

The changing role of organic nitrates in the removal and transport of NO_x

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Abstract. A better understanding of the chemistry of nitrogen oxides (NO_x) is crucial to effectively reducing air pollution and predicting future air quality. The response of NO_x lifetime to perturbations in emissions or in the climate system is set in large part by whether NO_x loss occurs primarily by the direct formation of HNO₃ or through the formation of alkyl and multifunctional nitrates (RONO₂). Using 15 years of detailed in situ observations, we show that in the summer daytime continental boundary layer the relative importance of these two pathways can be well approximated by the relative likelihood that OH will react with NO₂ or instead with a volatile organic compound (VOC). Over the past decades, changes in anthropogenic emissions of both NO_x and VOCs have led to a significant increase in the overall importance of RONO₂ chemistry to NO_x loss. We find that this shift is associated with a decreased effectiveness of NO_x emissions reductions on ozone production in polluted areas and increased transport of NO_x from source to receptor regions. This change in chemistry, combined with changes in the spatial pattern of NO_x emissions, is observed to be leading to a flatter distribution of NO₂ across the United States, potentially transforming ozone air pollution from a local issue into a regional one.

1 Introduction

Nitrogen oxides (NO_x ≡ NO + NO₂) play a central role in the formation of toxic air pollutants including O₃ and secondary aerosols. More broadly, NO_x chemistry controls the rates and pathways of atmospheric oxidation by determining the concentration of the three most important tropospheric oxidants: OH, O₃, and NO₃. NO_x emissions also directly contribute to nitrogen deposition in sensitive ecosystems (Fowler et al., 2013). Due to its harmful effects to the environment and human health, NO_x has been the target of emissions control strategies since the 1970s, causing anthropogenic NO_x emissions in the United States to have decreased by a factor of 2 or more over the past 30 years (United States Environmental Protection Agency, 2018). Understanding the consequences of these past changes and predicting the results of future emissions reductions on the atmosphere requires a quantitative description of feedbacks between NO_x concentrations and NO_x chemistry.

After emission to the atmosphere, removal of NO_x occurs through two primary pathways: conversion to HNO₃ and conversion to alkyl and multifunctional nitrates (RONO₂). Once formed, HNO₃ is nearly chemically inert in the troposphere, with a lifetime to reaction or photolysis of over 50 hours. HNO₃ is therefore removed almost entirely by wet and dry deposition. RONO₂ represents a class of diverse molecules, with atmospheric lifetimes ranging from hours to days depending on

the properties of the organic backbone (R-group). The loss of RONO_2 is divided among reactions that release NO_x from the R-group and recycle it back to the atmosphere, reactions that result in heterogeneous hydrolysis to form HNO_3 , and direct deposition. The latter two pathways permanently remove NO_x from the atmosphere (Nguyen et al., 2015; Romer et al., 2016; Fisher et al., 2016). Other NO_x oxidation products, such as peroxy acetyl nitrate (PAN) or HONO can play an important role in the transport and redistribution of NO_x but do not generally lead to permanent NO_x removal.

Historically, direct HNO_3 production was thought to be the only important NO_x loss pathway, with RONO_2 chemistry playing at most a minor role. However, several studies have shown that the formation rate of RONO_2 in cities or forested regions can be competitive with or greater than the direct production rate of nitric acid (Rosen et al., 2004; Farmer et al., 2011; Browne et al., 2013; Romer et al., 2016; Sobanski et al., 2017).

The relative importance of HNO_3 and RONO_2 production is an important factor in setting the lifetime of NO_x (Romer et al., 2016) and affects the response of NO_x loss to temperature (Romer et al., 2018). Due to their different production pathways, the relative importance of HNO_3 and RONO_2 production also controls how NO_x loss and ozone production are affected by changes to emissions of NO_x or volatile organic compounds (VOCs). By terminating the radical chain reactions, the formation of RONO_2 serves to suppress ozone formation in polluted areas (Perring et al., 2010; Farmer et al., 2011; Edwards et al., 2013; Lee et al., 2014). Several studies have also shown that RONO_2 can efficiently partition into aerosols, potentially explaining a large portion of secondary organic aerosol in a wide range of environments (Rollins et al., 2012; Pye et al., 2015; Xu et al., 2015b; Lee et al., 2016).

Multiple previous studies have used chemical transport models to investigate how the relative production of RONO_2 and HNO_3 varies in different environments. Browne and Cohen (2012) modeled NO_x loss over the Canadian boreal forest using WRF-Chem and Fisher et al. (2016) and Zare et al. (2018) studied NO_x loss in the southeast United States using GEOS-Chem and WRF-Chem respectively. These studies agree that in rural and forested areas with lower NO_x emissions and higher biogenic VOC emissions, RONO_2 chemistry is often the largest sink of NO_x .

However, these studies diverge in their conclusions about the overall importance of RONO_2 chemistry as a NO_x sink and how it is likely to change in the future. In a WRF-Chem simulation identical to those described in Zare et al. (2018), RONO_2 chemistry is found to be 60 % or more of the total NO_x loss across broad swathes of the southeast United States (Fig. 1), while Fisher et al. (2016) found RONO_2 production to be concentrated in rather small sections of the southeast. Furthermore, Fisher et al. (2016) suggested that the contribution of RONO_2 chemistry to NO_x loss across the region is unlikely to change significantly in the future due to the spatial segregation of NO_x and VOC emissions. On the other hand, Zare et al. (2018) and Browne and Cohen (2012) suggested that the contribution of RONO_2 chemistry to NO_x loss was likely to grow significantly if anthropogenic NO_x emissions decreased across the United States.

Here we use in situ observations from a collection of 13 different field deployments to investigate how the relative daytime production of RONO_2 and HNO_3 varies across the United States and how this fraction may change in the future. We show that the relative production of RONO_2 and HNO_3 can be well described by the relative OH reactivity of NO_2 and of the combined VOC mixture. As both anthropogenic NO_x and anthropogenic VOC emissions have decreased substantially in the United States over the past 20 years, the relative role of these two pathways has shifted as well. While the shift has generally

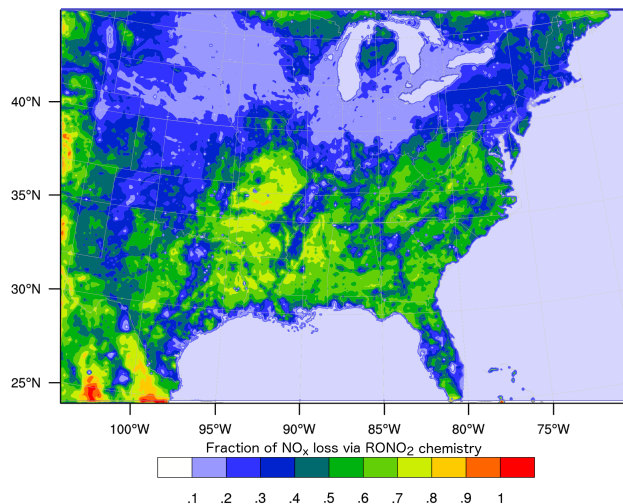


Figure 1. Average (24-hour) fraction of total NO_x loss via RONO_2 chemistry over the southeast United States in summer 2013 simulated using the RACM2_Berkeley2 mechanism in WRF-Chem (Zare et al., 2018).

been towards an increasing role for RONO_2 chemistry, the shift has been smallest in large cities and largest in the transitional regime around them. Combined with changing emission patterns of NO_x , the shift in NO_x chemistry is leading to a flatter distribution of NO_x across the continental United States.

2 NO_x chemistry and production of RONO_2 and HNO_3

- 5 NO_x is emitted to the atmosphere as NO from a range of anthropogenic and biogenic sources, including motor vehicles, power plants, lightning, fires, and soil bacteria. In the daytime, NO interconverts with NO_2 on a timescale of minutes through Reactions (R1–R2), forming the chemical family NO_x . When NO_x is combined with VOCs and hydrogen oxides (HO_x), a set of linked radical chain reactions is formed (R3–R6). As part of these reactions, two molecules of NO are oxidized to NO_2 , leading to the net production of O_3 through Reaction (R2).

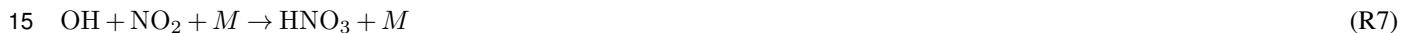




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The reactions that propagate the catalytic cycle occur at the same time as reactions that remove NO_x from the atmosphere, terminating the cycle. Direct HNO_3 production occurs through the association of OH with NO_2 (R7). RONO_2 compounds are produced as a minor channel of the $\text{RO}_2 + \text{NO}$ reaction (R4b). Some fraction of the time α , these two radicals will
 10 associate to form an organic nitrate, with the balance forming NO_2 and eventually producing O_3 (R4a). The branching ratio $k_{\text{R4b}}/(k_{\text{R4a}} + k_{\text{R4b}})$ is designated α and is determined by the nature of the R-group as well as the temperature and pressure. Longer carbon backbones and lower temperatures increase α , while lower pressures and oxygenated functional groups decrease it (Wennberg et al., 2018). Typical values of α in the summertime continental boundary layer range from near 0 for small hydrocarbons and highly oxygenated compounds to over 0.20 for large alkanes and alkenes (Perring et al., 2013).



The total rate of RONO_2 production can be calculated from the properties of individual VOCs measured in the atmosphere
 20 via Eq. (1). In Eq. (1), $Y_{\text{RO}_2 i}$ represents the yield of RO_2 radicals from VOC oxidation and f_{NO_i} represents the fraction of those RO_2 radicals that react with NO instead of reacting with HO_2 or undergoing unimolecular isomerization (e.g., Teng et al., 2017). f_{NO_i} is close to 1 under polluted or moderately-polluted conditions, but decreases as the concentration of NO_x decreases.

$$P(\text{RONO}_2) = [\text{OH}] \sum_{R_i} [\text{R}_i] \cdot k_{\text{OH}+\text{R}_i} \cdot Y_{\text{RO}_2 i} \cdot f_{\text{NO}_i} \cdot \alpha_i \quad (1)$$

25 If the contributions from individual VOCs are summed and averaged, the total production of RONO_2 can also be calculated from the effective behavior of the VOC mixture via Eq. (2), where VOCR is the sum of all measured VOC concentrations weighted by their reaction rate with OH.

$$P(\text{RONO}_2) = [\text{OH}] \cdot \text{VOCR} \cdot Y_{\text{RO}_2 \text{eff}} \cdot f_{\text{NOeff}} \cdot \alpha_{\text{eff}} \quad (2)$$

In a similar fashion, the production of HNO_3 can be calculated via Eq. (3), where NO_2R is the NO_2 reactivity, or the concentration of NO_2 multiplied by $k_{\text{OH}+\text{NO}_2}$. At 298 K and 1 atm, 10 ppb of NO_2 is equivalent to an NO_2R of 2.3 s^{-1} .

$$P(\text{HNO}_3) = [\text{OH}] \cdot [\text{NO}_2] \cdot k_{\text{OH}+\text{NO}_2} = [\text{OH}] \cdot \text{NO}_2\text{R} \quad (3)$$

Total NO_x loss is the sum of the conversion to HNO_3 and conversion to RONO_2 . The fraction of NO_x loss via RONO_2 production can be expressed analytically as Eq. (4).

$$\frac{P(\text{RONO}_2)}{P(\text{RONO}_2) + P(\text{HNO}_3)} = \left(1 + \frac{1}{\alpha_{\text{eff}} \cdot f_{\text{NO}_{\text{eff}}} \cdot Y_{\text{RO}_2\text{eff}}} \times \frac{\text{NO}_2\text{R}}{\text{VOCR}} \right)^{-1} \quad (4)$$

The relative production of RONO_2 and HNO_3 is seen to be controlled by two factors, the first describing the chemistry of RO_2 radicals (α_{eff} , $f_{\text{NO}_{\text{eff}}}$, $Y_{\text{RO}_2\text{eff}}$), and the second the ratio of NO_2R to VOCR , which describes whether OH is more likely to react with a VOC or with NO_2 . Because Eq. (4) concerns fractional loss of NO_x , the concentration of OH, which affects RONO_2 and HNO_3 production equally, does not appear in the result.

We show below that in the summertime continental boundary layer, the terms describing RO_2 radical chemistry vary significantly less than the $\text{NO}_2\text{R}/\text{VOCR}$ ratio, allowing the relative importance of RONO_2 and HNO_3 chemistry to be roughly estimated from only a single ratio.

3 Observed contributions of HNO_3 and RONO_2 chemistry to NO_x loss

3.1 Daytime chemistry

Relative RONO_2 and HNO_3 production rates were calculated for 13 separate campaign deployments in the northern hemisphere over the past 20 years. Campaigns were selected that included measurements of NO_x , HNO_3 , O_3 , HCHO , a wide range of VOCs, and total organic nitrates (ΣRONO_2). Although they do not include measurements of ΣRONO_2 , ITCT2k2 and CALNEX-P3 were also included to provide a pair of measurements of VOCs and NO_x in the same geographic location separated in time. A list of all campaigns used in this study is given in Table 1. Where available, measurements of OH and HO_2 were used to directly calculate RO_2 formation and loss. When these radicals were not available, OH, and HO_2 radical concentrations were also calculated iteratively based on the total rate of HO_x radical production by O_3 photolysis, HCHO photolysis, and alkene ozonolysis. When HONO was measured, HONO photolysis was also included as an OH source. In a small fraction of cases (3% of all data points), NO measurements were not available and NO concentrations were calculated based on the concentrations of O_3 and NO_2 . Details of the radical modeling, including the equations used to calculate the production and loss of these radicals, are given in Appendix A.

Although these field campaigns do not constitute a random sample of the atmosphere, the combined dataset provides an excellent survey of atmospheric chemistry over a wide range of conditions. The combined dataset includes nearly 8000 data points for which fractional NO_x loss can be calculated, spanning nearly 3 orders of magnitude in the ratio of NO_2R to VOCR with no significant gaps (Fig. 2).

Table 1. Field campaigns used in this analysis

Campaign name	Data Reference	Format	Year	Base of Operations	Date
ITCT2k2	ITCT Science Team (2002)	Airborne	2002	Monterey, CA	22 Apr – 19 May
INTEX-NA	INTEX-A Science Team (2006)	Airborne	2004	Palmdale, CA	2 Jul
				Mascoutah, IL	7 Jul – 14 Jul
				Portsmouth, NH	16 Jul – 10 Aug
				Mascoutah, IL	12 Aug
INTEX-B	INTEX-B Science Team (2011)	Airborne	2006	Houston, TX	4 Mar – 19 Mar
				Honolulu, HI	23 Apr – 28 Apr
				Anchorage, AK	1 May – 12 May
BEARPEX 2007	BEARPEX 07 Science Team (2007)	Ground	2007	Georgetown, CA	15 Aug – 10 Oct
ARCTAS-B	ARCTAS-B Science Team (2011)	Airborne	2008	Palmdale, CA	18 Jun – 24 Jun
				Cold Lake, Alberta, CAN	29 Jun – 8 Jul
				Thule, Greenland	8 Jul – 10 Jul
BEARPEX 2009	BEARPEX 09 Science Team (2009)	Ground	2009	Georgetown, CA	15 Jun – 31 Jul
CALNEX-P3	CALNEX Science Team (2002a)	Airborne	2010	Ontario, CA	1 May – 22 Jun
CALNEX-SJV	CALNEX Science Team (2002b)	Ground	2010	Bakersfield, CA	15 May – 30 Jun
DC3	DC3 Science Team (2013)	Airborne	2012	Salina, KS	13 May – 30 Jun
SOAS	SOAS Science Team (2013)	Ground	2013	Centreville, AL	1 Jun – 15 Jul
SEAC4RS	SEAC4RS Science Team (2014)	Airborne	2013	Houston, TX	8 Aug – 23 Sep
FRAPPÉ	FRAPPÉ Science Team (2014)	Airborne	2014	Broomfield, CO	16 Jul – 16 Aug
KORUS-AQ	KORUS-AQ Science Team (2018)	Airborne	2016	Pyeongtaek, ROK	1 May – 14 Jun
				Palmdale, CA	17 Jun – 18 Jun

The fraction of total NO_x loss occurring via RONO_2 chemistry from all 13 of these campaigns is shown in Fig. 3a for points within the continental summertime boundary layer. Despite spanning a large range of environments, all 13 campaigns are well described by a single function of the form $(1 + b \cdot (\frac{\text{NO}_2\text{R}}{\text{VOCR}})^m)^{-1}$ (red line in Fig. 3a). This functional form corresponds to a linear relationship between $P(\text{RONO}_2)/P(\text{HNO}_3)$ and $\text{NO}_2\text{R}/\text{VOCR}$ on a log-log scale. If m is fixed to 1, then this form also corresponds to the expected behavior if the VOC mixture did not change between environments, and so all parameters other than $\text{NO}_2\text{R}/\text{VOCR}$ remained constant (gray line in Fig. 3a).

The calculated increase in fractional NO_x loss via RONO_2 chemistry as $\text{NO}_2\text{R}/\text{VOCR}$ decreases is matched by an increase in the observed ratio of ΣRONO_2 to the sum of ΣRONO_2 and HNO_3 (Fig. 3b). However, the increase in fractional concentrations as $\text{NO}_2\text{R}/\text{VOCR}$ decreases is much less than the increase in fractional production. At low $\text{NO}_2\text{R}/\text{VOCR}$ ratios, the dominant RONO_2 species are typically short lived and can undergo heterogeneous hydrolysis to produce HNO_3 (e.g., Browne

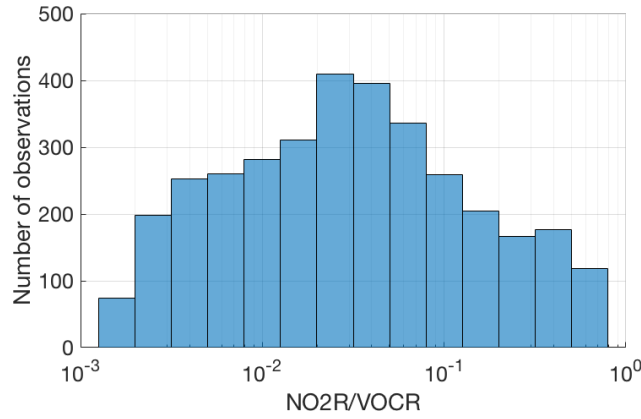


Figure 2. Number of points in each bin for which the fraction of NO_x loss occurring via RONO_2 chemistry could be calculated.

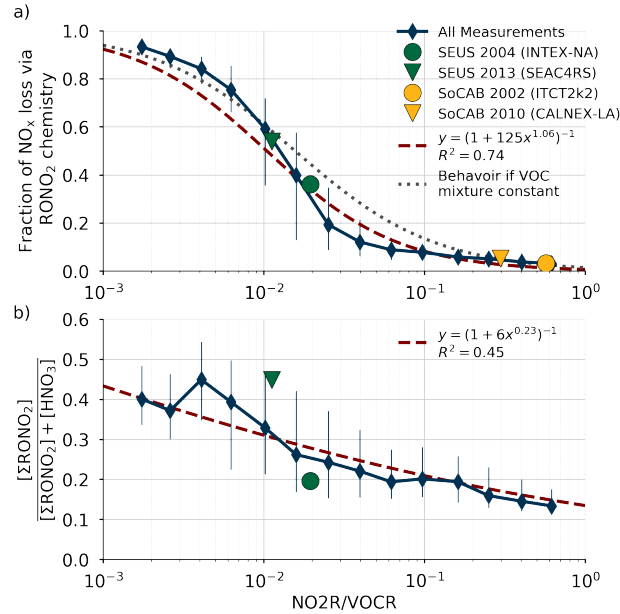


Figure 3. Comparison of the relative production rates of RONO_2 and HNO_3 as a function of $\text{NO}_2\text{R}/\text{VOCR}$. Used data points are restricted to the continental summer daytime boundary layer (i.e., over land, less than 1.5 km above ground level, and average temperature $> 10^\circ\text{C}$). The top panel shows the fraction of NO_x loss attributable to RONO_2 chemistry, as well as a least-squares fit to the data and the expected behavior if α_{eff} , $f_{\text{NO}_{\text{eff}}}$, $Y_{\text{RO}_{2\text{eff}}}$ were constant. The bottom panel shows the ratio of ΣRONO_2 to the sum of HNO_3 and ΣRONO_2 . In each panel, the blue diamonds show the median in each bin and the vertical lines show the interquartile range.

et al., 2013). This indirect source of HNO_3 can be the greatest source of HNO_3 in forested environments, and leads to the relatively weak dependence of fractional concentration on $\text{NO}_2\text{R}/\text{VOCR}$.

While the fraction of NO_x loss occurring via RONO_2 chemistry can be well predicted from just the $\text{NO}_2\text{R}/\text{VOCR}$ ratio, the observations exhibit a sharper transition from HNO_3 -dominated to RONO_2 -dominated NO_x loss than would be expected if the VOC mixture remained constant. This effect can be explained by variation in $Y_{\text{RO}_2\text{eff}}$, α_{eff} , and $f_{\text{NO}_{\text{eff}}}$ as $\text{NO}_2\text{R}/\text{VOCR}$ changes. The behavior of these three parameters is shown in Fig. 4. As $\text{NO}_2\text{R}/\text{VOCR}$ decreases, $f_{\text{NO}_{\text{eff}}}$ consistently decreases from 0.8 to 0.2, due almost entirely to the decrease in NO_x concentrations. In contrast, both $Y_{\text{RO}_2\text{eff}}$ and α_{eff} are larger in areas with low $\text{NO}_2\text{R}/\text{VOCR}$ ratios, due to changes in the VOC mixture between environments. In areas where $\text{NO}_2\text{R}/\text{VOCR}$ is high, many of the predominant VOCs, including CO, HCHO, and aromatics, either do not produce RO_2 radicals when oxidized by OH or produce RO_2 radicals that do not efficiently produce organic nitrates, leading to the relatively low values of $Y_{\text{RO}_2\text{eff}}$ and α_{eff} . In areas with low $\text{NO}_2\text{R}/\text{VOCR}$ ratios, the VOC mixture is often dominated by biogenic alkenes such as isoprene and monoterpenes that efficiently produce organic nitrates, leading to higher values of both $Y_{\text{RO}_2\text{eff}}$ and α_{eff} . However, although variation in these parameters can help explain some of the observed behavior of fractional NO_x loss, the overall variation is much smaller than the variation of the $\text{NO}_2\text{R}/\text{VOCR}$ ratio. Each of the three parameters varies by a factor of 4 or less, while the $\text{NO}_2\text{R}/\text{VOCR}$ ratio varies by a factor of 1000.

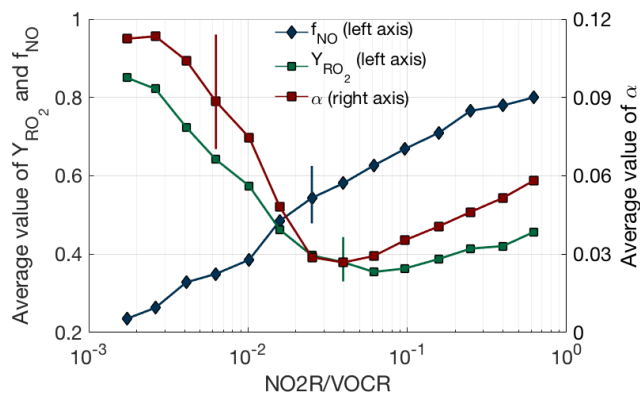


Figure 4. VOC oxidation parameters (α_{eff} , $f_{\text{NO}_{\text{eff}}}$, $Y_{\text{RO}_2\text{eff}}$) as a function of $\text{NO}_2\text{R}/\text{VOCR}$. Used data points are restricted to the continental summer daytime boundary layer (i.e., over land, less than 1.5 km above ground level, and average temperature $> 10^\circ\text{C}$). The line and solid shapes show the median in each bin, and the vertical lines show an example of the interquartile range for each binned parameter.

The conclusion that variation in VOC parameters is small compared to the variation in the $\text{NO}_2\text{R}/\text{VOCR}$ ratio does not hold outside of the summertime continental boundary layer. In the remote marine boundary layer or in the upper troposphere, α_{eff} is extremely low, as the dominant VOCs produce alkyl nitrates at yields of 0.01 or less (Mao et al., 2009; Perring et al., 2013). Under these conditions, HNO_3 dominates NO_x loss even when $\text{NO}_2\text{R}/\text{VOCR}$ is less than 3×10^{-2} .

The trend calculated from the in situ observations matches that found in model simulations, that in areas with high ratios of NO_2R to VOCR , HNO_3 is the dominant NO_x sink, but as concentrations of NO_x decrease and concentrations of VOCs increase, the opposite is true. The combined in situ observations show that the importance of RONO_2 chemistry to NO_x loss is a non-linear function of the $\text{NO}_2\text{R}/\text{VOCR}$ ratio, leading to a sharp transition between the HNO_3 -dominated and RONO_2 -

dominated regimes. The sharp transition suggests there is a strong gradient in chemical NO_x loss between urban and rural areas, especially in areas with significant biogenic VOC emissions. Furthermore, the sharp transition indicates that some regions may quickly shift from being HNO_3 -dominated to RONO_2 -dominated if NO_2/VOCR decreases.

3.2 Nighttime chemistry

- 5 While the primary focus of this analysis is on daytime chemistry, a conceptually similar transition may also occur at night. At night, OH concentrations are near zero, and the first step in NO_x oxidation is the reaction of NO_2 with O_3 to produce NO_3 . This radical can in turn react either with NO_2 to form N_2O_5 or with an alkene to form an organic nitrate (R8 – R9).



Finally, N_2O_5 can either thermally decompose to reform NO_3 and NO_2 or it can hydrolyze on aerosol surfaces to produce HNO_3 (R9 – R10).



- Although the details of the nighttime chemical system are different, it shares some fundamental similarities with the daytime system: NO_x can be lost through the production of RONO_2 or of HNO_3 , and a key step controlling the relative importance of these two sinks is whether an oxidant reacts with NO_2 or with a VOC. These similarities suggest that the relative importance of RONO_2 and HNO_3 as NO_x sinks at night may be controlled by the relative reactivities of NO_2 and VOCs towards NO_3 . In areas where NO_3 is more likely to react with NO_2 , HNO_3 production is likely to dominate NO_x loss, while the opposite is likely to be true in areas where NO_3 is more likely to react with a VOC.

- 20 However, quantitatively estimating the relative fraction of NO_x lost through these different pathways is not practical with the combined dataset presented here. There have been relatively few measurements of the nocturnal atmosphere (only 4 of the 13 campaigns in Table 1 include nighttime measurements) and there remain significant uncertainties in the kinetics of nighttime NO_x loss. In particular, the overall rate of N_2O_5 hydrolysis is controlled by the reactive uptake parameter γ and the aerosol surface area, both of which can vary by multiple orders of magnitude (Brown et al., 2009; McDuffie et al., 2018). Variation in
25 the rate of N_2O_5 hydrolysis may therefore also play a major role in controlling the relative importance of RONO_2 and HNO_3 chemistry to NO_x loss at night. While developing a more quantitative understanding of the trends in the chemical mechanisms of nocturnal NO_x loss is an important area for future research, the conceptual similarity between the daytime and nighttime regimes suggests that conclusions based on daytime NO_x chemistry may also be relevant to the nighttime.

4 Predicted trends over time

Using the trends in Fig. 3a to understand trends in NO_x chemistry over time is only possible if the response to variation across space is equivalent to the response to variation across time. Two direct comparisons of fractional NO_x loss in the same environment but at different times are found to fall along the same curve as the variation between campaigns in different locations (Fig. 3), indicating that such a substitution is valid in this analysis. The first case, INTEX-NA and SEAC4RS, sampled the southeast United States (SEUS) in 2004 and 2013; the second case, ITCT2k2 and CALNEX-P3, sampled the South Coast Air Basin (SoCAB) around Los Angeles in 2002 and 2010. Averages from these pairs of campaigns are shown in Fig. 3a and all four points fall along the same overall curve. For INTEX-NA and SEAC4RS, the shift in chemistry towards the RONO_2 -dominated regime is accompanied by a dramatic shift in the ratio of ΣRONO_2 and HNO_3 concentrations, where ΣRONO_2 concentrations were only one quarter of HNO_3 in 2004 but were nearly equal to HNO_3 in 2013. ΣRONO_2 measurements are not available for ITCT2k2 or CALNEX-P3, preventing a similar comparison from being made for those campaigns.

Together, these cases indicate that the trend from Fig. 3a can be used to predict changes in fractional loss if the trend in $\text{NO}_2\text{R}/\text{VOCR}$ is known. Over the past decade, satellite measurements of NO_2 show a significant decrease in national NO_2 concentrations, reporting an average decrease of 4.5–7 % per year between 2005 and 2011 (Russell et al., 2012). No comparable satellite observations of VOCs exist, but studies in multiple locations have reported a decrease in primary anthropogenic VOC concentrations of 5.5–7.5 % per year over 2000–2010 (Geddes et al., 2009; Warneke et al., 2012; Pollack et al., 2013; Pusede et al., 2014). In contrast, biogenic VOC concentrations have been either constant or increasing over that same time period (Geddes et al., 2009; Hidy et al., 2014). Oxygenated VOCs show no major trend with time, although there are few long-term measurements of these species (Geddes et al., 2009; Pusede et al., 2014).

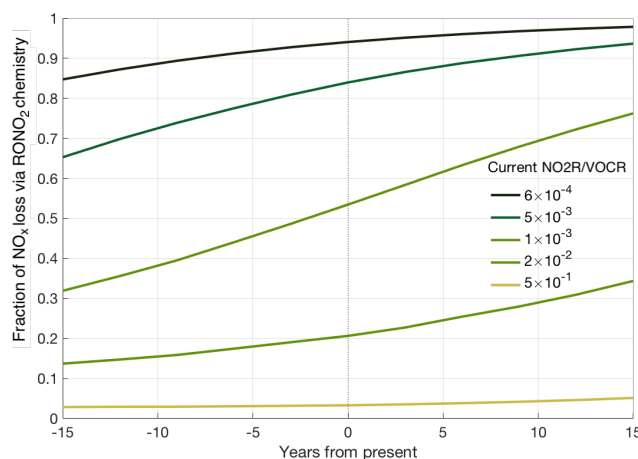


Figure 5. Predicted trends in fractional NO_x loss over time, calculated from the estimated $\text{NO}_2\text{R}/\text{VOCR}$ ratio assuming a constant -6.5 \% yr^{-1} decrease in anthropogenic VOC concentrations, a 5.5 \% yr^{-1} decrease in NO_x concentrations, and a 1.5 \% yr^{-1} increase in biogenic VOC concentrations.

These varied trends in NO_x, anthropogenic VOCs, and biogenic VOCs mean that NO₂R/VOCR has not changed uniformly over the past decade. Past NO₂R/VOCR ratios were calculated by assuming a 6.5 % yr⁻¹ decrease to anthropogenic VOC concentrations, a 5.5 % yr⁻¹ decrease to NO_x concentrations, and a 1.5 % yr⁻¹ increase in biogenic VOC concentrations over the past 15 years. We also extrapolate these same trends to estimate NO₂R/VOCR 15 years into the future. The calculated

5 NO₂R/VOCR ratios are combined with the relationship from Fig. 3 to estimate fractional NO_x loss at different times (Fig. 5). Based on these trends, RONO₂ chemistry is seen to have become a larger portion of total NO_x loss over the past 15 years, although the change is not evenly distributed. The similar trends in NO_x and anthropogenic VOCs cause there to have been little to no change in the regions with the highest NO₂R/VOCR ratios (typically large cities). The largest changes are projected to occur in regions with moderate NO₂R/VOCR ratios. In these regions, biogenic VOCs often account for a greater fraction

10 of the VOCR, leading to significant decreases in NO₂R/VOCR over the past 15 years. In addition, the response of fractional NO_x loss to changes in the NO₂R/VOCR ratio is magnified in areas where both RONO₂ and HNO₃ chemistry contribute to NO_x loss. In this transitional regime, if recent trends continue, the fraction of NO_x loss occurring via RONO₂ chemistry could double in the next 15 years. Given the large number of data points sampled in this transition regime (Fig. 2), many regions of the United States are therefore likely to transition from a regime where HNO₃ dominates NO_x loss to a mixed or

15 RONO₂-dominated regime.

5 Impacts of the transition from the HNO₃ to the RONO₂ regime

The growing importance of RONO₂ chemistry to NO_x loss has several implications for air quality. Most directly, it means that understanding NO_x chemistry in all but the most polluted megacities requires including the effects of RONO₂ chemistry. More theoretically, the transition from HNO₃- to RONO₂-dominated NO_x loss affects how atmospheric chemistry will respond to

20 changes in emissions of NO_x and VOCs. Because RONO₂ are produced in the same set of reactions that produce O₃, the fractional loss of NO_x via RONO₂ chemistry is directly proportional to the ozone production efficiency (OPE), the ratio of ozone production to NO_x loss (Eq. 5).

$$\text{OPE} = \frac{P(\text{O}_3)}{L(\text{NO}_x)} = \frac{2 \cdot \text{VOCR} \cdot Y_{\text{RO}_2\text{eff}} \cdot f_{\text{NO}_{\text{eff}}} \cdot (1 - \alpha_{\text{eff}})}{\text{NO}_2\text{R} + \text{VOCR} \cdot Y_{\text{RO}_2\text{eff}} \cdot f_{\text{NO}_{\text{eff}}} \cdot \alpha_{\text{eff}}} \propto \frac{P(\text{RONO}_2)}{P(\text{RONO}_2) + P(\text{HNO}_3)} \quad (5)$$

Fundamentally, OPE represents the total amount of ozone produced for each molecule of NO_x emitted. When considering

25 ozone pollution on regional scales, OPE is a more appropriate metric than instantaneous ozone production because it accounts for ozone production both locally and further afield.

Figure 6 uses the theoretic framework described in Romer et al. (2018) to investigate how ozone and NO_x chemistry change as a function of NO₂R/VOCR. As the NO₂R/VOCR ratio decreases, OPE increases, reaching an inflection point exactly at the crossover point between the HNO₃-dominated and RONO₂-dominated regimes (Fig. 6a–b). For the polluted areas of the

30 country, where HNO₃ is currently the dominant NO_x loss pathway, this means that, for example, interventions to improve air quality by reducing NO_x emissions will be fighting uphill, because every incremental fractional decrease in NO_x emissions will be associated with a growing incremental increase in OPE (Fig. 6c).

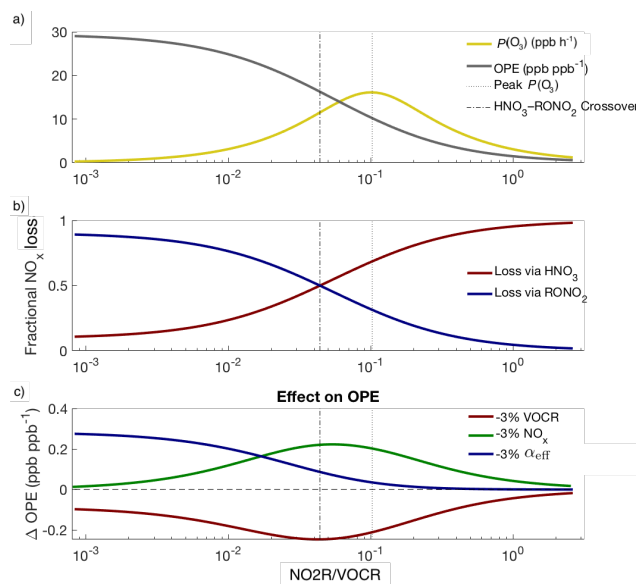


Figure 6. Theoretical picture of NO_x and O₃ chemistry, calculated using variable NO_x concentrations and fixed VOCR, $P(HO_x)$, and α_{eff} . Panel a shows how $P(O_3)$ and OPE change as NO_x changes; Panel b shows how the fractional NO_x loss changes as NO₂R/VOCR decreases; Panel c shows that changes to NO_x and VOCR have their greatest effect on OPE not when $P(O_3)$ is at a maximum, but at the crossover point between the RONO₂-dominated and HNO₃-dominated regimes.

In addition, as RONO₂ chemistry becomes a more important part of the NO_x budget, changes to α_{eff} have an increasing effect on OPE (Fig. 6c). Policy interventions that reduce VOCR but preferentially target high- α compounds (e.g., long-chain alkanes) could inadvertently increase ozone production or OPE (Farmer et al., 2011; Perring et al., 2013).

In addition to the large effects on aerosol yield that changes to NO_x and VOC emissions have directly (e.g., Xu et al., 2015a; Pusede et al., 2016), they also affect aerosols by changing the fate of NO_x. While both HNO₃ and RONO₂ can form aerosols (Stelson and Seinfeld, 1982; Pye et al., 2015), the properties of the resulting aerosols are likely to differ. Because HNO₃ is a strong acid, a shift towards RONO₂ chemistry is likely to increase aerosol pH. An increase in the role of RONO₂ chemistry will also cause more of the nitrate aerosol to be organic rather than inorganic, potentially affecting the viscosity and morphology of aerosols.

Further effects of changing NO_x chemistry arise from the distinct fates of RONO₂ and HNO₃. Many RONO₂ compounds, especially those derived from isoprene, are remarkably reactive in the troposphere, with lifetimes of a few hours or less. A fraction of this RONO₂ loss returns NO_x to the atmosphere, allowing RONO₂ production to effectively transport NO_x downwind (Romer et al., 2016; Xiong et al., 2016). In contrast, HNO₃ is effectively chemically inert in the troposphere, with a chemical lifetime of 50 hours or more.

As a result of the differing chemical fates and lifetimes, transitioning from a HNO₃-dominated regime to a mixed or RONO₂-dominated regime has implications for the distribution of NO_x on regional to continental scales. If a greater fraction

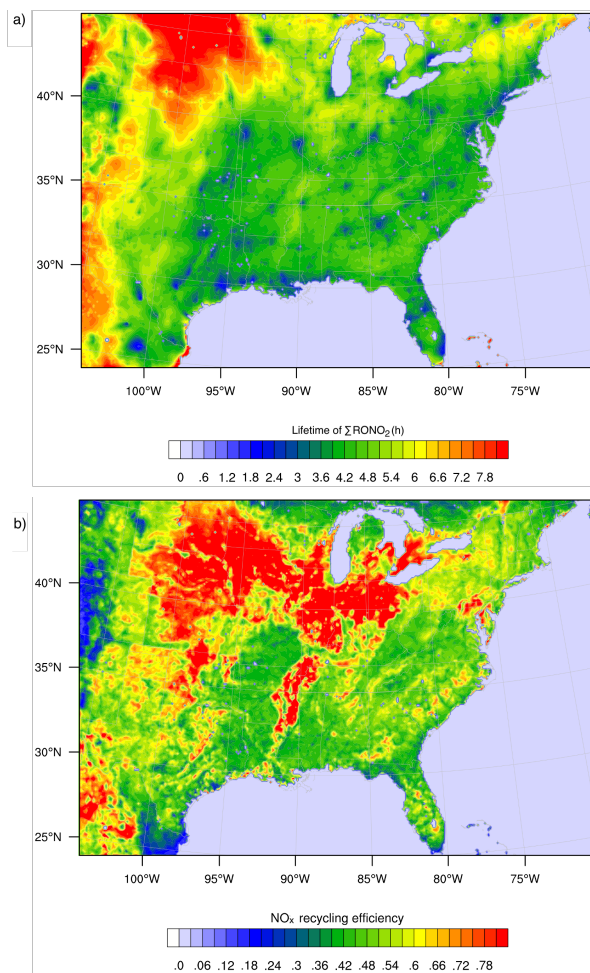


Figure 7. WRF-Chem simulation of RONO_2 chemistry over the southeast United States for summer 2013 as described in Zare et al. (2018). Panel a shows the overall lifetime of ΣRONO_2 , defined as the concentration of ΣRONO_2 divided by their chemical loss rate for the daytime boundary layer. Panel b shows the average NO_x recycling efficiency, defined as the local rate of NO_x production from RONO_2 oxidation divided by the rate of RONO_2 production.

of NO_x in polluted or moderately polluted regions is converted into RONO_2 compounds rather than into HNO_3 , then more of the NO_x may be re-released downwind, where it can participate in radical chemistry and ozone production. Simulations of RONO_2 chemistry using WRF-Chem and the RACM2_Berkeley2 mechanism (Zare et al., 2018) were used to investigate the RONO_2 lifetime and NO_x recycling efficiency of RONO_2 across the southeast United States in summer 2013 (Fig. 7). Across

5 much of the region, ΣRONO_2 are calculated to have a lifetime of roughly 4 hours, and the release of NO_x from RONO_2 oxidation was between 40 and 75 % of the instantaneous RONO_2 production rate. Combined, these findings demonstrate a significant role for RONO_2 chemistry in the transport of NO_x between regions in the southeast United States. The effects of

organic nitrate chemistry on the distribution of NO_x is likely to vary greatly across different regions of the United States and should be studied in further detail.

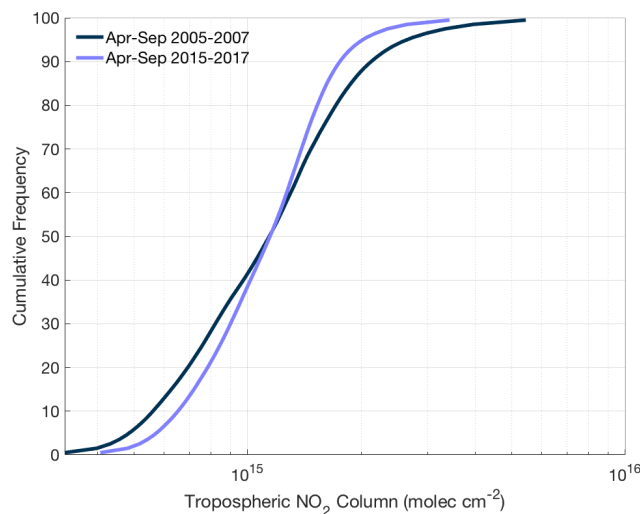


Figure 8. Cumulative frequency distribution of OMI tropospheric NO_2 columns over the continental United States using the BEHR v3.0A retrieval for summer (Apr-Sep) in 2005–2007 and 2015–2017.

Enhanced NO_x transport between source and receptor regions is one aspect of a combined trend that is transforming the spatial distribution of NO_x . Over the past decade, NO_x emission reductions have been concentrated in the most polluted environments. In these areas, motor vehicles and power plants, targets of emission control strategies, account for almost all of the NO_x emissions. In less polluted regions, other sources of NO_x , including soil microbes (both in agricultural and non-agricultural regions), off-road vehicles, fires, and lightning, play a greater role in the NO_x budget, reducing the effectiveness of typical combustion-related NO_x emission controls. In addition, hemispheric background concentrations of NO_x and O_3 have risen slightly over the past two decades (Cooper et al., 2012). The combination of all three of these trends suggests that the distribution of NO_x across the United States is getting flatter over time. This trend matches satellite observations of NO_2 over the continental United States. Figure 8 shows the cumulative frequency distribution of summertime tropospheric NO_2 columns from 2005–2007 and 2015–2017 using the BErkeley High-Resolution (BEHR) v3.0A retrieval (Laughner et al., 2018) of slant-column measurements from OMI. Over this time, the highest percentiles of NO_2 concentrations have decreased and the lowest percentiles increased, leading to a significantly narrower distribution of NO_2 concentrations.

In summary, over the past 15 years, decreases in anthropogenic NO_x and VOC emissions have led to a significant shift in the mechanisms of daytime NO_x loss. Many places where HNO_3 production dominated NO_x loss are now mixed or have switched to a situation where the majority of NO_x loss occurs through RONO_2 chemistry. If past trends continue, RONO_2 chemistry will grow to become an even more important fraction of NO_x chemistry in coming decades. As a result of this combination of changing NO_x chemistry, decreasing NO_x emissions, and increasing background concentrations, air pollution in the United

States may transform from a highly local issue to a more extended regional one. Efforts to control air pollution focused only on local sources are less likely to be effective; future improvements in air quality and attaining the most recent National Ambient Air Quality Standards are likely to require coordinated efforts on regional scales to broadly reduce NO_x emissions.

Data availability. Data from ARCTAS, DC3, FRAPPÉ, INTEX-NA, INTEX-B, KORUS-AQ and SEAC4RS are available from <https://www-air.larc.nasa.gov/missions.htm>. Data from ITCT2k2, CALNEX, SOAS, UBWOS, and WINTER are available from <https://www.esrl.noaa.gov/csd/field.html>. The BEHR retrieval of OMI NO₂ columns is available at <http://behr.cchem.berkeley.edu/>.

Appendix A: Calculation of the RONO₂ production rate

A1 Steady-state calculation of unmeasured radicals

The formation rates of RONO₂, HNO₃, and O₃ depend either directly or indirectly on the concentration of OH, HO₂, RO₂, NO, and NO₂. Speciated RO₂ radicals are not currently observable in the atmosphere, and thus all RO₂ concentrations were calculated assuming they were in steady-state, with their production and loss rates equal.

There were additional periods in which some combination of OH, HO₂, and NO were also not measured, and these radicals were also assumed to be in steady state. Concentrations of VOCs, NO₂, and O₃ were always taken from measurements. In order to calculate the steady-state concentrations of unmeasured radicals, reaction rate constants and RO₂ yields for the different VOCs were taken from the MCM v3.3.1 (Jenkin et al., 2015). Concentrations of all unmeasured species were calculated iteratively until all the concentrations converged. Equations (A1–A8) were used to calculate the steady-state concentration of unmeasured radicals. In Eq. (A8), the symbol XR is used to represent the OH reactivity of species such as SO₂ and O₃ that are not included in either VOCR or NO₂R. Although it is not often categorized as a VOC, CO is included as a contributor to VOCR. The reaction rate constant for NO₂ with OH was taken from Mollner et al. (2010), with temperature- and pressure-dependencies from Henderson et al. (2012).

$$P(\text{RO}_2) = [\text{OH}] \cdot \text{VOCR} \cdot Y_{\text{RO}_2} \quad (\text{A1})$$

$$L(\text{RO}_2) = k_{\text{RO}_2+\text{NO}}[\text{RO}_2][\text{NO}] + k_{\text{RO}_2+\text{HO}_2}[\text{RO}_2][\text{HO}_2] + 2k_{\text{RO}_2+\text{RO}_2}[\text{RO}_2][\text{RO}_2] + k_{\text{isom}}[\text{RO}_2] \quad (\text{A2})$$

$$P(\text{HO}_2) = k_{\text{RO}_2+\text{NO}}[\text{RO}_2][\text{NO}](1 - \alpha) + [\text{OH}] \cdot \text{VOCR} \cdot Y_{\text{HO}_2} + 2j_{\text{HCHO}}[\text{HCHO}] \quad (\text{A3})$$

$$L(\text{HO}_2) = k_{\text{HO}_2+\text{NO}}[\text{HO}_2][\text{NO}] + 2k_{\text{HO}_2+\text{HO}_2}[\text{HO}_2][\text{HO}_2] + k_{\text{HO}_2+\text{RO}_2}[\text{HO}_2][\text{RO}_2] \quad (\text{A4})$$

$$P(\text{NO}) = j_{\text{NO}_2}[\text{NO}_2] \quad (\text{A5})$$

$$L(\text{NO}) = k_{\text{O}_3+\text{NO}}[\text{O}_3][\text{NO}] + k_{\text{RO}_2+\text{NO}}[\text{RO}_2][\text{NO}] + k_{\text{HO}_2+\text{NO}}[\text{HO}_2][\text{NO}] \quad (\text{A6})$$

$$P(\text{OH}) = \frac{2j_{\text{O}_3 \rightarrow \text{O}^1\text{D}}[\text{O}_3] \cdot k_{\text{O}^1\text{D}+\text{H}_2\text{O}}[\text{H}_2\text{O}]}{k_{\text{O}^1\text{D}+\text{H}_2\text{O}}[\text{H}_2\text{O}] + k_{\text{O}^1\text{D}+\text{M}}[\text{M}]} + j_{\text{HONO}}[\text{HONO}] + k_{\text{HO}_2+\text{NO}}[\text{HO}_2][\text{NO}] + k_{\text{O}_3+\text{RH}}[\text{O}_3][\text{RH}]Y_{\text{OH}} \quad (\text{A7})$$

$$L(\text{OH}) = (\text{VOCR} + \text{NO}_2\text{R} + \text{XR})[\text{OH}] \quad (\text{A8})$$

In order to test the accuracy of the modeling, we used periods when HO_2 , OH , and NO were all measured and calculated how the production ratio $P(\text{RONO}_2)/P(\text{HNO}_3)$ changed if modeled radical concentrations were substituted for the measured values. These results are shown in Fig. A1. Even in the worst-case scenario (modeled concentrations used for all radicals), the slope is close to one (Fig. A1a), indicating that the use of modeled radicals does not significantly affect our results. Furthermore, Fig. A1b–d show that the use of modeled OH or HO_2 concentrations alone does not lead to noticeable changes in $P(\text{RONO}_2)/P(\text{HNO}_3)$. Use of modeled NO concentrations can cause small but noticeable changes in $P(\text{RONO}_2)/P(\text{HNO}_3)$, but modeled NO concentrations are used in less than 3% of all data points used in this analysis (238 out of 7988 data points).

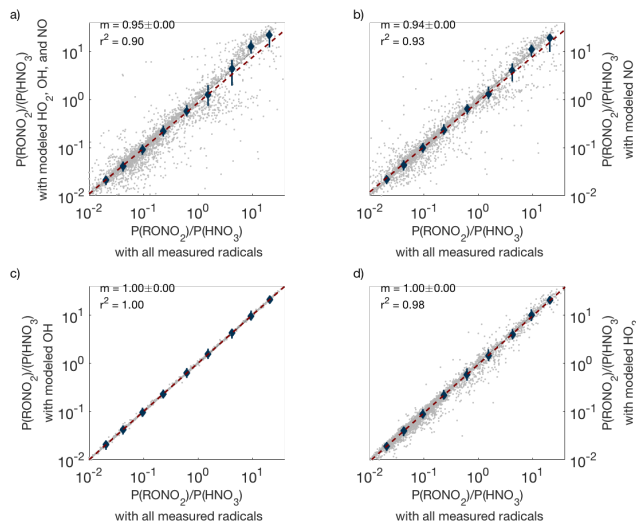


Figure A1. Comparison of $P(\text{RONO}_2)/P(\text{HNO}_3)$ when measured concentrations of all possible radicals are used (x -axis) versus when measured concentrations are replaced by modeled concentrations (y -axis). Panel a shows the result when modeled concentrations of OH , HO_2 , and NO are all used simultaneously; Panels b–d show the effect of replacing measured with modeled values one species at a time.

A2 Determination of α

- 10 Accurately calculating the RONO_2 production rate requires accurate knowledge of α_i for all VOCs. If values of α had been reported for a specific compound from laboratory measurements, the most recent value was applied (Perring et al., 2013; Teng et al., 2015; Rindelaub et al., 2015; Praske et al., 2015; Wennberg et al., 2018). In cases where no reliable laboratory measurements are available, the parameterization for α from Wennberg et al. (2018) was used. In all cases, the temperature- and pressure-dependencies described in Wennberg et al. (2018) were used to scale the laboratory measurements of α to the
- 15 conditions of the atmosphere.

Author contributions. PSRP and RCC designed the experiment, PSRP performed the analysis of field campaign data and wrote the paper with contributions from all authors, AZ designed, ran, and analyzed the modeling simulations, and RCC supervised the project.

Competing interests. The authors declare that they have no conflict of interest.

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