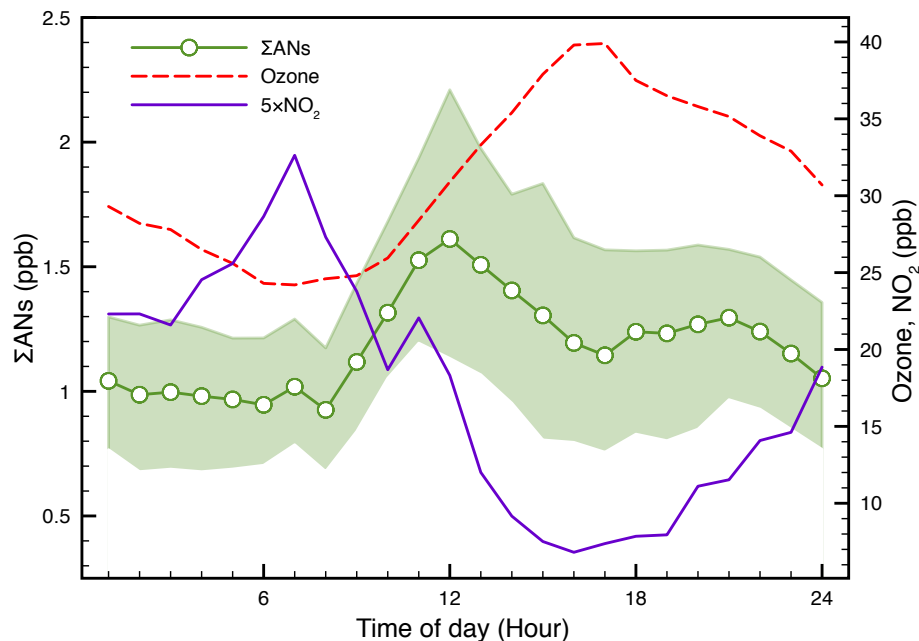


**Figure 1.** Hourly-averaged time series of  $\text{NO}_2$ , total alkyl nitrates ( $\Sigma\text{ANs}$ ),  $\text{O}_3$  and windspeed measured during UBWOS 2012. The concentrations are measured at height of 16 m from a 19 m scaffolding tower on site. The windspeed is measured at the tower top. Ticks on the x-axis mark local midnight.

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**Figure 2.** Diurnal variations of  $\Sigma\text{ANs}$ , ozone and  $\text{NO}_2$ . Lines represent median values while the shaded area of  $\Sigma\text{ANs}$  represents the interquartile (25–75%) coverage. The  $\Sigma\text{AN}$  data have been corrected for  $\text{O}_3$  and  $\text{ClNO}_2$  interferences (see text).

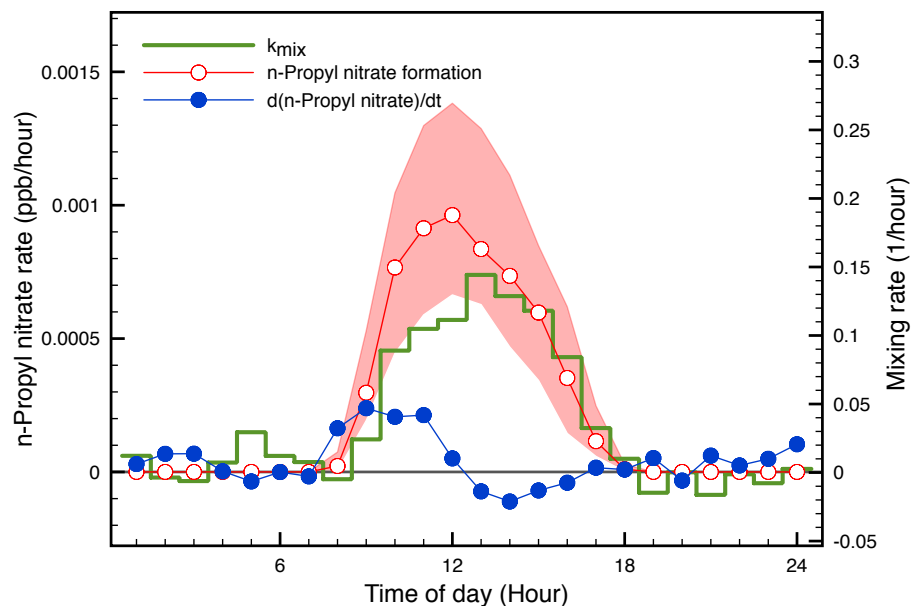
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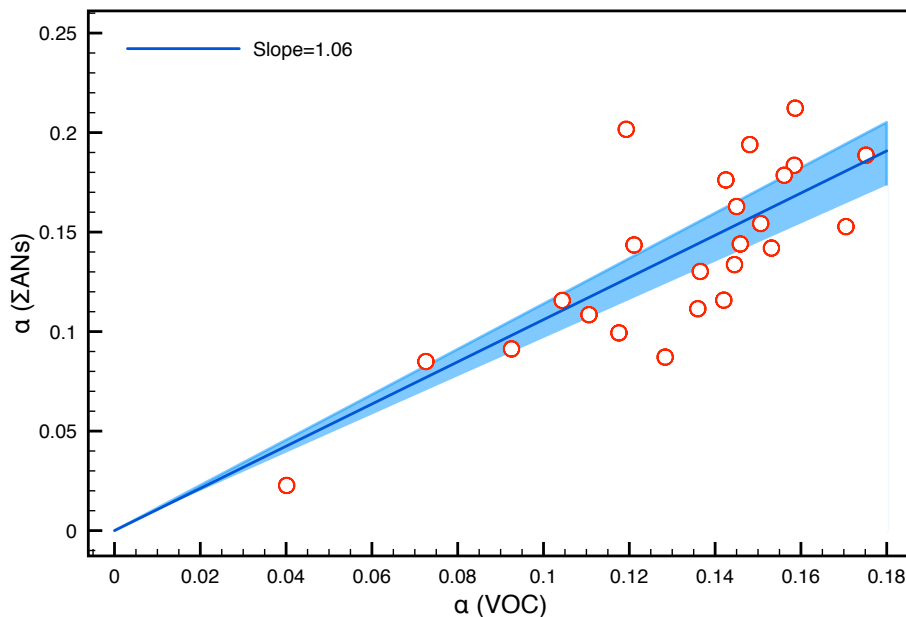
**Figure 5.** The production rate and concentration change of n-propyl nitrate calculated from field observations. The difference between the red and blue traces represent the mixing loss promoted by solar surface heating. The green trace is the calculated effective first order mixing rate,  $k_{\text{mix}}$ .

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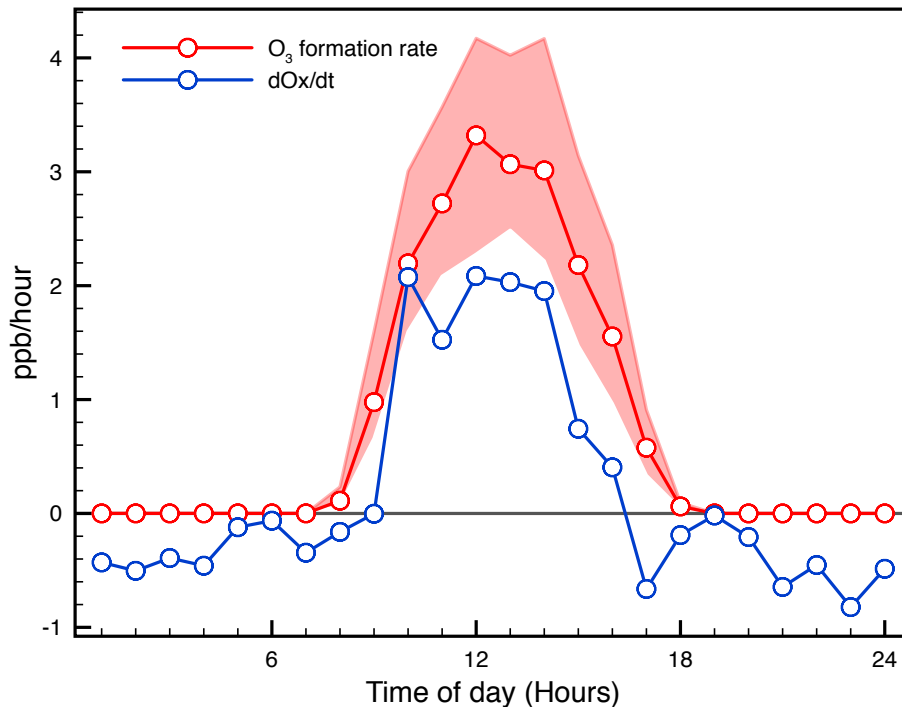
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**Figure 6.** Correlation between daytime averaged  $\alpha$  estimated using the VOC-ensemble method (VOC, Sect. 3.2.1) and oxidation-production method ( $\Sigma$ ANs, Sect. 3.2.2). The shaded area corresponds to the 95 % confidence interval for the regression slope passing through origin. The 1 : 1 line is within this interval.

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**Figure 7.** Calculated daytime O<sub>3</sub> formation rate and the rate of change of O<sub>x</sub> (NO<sub>2</sub> + O<sub>3</sub>) observed. The difference between traces can be attributed to mixing using the same mixing rate estimated from n-propyl nitrate. The existence of non-negligible background O<sub>3</sub> concentration (30 ppb) suppresses the net dilution.

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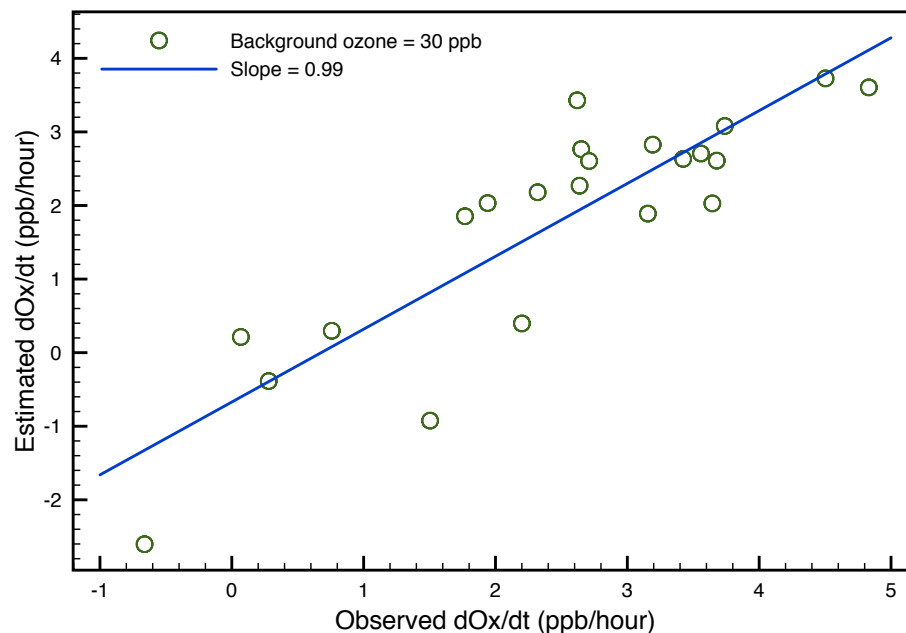
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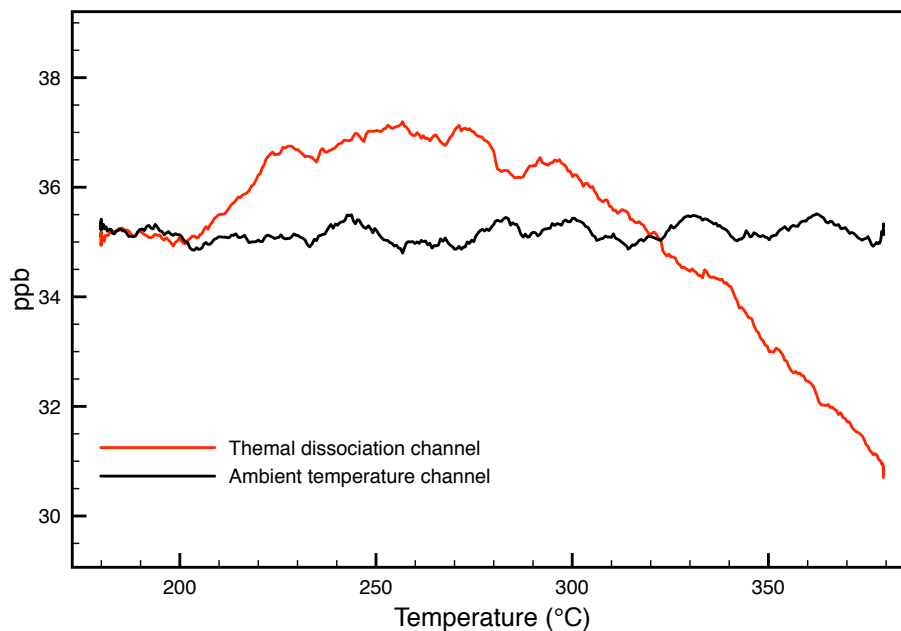
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**Figure 8.** Correlation of the estimated daytime hourly  $O_3$  production rate corrected for dilution loss to what was observed from  $O_3$  and  $NO_2$  data. A background  $O_3$  concentration of 30 ppb was assumed.

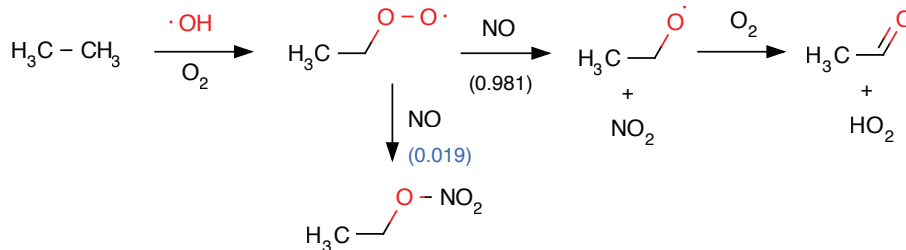
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**Figure A1.** Laser induced fluorescence signal from samples containing  $\sim 35$  ppb  $\text{NO}_2$  and 2 ppb 2-ethylhexyl nitrate passing through the unheated channel (ambient temperature, black trace) and thermal dissociation channel (red trace) in the presence of  $\text{O}_3$ .

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**Figure B1.** Ethane oxidation by OH radical in the presence of NO.

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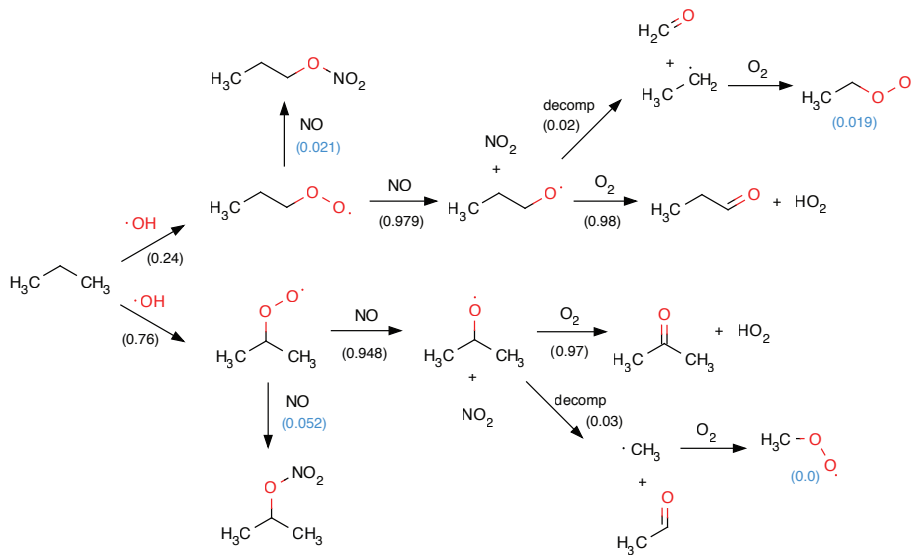
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**Figure B2.** Propane oxidation by OH radical in the presence of NO.

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