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# Effects of biogenic nitrate chemistry on the $\text{NO}_x$ lifetime in remote continental regions

**E. C. Browne<sup>1</sup> and R. C. Cohen<sup>1,2</sup>**

<sup>1</sup>Department of Chemistry, University of California Berkeley, Berkeley, CA, USA

<sup>2</sup>Department of Earth and Planetary Sciences, University of California Berkeley, Berkeley, CA, USA

Received: 21 June 2012 – Accepted: 6 August 2012 – Published: 17 August 2012

Correspondence to: R. C. Cohen (rccohen@berkeley.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.

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## Abstract

We present an analysis of the  $\text{NO}_x$  budget in conditions of low  $\text{NO}_x$  ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) chemistry and high biogenic volatile organic compound (BVOC) concentrations that are characteristic of most continental boundary layers. Using a steady-state model, we show that below 500 pptv of  $\text{NO}_x$ , the  $\text{NO}_x$  lifetime is extremely sensitive to organic nitrate ( $\text{RONO}_2$ ) formation rates. We find that even for  $\text{RONO}_2$  formation values that are an order of magnitude smaller than is typical for continental conditions significant reductions in  $\text{NO}_x$  lifetime are caused by nitrate forming reactions. Comparison of the steady-state box model to a 3-D chemical transport model (CTM) confirms that the concepts illustrated by the simpler model are a useful approximation of predictions provided by the full CTM.

## 1 Introduction

Nitrogen oxides enter the atmosphere as a result of bacterial processes in soils, high temperature chemistry in lightning, and combustion of fossil fuels and biomass. Current estimates are that human creation of reactive nitrogen (both oxidized and reduced nitrogen) has increased by over an order of magnitude from  $\sim 15 \text{ Tg N yr}^{-1}$  to  $\sim 187 \text{ Tg N yr}^{-1}$  from 1860 to 2005 (Galloway et al., 2008). This increase is one of the primary causes of air pollution, contributing directly to the production of urban ozone and secondary organic aerosol. The increase in  $\text{NO}_x$  also results in an increase in the global background of OH and thus affects air pollution by increasing the global background ozone concentration and making it more difficult for individual cities to reduce ozone. This increase in ozone also affects climate directly, and both the  $\text{NO}_x$  and the ozone affect climate indirectly by their influence on the global lifetime of  $\text{CH}_4$  (e.g., Fuglestedt et al., 1999; Wild et al., 2001; Derwent et al., 2008; Fry et al., 2012). Several studies have shown that the net global impact of  $\text{NO}_x$  emissions on climate forcing is highly dependent on the location and seasonal cycle of the emissions (e.g., Fuglestedt

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et al., 1999; Derwent et al., 2008; Fry et al., 2012). Consequently, there has been a significant research effort to understand emissions of  $\text{NO}_x$  from different sources such as fossil fuel combustion (e.g., van der A et al., 2008; Dallmann and Harley, 2010; Jaeglé et al., 2005), lightning (e.g., van der A et al., 2008; Hudman et al., 2007; Schumann and Huntrieser, 2007), biomass burning (e.g., van der A et al., 2008; Alvarado et al., 2010; Jaeglé et al., 2005; Mebust et al., 2011; Wiedinmyer et al., 2006), and soils (e.g., van der A et al., 2008; Bertram et al., 2005; Ghude et al., 2010; Hudman et al., 2010; Jaeglé et al., 2005). In contrast, the lifetime of  $\text{NO}_x$ , knowledge of which is necessary to determine concentrations from emissions, is not as well studied.

In the vicinity of emissions, the lifetime of  $\text{NO}_x$  is a steeply nonlinear function of the concentration of  $\text{NO}_x$  (Valin et al., 2011 and references therein). In the remote continental atmosphere, emissions are more uniformly distributed and  $\text{NO}_x$  concentrations vary more slowly. Textbooks suggest that the chemical lifetime of  $\text{NO}_x$  in these regions is largely set by its reaction with OH to produce  $\text{HNO}_3$ . However, several analyses have quantified the effect of isoprene nitrate formation on the  $\text{NO}_x$  budget, showing that isoprene nitrate formation is a major sink of  $\text{NO}_x$  and implying a strong effect on  $\text{NO}_x$  lifetime (e.g., Trainer et al., 1991; Horowitz et al., 2007; Ito et al., 2007; Wu et al., 2007; Paulot et al., 2012).

In this paper we investigate how changes in the formation rate of organic nitrates ( $\text{RONO}_2$ ) affect the  $\text{NO}_x$  budget in low  $\text{NO}_x$ , high BVOC environments. Using a steady-state model we find that the instantaneous  $\text{NO}_x$  lifetime, and consequently ozone production efficiency, is extremely sensitive to  $\text{RONO}_2$  production even when production rates are an order of magnitude smaller than typical for continental conditions. Calculations using the WRF-Chem model (Weather Research and Forecasting model with chemistry (Grell et al., 2005) with detailed  $\text{RONO}_2$  chemistry added to the chemical mechanism are shown to be consistent with the conceptual model; this indicates that the steady-state model is sufficient to serve as a guide for thinking about how changes in  $\text{RONO}_2$  chemistry affect  $\text{NO}_x$ .

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## 2 Background

Daytime chemistry in the lower troposphere encompasses two chemical regimes: a low  $\text{NO}_x$  ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) regime in which  $\text{HO}_x$  ( $\text{HO}_x = \text{OH} + \text{HO}_2 + \text{RO}_2$ ) self-reactions (e.g.,  $\text{HO}_2 + \text{RO}_2$ ) dominate  $\text{HO}_x$  loss processes, and a high  $\text{NO}_x$  regime in which radicals are lost through nitric acid production. Although low  $\text{NO}_x$  chemistry has generally been synonymous with methane and carbon monoxide chemistry, recent field observations have shown that in the presence of high biogenic volatile organic compound (BVOC) concentrations, low  $\text{NO}_x$  chemistry is significantly more complex than this textbook view. Most of these recent low  $\text{NO}_x$ , high BVOC studies have focused on understanding the production and loss processes of  $\text{HO}_x$  radicals (Lelieveld et al., 2008; Stavrou et al., 2010; Stone et al., 2011; Taraborrelli et al., 2012; Whalley et al., 2011; Mao et al., 2012). Here, we focus on understanding the nitrogen radical budget under these conditions.

Chemical loss of  $\text{NO}_x$  is generally considered to be dominated by nitric acid formation:



Close to source regions, where  $\text{NO}_x$  concentrations are high,  $\text{NO}_x$  will also be lost through the formation of peroxy nitrates:



It is well known that peroxy nitrates act as a  $\text{NO}_x$  reservoir; they may be transported to rural and remote locations where they will dissociate, resulting in a net source of  $\text{NO}_x$  downwind from the emissions.

Chemical  $\text{NO}_x$  loss also occurs via the formation of alkyl and multifunctional organic nitrates of the form  $\text{RONO}_2$  from the minor branch of the NO and peroxy radical reaction:



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Measurements of total  $\text{RONO}_2$  by thermal dissociation laser induced fluorescence (Day et al., 2002) have shown that  $\text{RONO}_2$  account for a substantial fraction of oxidized nitrogen ( $\text{NO}_y = \text{NO} + \text{NO}_2 + \text{NO}_3 + \text{total peroxy nitrates} + \text{total alkyl and multifunctional nitrates} + \text{HNO}_3 + 2^*\text{N}_2\text{O}_5 + \text{HONO} + \dots$ ) in urban (Rosen et al., 2004; Cleary et al., 2005; Perring et al., 2010; Farmer et al., 2011) and rural (Murphy et al., 2006; Farmer and Cohen, 2008; Day et al., 2009; Perring et al., 2009a; Beaver et al., 2012) locations as well as downwind of the continents (Perring et al., 2010).

Isoprene nitrates are thought to be a large fraction of the organic nitrate source. Global modeling studies investigating the impact of isoprene-derived nitrates on  $\text{NO}_x$  and  $\text{O}_3$  have found large sensitivities in the net global and regional budgets of  $\text{O}_3$  and OH to assumptions about formation, lifetime, and oxidation products of isoprene-derived nitrates (e.g., Horowitz et al., 1998, 2007; von Kuhlmann et al., 2004; Fiore et al., 2005; Ito et al., 2007, 2009; Wu et al., 2007; Paulot et al., 2012). Paulot et al. (2012) used a global CTM to calculate the impact of isoprene-derived nitrates on the  $\text{NO}_x$  budget in the tropics and found that up to 70% of the local net  $\text{NO}_x$  sink is from the formation of isoprene-derived nitrates.

Recently, simultaneous field measurements of speciated multifunctional nitrates using chemical ionization mass-spectrometry (St. Clair et al., 2010) and measurements of total  $\text{RONO}_2$  by thermal dissociation laser induced fluorescence provided the first opportunity for a comparison of the total  $\text{RONO}_2$  measurement in a complex chemical environment. The sum of the individual compounds was  $\sim 65\%$  of the total  $\text{RONO}_2$  when only isoprene (first and second generation) and 2-methyl-3-buten-2-ol nitrates were included, and was almost closed when all nitrogen containing masses were included. The measurements confirmed that biogenic  $\text{RONO}_2$  represent the vast majority of the total in a rural environment (Beaver et al., 2012). Recent measurements from the NASA Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) campaign (Jacob et al., 2010) show that in the low  $\text{NO}_x$ , high BVOC

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environment of the Canadian boreal forest,  $\text{RONO}_2$  account for 18 % of  $\text{NO}_y$  and often account for at least half of the instantaneous  $\text{NO}_x$  sink (Browne et al., 2012).

### 3 Steady-state calculations

Low  $\text{NO}_x$ , high BVOC environments, such as boreal and tropical forests, are generally characterized by large expanses of relatively homogeneous emissions. Consequently, even while transport can be long-range, the lifetime of  $\text{NO}_x$  can be short relative to changes in sources and sinks. Thus,  $\text{NO}_x$  is expected to be in steady-state where sources are balanced by chemical loss.  $\text{HO}_x$  radicals have a shorter lifetime and are also expected to be in a steady-state. Using this assumption, we calculate the rate of  $\text{NO}_x$  loss to  $\text{RONO}_2$  and to  $\text{HNO}_3$  during the day and night. Analysis is restricted to  $\text{NO}_x$  concentrations less than 500 pptv. Discussion on the effects of  $\text{RONO}_2$  chemistry at higher  $\text{NO}_x$  concentrations can be found in Farmer et al. (2011) and are reviewed by Perring et al. (2012).

#### 3.1 Daytime

Here, we use a simplified representation of daytime chemistry (Table 1) where  $P(\text{HO}_x)$  represents primary  $\text{HO}_x$  production from all sources including  $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ , photolysis of species such as  $\text{H}_2\text{O}_2$  and  $\text{HCHO}$ , and any others. We assume that 80 % of  $\text{HO}_x$  production results in  $\text{OH}$  and the remainder in  $\text{HO}_2$  (from  $\text{HCHO}$  photolysis). In addition to  $\text{CO}$  and  $\text{CH}_4$  chemistry, we include a lumped VOC that reacts with  $\text{OH}$  to form a lumped peroxy radical ( $\text{RO}_2$  in Table 1). When this lumped  $\text{RO}_2$  species reacts with  $\text{NO}$ , it either propagates the radicals (R3a) or forms an organic nitrate (R3b). The fraction of the time that an organic nitrate is formed ( $\text{R3b}/(\text{R3a} + \text{R3b})$ ) is referred to as the branching ratio ( $\alpha$ ). For specific molecules,  $\alpha$  increases with increasing carbon number, lower temperature, and higher pressure (Arey et al., 2001).

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For the other RO<sub>2</sub> reactions, we assume that the RO<sub>2</sub> species behaves like a primary or secondary peroxy radical. Following the MCM protocol, the RO<sub>2</sub>+RO<sub>2</sub> reaction then results in 1.2 alkoxy radicals (Jenkin et al., 1997). In the model, the alkoxy radical either instantaneously isomerizes or decomposes (i.e., we ignore the reaction with O<sub>2</sub>) to produce a peroxy radical that is lumped with CH<sub>3</sub>O<sub>2</sub> (i.e., no formation of organic nitrates upon reaction with NO). The RO<sub>2</sub>+CH<sub>3</sub>O<sub>2</sub> reaction follows the same assumptions resulting in 0.6 CH<sub>3</sub>O<sub>2</sub> and 0.6 HO<sub>2</sub>. The RO<sub>2</sub> species undergoes an isomerization reaction with products of OH and HO<sub>2</sub>. This reduced complexity is designed to mimic the low NO<sub>x</sub> chemistry of isoprene (e.g., Peeters et al., 2009; Peeters and Müller, 2010; Crouse et al., 2011, 2012).

For illustrative purposes, we use the mean conditions sampled during ARCTAS at low altitude and removed from recent biomass burning influence (Table 2) as inputs to the model. We run the model at specified NO concentrations until the radicals (RO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub>, HO<sub>2</sub>, OH, and NO<sub>2</sub>) are in steady-state and then calculate the formation of RONO<sub>2</sub> and nitric acid.

Values of  $\alpha$  equal to 0 %, 0.1 %, 1 %, 5 %, and 10 % are used to illustrate a range of conditions that vary from remote conditions removed from the continents ( $\alpha = 0$  % and  $\alpha = 0.1$  %) to areas influenced primarily by BVOCs (e.g., monoterpenes, isoprene) with high RONO<sub>2</sub> formation ( $\alpha = 5$ –10 %).

It should be noted that the  $\alpha$  value in the steady-state model is different from what has been referred to in the literature as the “effective branching ratio” (Rosen et al., 2004; Cleary et al., 2005; Perring et al., 2010; Farmer et al., 2011). The effective branching ratio refers to the average branching ratio of the entire VOC mixture (including CO, CH<sub>4</sub>, etc) and is therefore smaller than the branching ratio of the RO<sub>2</sub> species. Observations suggest that the effective branching ratio for VOC mixtures for urban regions ranges from 4–7 % (Cleary et al., 2005; Farmer et al., 2011; Perring et al., 2010; Rosen et al., 2004). The effective branching ratio for the situations calculated here ranges from 0.06–8.74 % and is dependent on NO<sub>x</sub> due to changes in the ratio of CH<sub>3</sub>O<sub>2</sub> to RO<sub>2</sub>

with  $\text{NO}_x$  (Table 3). Full details regarding the calculation of  $\alpha_{\text{eff}}$  and discussion of how it varies with  $\text{NO}_x$  can be found in Appendix A.

### 3.2 Nighttime

Nighttime chemical loss of  $\text{NO}_x$  occurs via  $\text{NO}_3$  reactions with alkenes that have organic nitrate products, heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$ , and reactions of  $\text{NO}_3$  with aldehydes. The latter two loss processes both result in the formation of  $\text{HNO}_3$ . We consider a nighttime VOC mix that consists of three VOCs: isoprene,  $\alpha$ -pinene, and acetaldehyde.

The reaction of  $\text{NO}_3$  with alkenes results in an  $\text{NO}_3$ -alkene adduct that either retains or releases the nitrate functionality upon reaction with other radicals. We use the parameter  $\beta$  to represent the fraction that retains the nitrate functionality. Recent measurements of organic  $\text{RONO}_2$  yields for the reaction of biogenic VOC with  $\text{NO}_3$  suggest that  $\beta$  for isoprene is  $\sim 65\text{--}70\%$  (Rollins et al., 2009; Perring et al., 2009b),  $\sim 40\text{--}45\%$  for  $\beta$ -pinene (Fry et al., 2009), and  $\sim 30\%$  for limonene (Fry et al., 2011). We assign a  $\beta$  value of 30% for  $\alpha$ -pinene, and 70% for isoprene.

Since there is no suitable ARCTAS data to constrain the nighttime concentrations of alkenes and aldehydes, we use output from the WRF-Chem model to guide our choice of input concentrations (Table 5). We choose a lower estimate of 400 pptv of alkenes (which we split evenly between isoprene and  $\alpha$ -pinene) and a mid-range concentration of 2 ppbv of acetaldehyde. We run the model using lifetimes of  $\text{N}_2\text{O}_5$  (ranging from 10 min to 3 h) with respect to heterogeneous hydrolysis. With this simplified representation of the chemistry of these VOCs and the inorganic reactions of  $\text{NO}_x$  and  $\text{O}_3$  shown in Table 4, we calculate the loss of  $\text{NO}_x$  to  $\text{HNO}_3$  and to  $\text{RONO}_2$  by prescribing the  $\text{NO}_2$  concentration and assuming  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  are in instantaneous steady-state.

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## 4 NO<sub>x</sub> lifetime

### 4.1 Daytime

We compute the lifetime of NO<sub>x</sub> with respect to chemical loss to RONO<sub>2</sub> and nitric acid using Eq. (1):

$$\tau_{\text{NO}_x} = \frac{[\text{NO}_x]}{\text{Loss}(\text{NO}_x)} = \frac{[\text{NO}_x]}{\sum_i \alpha_i k_{\text{RO}_2_i + \text{NO}} [\text{RO}_2_i] [\text{NO}] + k_{\text{OH} + \text{NO}_2} [\text{OH}] [\text{NO}_2]} \quad (1)$$

For NO<sub>x</sub> concentrations less than 500 pptv when  $\alpha = 0\%$ , HNO<sub>3</sub> formation is the sole mechanism for NO<sub>x</sub> loss, and the NO<sub>x</sub> lifetime is longest at low NO<sub>x</sub> and decreases as NO<sub>x</sub> increases (Fig. 1). This decrease is roughly proportional to 1/OH (not shown) which, at low NO<sub>x</sub> concentrations, increases as NO<sub>x</sub> concentrations increase due to an increase of OH recycling from HO<sub>2</sub> + NO.

As  $\alpha$  increases, the NO<sub>x</sub> lifetime decreases, most significantly at the lowest NO<sub>x</sub> concentrations. At 100 pptv NO<sub>x</sub>, for  $\alpha$  values in the range expected in remote forested regions, RONO<sub>2</sub> production results in a NO<sub>x</sub> lifetime of less than 8 h ( $\alpha = 5\%$ ) and less than 5 h ( $\alpha = 10\%$ ), compared to a NO<sub>x</sub> lifetime of greater than one day ( $\sim 27$  h) for  $\alpha = 0\%$ . The lifetime of NO<sub>x</sub> peaks near NO<sub>x</sub> concentrations of  $\sim 20$  pptv ( $\alpha = 1\%$ ) to  $\sim 210$  pptv ( $\alpha = 10\%$ ) for  $\alpha$  values of at least 1% (Fig. 1). This reflects the dependence of RONO<sub>2</sub> production on RO<sub>2</sub> concentrations. At low NO<sub>x</sub> concentrations, RO<sub>2</sub> concentrations change rapidly as a function of NO<sub>x</sub>, resulting in the NO<sub>x</sub> lifetime curve behaving approximately as is roughly proportional to 1/[RO<sub>2</sub>]. As NO<sub>x</sub> increases, the change in RO<sub>2</sub> with NO<sub>x</sub> slows, and the OH term becomes more important. The resulting maximum in NO<sub>x</sub> lifetime depends on the weighting of the RO<sub>2</sub> term (the  $\alpha$  value) and shifts to higher NO<sub>x</sub> concentrations as  $\alpha$  increases (Fig. 1).

The relative effects of HNO<sub>3</sub> versus RONO<sub>2</sub> formation on NO<sub>x</sub> lifetime are shown in Fig. 2, where the fraction of NO<sub>x</sub> loss to RONO<sub>2</sub> (solid lines) and to HNO<sub>3</sub> (dashed

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lines) is shown versus  $\text{NO}_x$ . The fraction of  $\text{NO}_x$  loss to  $\text{RONO}_2$  is significant at  $\text{NO}_x$  below 100 pptv—even if  $\alpha$  is as low as 1 %. That fraction decreases as  $\text{NO}_x$  increases.

For the  $\alpha = 5\%$  and  $\alpha = 10\%$  cases that are expected to be typical of BVOC emissions from forests,  $\text{RONO}_2$  production represents more than half of the  $\text{NO}_x$  loss at  $\text{NO}_x$  concentrations below  $\sim 400$  pptv and  $\sim 950$  pptv, respectively. Consequently, in remote regions with high BVOC emissions where we expect  $\text{NO}_x$  concentrations of  $\sim 20$ – $300$  pptv,  $\text{RONO}_2$  formation accounts for over 50 % of the instantaneous  $\text{NO}_x$  loss. It is notable that even for the  $\alpha = 1\%$ , which is similar to the measured value for ethane of  $1.2\% \pm 0.2\%$  (Atkinson et al., 1982),  $\sim 31\%$  of  $\text{NO}_x$  loss is due to  $\text{RONO}_2$  at 100 pptv  $\text{NO}_x$  and  $\sim 15\%$  of  $\text{NO}_x$  loss at 500 pptv  $\text{NO}_x$ . We note that the total VOC reactivity of  $2\text{ s}^{-1}$  that we use in these calculations is much too high for ethane to affect the  $\text{RONO}_2$  yield ( $\sim 370$  ppbv of ethane are required to have a reactivity of  $2\text{ s}^{-1}$ ). Since the importance of  $\text{RONO}_2$  decreases with decreasing VOC reactivity, we expect that  $\text{RONO}_2$  formation would be low in pure ethane, CO,  $\text{CH}_4$  chemistry. However, only  $\sim 740$  pptv of isoprene ( $\alpha \sim 10\%$ ) is needed to achieve a reactivity of  $2\text{ s}^{-1}$  and 74 pptv of isoprene with a reactivity of  $0.2\text{ s}^{-1}$  would have the effect of  $\alpha \sim 1\%$ . Even a small addition of isoprene or other highly reactive BVOC will result in a reactivity and  $\alpha$  in the range of these calculations.

The exact numbers presented in Figs. 1 and 2 are sensitive to the parameters chosen for  $\text{HO}_x$  production, VOC reactivity, and peroxy radical reaction rates. We have tested the effects of much slower or faster peroxy radical self reaction rates and the effects of varying the  $\text{HO}_x$  production and NMVOC reactivity. We find that the basic structure of the results is insensitive to wide variations in the assumed parameters.

## 4.2 Nighttime

The nighttime formation of  $\text{RONO}_2$  from  $\text{NO}_3$  chemistry also has important implications for the chemical loss of  $\text{NO}_x$ , especially since the branching ratio for  $\text{RONO}_2$  formation is much higher for  $\text{NO}_3$  chemistry and  $\text{N}_2\text{O}_5$  is present at very low concentrations due

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to low concentrations of  $\text{NO}_2$ . We calculate the  $\text{NO}_x$  lifetime at night with respect to the formation of  $\text{RONO}_2$  and  $\text{HNO}_3$  using Eq. (2) and Eq. (3) respectively.

$$\tau_{\text{NO}_x \rightarrow \text{RONO}_2} = \frac{[\text{NO}_2] + [\text{NO}_3] + 2 * [\text{N}_2\text{O}_5]}{\beta_{\alpha\text{-pinene}} k_{\text{NO}_3 + \alpha\text{-pinene}} [\alpha\text{-pinene}] [\text{NO}_3] + \beta_{\text{isoprene}} k_{\text{NO}_3 + \text{isoprene}} [\text{Isoprene}] [\text{NO}_3]} \quad (2)$$

$$\tau_{\text{NO}_x \rightarrow \text{HNO}_3} = \frac{[\text{NO}_2] + [\text{NO}_3] + 2 * [\text{N}_2\text{O}_5]}{2k_{\text{N}_2\text{O}_5 \text{ hydrolysis}} [\text{N}_2\text{O}_5] + k_{\text{NO}_3 + \text{aldehyde}} [\text{Aldehyde}] [\text{NO}_3]} \quad (3)$$

For  $\text{NO}_x$  concentrations less than 500 pptv, the  $\text{NO}_x$  lifetime with respect to  $\text{RONO}_2$  formation is just under 40 h and varies by  $\sim 8\%$  for a range of assumptions about the  $\text{N}_2\text{O}_5$  lifetime to hydrolysis and acetaldehyde concentrations (Fig. 3a). The lifetime shows relatively little sensitivity to reasonable changes in alkene concentration since any increase in alkenes decreases the steady-state  $\text{NO}_3$  concentration. The  $\text{NO}_x$  lifetime with respect to nighttime production of  $\text{HNO}_3$  is much longer (at least several days – Fig. 3b) and varies by over an order of magnitude. Consequently, at  $\text{NO}_x$  concentrations less than 500 pptv, the  $\text{NO}_x$  lifetime at night (not shown) is dominated by the loss to  $\text{RONO}_2$ . The net lifetime with respect to both sinks at 100 pptv  $\text{NO}_x$  is  $\sim 34\text{--}36$  h (for all cases). At 500 pptv  $\text{NO}_x$ , the lifetime varies from  $\sim 27$  h for an  $\text{N}_2\text{O}_5$  hydrolysis lifetime of 10 min, to just under 36 h for an  $\text{N}_2\text{O}_5$  hydrolysis lifetime of 180 min (and 2 ppbv acetaldehyde concentration).

This lifetime is highly sensitive to the assumed value of  $\beta$ ; as  $\beta$  increases and the loss of  $\text{NO}_x$  through  $\text{NO}_3$  reactions becomes more efficient, the  $\text{NO}_x$  lifetime will be limited by the  $\text{NO}_2 + \text{O}_3$  rate. Under this condition, the  $\text{NO}_x$  lifetime is

$$\tau = \frac{[\text{NO}_x]}{F k_{\text{NO}_2 + \text{O}_3} [\text{NO}_2] [\text{O}_3]} \quad (4)$$

where  $F$  is a number between 1 (loss through  $\text{NO}_3$  dominates) and 2 (loss through  $\text{N}_2\text{O}_5$  dominates). Under low  $\text{NO}_x$  conditions  $F$  will be close to 1 and the lifetime has a limiting value at high BVOC or high  $\beta$  of  $\sim 12$  h.

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The fractional  $\text{NO}_x$  loss to  $\text{HNO}_3$  and  $\text{RONO}_2$  is shown in Fig. 4. Loss to  $\text{HNO}_3$  becomes important only for the shortest  $\text{N}_2\text{O}_5$  hydrolysis lifetime; a lifetime that is likely much too fast for a remote environment. Furthermore, increasing the  $\text{HNO}_3$  production through the aldehyde +  $\text{NO}_3$  reaction by increasing the acetaldehyde concentration by a factor of 3 (to 6 ppbv) results in minor differences. Even if we replace acetaldehyde with pinonaldehyde (which reacts an order of magnitude more quickly), the fraction of  $\text{NO}_x$  loss to  $\text{RONO}_2$  is high: at 100 pptv  $\text{NO}_x$  it is  $\sim 92\%$  for pinonaldehyde concentrations of 2 ppbv and  $80\%$  for 6 ppbv pinonaldehyde (for a  $\text{N}_2\text{O}_5$  lifetime of 180 min).

### 4.3 Twenty-four hour average lifetime

The average  $\text{NO}_x$  lifetime will be a combination of the nighttime and daytime sinks. However, the  $\text{NO}_x$  lifetime at night is much longer than the daytime value except at  $\alpha = 0\%$  where the two are nearly equal. Thus, the diurnal average lifetime will be similar to the daytime lifetime (Fig. 1).

## 5 Ozone production efficiency

Since the production of  $\text{RONO}_2$  reduces the  $\text{NO}_x$  lifetime, it will reduce the number of ozone molecules produced per  $\text{NO}_x$  removed (the ozone production efficiency-OPE) (Fig. 5). OPE is calculated using Eq. (5):

$$\text{OPE} = \frac{P(\text{O}_3)}{L(\text{NO}_x)} = \frac{k_{\text{HO}_2+\text{NO}}[\text{HO}_2][\text{NO}] + k_{\text{CH}_3\text{O}_2+\text{NO}}[\text{CH}_3\text{O}_2][\text{NO}] + (1 - \alpha)k_{\text{RO}_2+\text{NO}}[\text{RO}_2][\text{NO}]}{k_{\text{OH}+\text{NO}_2}[\text{NO}_2][\text{OH}] + \alpha k_{\text{RO}_2+\text{NO}}[\text{RO}_2][\text{NO}]} \quad (5)$$

At 100 pptv  $\text{NO}_x$  OPE decreases from  $\sim 110$  for  $\alpha = 0\%$  to  $\sim 19$  for the  $\alpha = 10\%$  case. The shape of the OPE versus  $\text{NO}_x$  curve also changes with  $\alpha$ ; the slope of the OPE versus  $\text{NO}_x$  line decreases in steepness as  $\alpha$  increases. The shallow slope of OPE versus  $\text{NO}_x$  for the higher  $\alpha$  cases occurs because both ozone production and ozone loss depend on  $\text{RO}_2$ . For the low  $\alpha$  cases,  $\text{NO}_x$  loss depends primarily on OH concentration,

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which, as discussed earlier, decreases as  $\text{NO}_x$  decreases. Since the  $\text{RO}_2$  concentration increases as  $\text{NO}_x$  decreases, this results in a high OPE at low  $\text{NO}_x$ .

$\text{NO}_x$  reservoirs, such as peroxy nitrates, transport  $\text{NO}_x$  from high  $\text{NO}_x$ , low OPE environments (urban areas) to areas downwind at lower  $\text{NO}_x$  and high OPE. Figure 5 suggests that if this downwind area is over the continents, that the OPE may be significantly lower than the traditional textbook view of low  $\text{NO}_x$  chemistry would assume. This high sensitivity of OPE to the  $\text{RONO}_2$  formation potential also suggests that small errors in  $\text{RONO}_2$  representation may lead to larger errors in the calculated ozone burden.

The value of OPE in the atmosphere has often been estimated using the correlation between  $\text{NO}_z$  ( $\text{NO}_z = \text{NO}_y - \text{NO}_x$ ) and  $\text{O}_3$ , however, this is a difficult comparison due to the different lifetimes of  $\text{O}_3$  and  $\text{NO}_z$ , as well as the variability in lifetimes of the different  $\text{NO}_z$  components. These problems are more significant in the boundary layer of remote environments where there are large contributions of peroxy nitrates and  $\text{HNO}_3$  to  $\text{NO}_z$ . However, measurements from a forest in northern Michigan suggest an OPE of  $\sim 22$  for  $\text{NO}_x$  concentrations around 300 pptv (Thornberry et al., 2001), an OPE value that lies between our  $\alpha = 5\%$  and  $\alpha = 10\%$  values expected for a forested environment.

## 6 Boreal forest: comparison to a 3-D chemical transport model

We compare the steady state calculations described above to the WRF-Chem 3-D chemical transport model simulations carried out using a domain that includes a large fraction of Canada where we expect low  $\text{NO}_x$  concentrations coupled with high BVOC emissions from the boreal forest to have a strong effect on  $\text{NO}_x$  lifetime. Details regarding the WRF-Chem model simulations can be found in Appendix B.

The WRF-Chem model allows us to account for effects from  $\text{NO}_x$  reservoirs with long lifetimes relative to changes in sources and sinks (i.e. ones for which transport plays an important role in determining concentration) such as: formation and decomposition of peroxy nitrates and the release of  $\text{NO}_x$  from oxidation and photolysis of  $\text{RONO}_2$ .

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We define the NO<sub>x</sub> lifetime with respect to the net chemical loss of NO<sub>x</sub>. If the net chemical loss to any class of species (e.g., peroxy nitrates, RONO<sub>2</sub>, nitric acid) is less than zero, then that species has zero contribution to the chemical loss of NO<sub>x</sub> at that NO<sub>x</sub> concentration. Figure 6 shows the NO<sub>x</sub> lifetime to net chemical loss as a function of NO<sub>x</sub>, binned by the effective  $\alpha$  value calculated using Eq. (A2). In the calculation of  $\alpha_{\text{eff}}$  we assume that the ozone production rate defined in Eq. (A3) is equivalent to Eq. (6):

$$P(\text{O}_3) = j_{\text{NO}_2}[\text{NO}_2] - k_{\text{NO}+\text{O}_3}[\text{NO}][\text{O}_3] \quad (6)$$

We note that in the WRF-Chem results we report use 24-h averaged data to calculate  $\alpha_{\text{eff}}$ . This allows us to sort the airmasses by their RONO<sub>2</sub> production rates; however, the exact value of  $\alpha_{\text{eff}}$  differs slightly from what would be calculated using only the daytime data.

Within the domain we find examples of airmasses with  $\alpha_{\text{eff}}$  ranging from  $\sim 0.4$ – $8\%$ . Both the full 3-D calculations (Fig. 6) and the box model (Fig. 1) show the same general dependence of the lifetime on  $\alpha$ . The most notable difference between the two is that the NO<sub>x</sub> lifetime from the 3-D calculations decreases more steeply as NO<sub>x</sub> increases than it does for the steady-state results. This is due to an increase in the loss due to peroxy nitrate formation (Fig. 7c) as NO<sub>x</sub> increases, an effect that is not represented in the steady-state model which assumed peroxy nitrates were at steady-state and thus could be ignored.

The fractional net NO<sub>x</sub> loss to RONO<sub>2</sub>, peroxy nitrates, and HNO<sub>3</sub> is shown in Fig. 7. The NO<sub>x</sub> concentrations predicted by WRF-Chem cover the range ( $\sim 30$ – $250$  pptv); over this small range, large changes in the fractional composition of the products of NO<sub>x</sub> loss reactions are predicted by both the steady-state model (Fig. 2) and the WRF-Chem calculations (Fig. 7). In both calculations the fraction of net NO<sub>x</sub> loss to RONO<sub>2</sub> (Fig. 7a) approaches unity as NO<sub>x</sub> decreases and as the effective  $\alpha$  value increases. Interestingly, the WRF-Chem predictions for the fractional net NO<sub>x</sub> loss to HNO<sub>3</sub> shows only a slight increase as a function of NO<sub>x</sub> (Fig. 7b) and the decrease in fractional NO<sub>x</sub>

loss to  $\text{RONO}_2$  is compensated by an increase in the net  $\text{NO}_x$  loss to peroxy nitrates when  $\text{NO}_x$  is greater than  $\sim 50\text{--}80$  pptv (Fig. 7c). We note that a plot of the fractional instantaneous gross loss when only  $\text{RONO}_2$  and  $\text{HNO}_3$  are considered (which is a direct comparison to Fig. 2), does show the fractional contribution of  $\text{HNO}_3$  decreasing with increasing  $\text{NO}_x$  (not shown). The fractional net  $\text{NO}_x$  loss to peroxy nitrates exhibits little variation with respect to  $\alpha_{\text{eff}}$ , indicating that peroxy nitrates are acting to buffer  $\text{NO}_x$ . A full investigation of this effect, however, would require a larger  $\text{NO}_x$  range and attention to the effects of temperature and transport. Many of these aspects have been discussed previously (Sillman and Samson, 1995). We note that due to the thermal instability of peroxy nitrates, the importance of peroxy nitrates as a  $\text{NO}_x$  reservoir will be highly dependent on temperature and we expect large differences between seasons and between boreal and tropical forests. In no regime does peroxy nitrate chemistry change the conclusion that the lifetime of  $\text{NO}_x$  is controlled by  $\text{RONO}_2$  production rates at low  $\text{NO}_x$  concentrations.

## 7 Discussion

In low  $\text{NO}_x$ , high BVOC environments, the formation of  $\text{RONO}_2$  accounts for the majority of the instantaneous  $\text{NO}_x$  sink, resulting in decreased  $\text{NO}_x$  lifetime and decreased OPE relative to chemistry dominated by CO and  $\text{CH}_4$ . However, the ultimate regional and global impact of the  $\text{RONO}_2$  chemistry is dependent on the extent to which these molecules serve as permanent versus temporary  $\text{NO}_x$  sinks; a value which, in general, is not well known. For instance, if we assume that  $\text{RONO}_2$  predominately serve as temporary  $\text{NO}_x$  sinks that transport  $\text{NO}_x$  to areas with higher OPE (e.g., areas with lower  $\text{NO}_x$  or areas at the same  $\text{NO}_x$  but lower  $\alpha$ ), we expect an increase in the ozone burden as a result of accounting for  $\text{RONO}_2$  chemistry. In contrast, if the  $\text{RONO}_2$  are lost primarily through deposition, they may increase nitrogen availability in the biosphere. Since many areas are nitrogen limited, introduction of nitrogen will also affect the carbon storage capacity of an ecosystem (e.g., Holland et al., 1997; Thornton et al.,

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2007, 2009; Bonan and Levis, 2010). A recent study observed the direct foliar uptake of  $\text{RONO}_2$  and subsequent incorporation of the nitrogen into amino acids (Lockwood et al., 2008), indicating that (at least some)  $\text{RONO}_2$  will affect plant growth.

It is interesting to consider how the effects of  $\text{RONO}_2$  on climate and air quality may impact our understanding of both preindustrial and future climates. For instance, it is likely that during the preindustrial era when  $\text{NO}_x$  concentrations were lower, that  $\text{RONO}_2$  formation was a more important  $\text{NO}_x$  sink than it is today. Model predictions of preindustrial climate often predict larger ozone concentrations than the semi-quantitative measurements of the late 19th/early 20th century indicate (e.g., Mickley et al., 2001; Archibald et al., 2011). Although there may be problems with the ozone measurements or with the emissions estimates used in the models, this may also indicate that models are missing a  $\text{NO}_x$  sink in the preindustrial era. As shown in Fig. 5, we calculate that the OPE is very sensitive to the assumed branching ratio, indicating that a small error in  $\text{RONO}_2$  formation may have a large effect on the ozone burden.

In industrialized countries,  $\text{NO}_x$  emissions are currently decreasing due to air quality control measures (e.g., van der A et al., 2008; Dallmann and Harley, 2010; Russell et al., 2010, 2012). Coupling this decrease in  $\text{NO}_x$  with the increase in biogenic VOC emissions expected in a warmer climate, suggests that  $\text{RONO}_2$  chemistry will begin to play a more important role in  $\text{NO}_x$  termination in urban and suburban areas. As discussed in Sect. 4.1, the crossover from  $\text{RONO}_2$  to nitric acid accounting for over 50 % of  $\text{NO}_x$  loss occurs at  $\sim 400$  pptv for a 5 % branching ratio and at  $\sim 950$  pptv for a 10 % branching ratio. Past studies have constrained the effective branching ratio in urban areas at 4–7 % (Cleary et al., 2005; Farmer et al., 2011; Perring et al., 2010; Rosen et al., 2004), which suggests that in future climates, it will be necessary to correctly simulate  $\text{RONO}_2$  chemistry in order to understand regional pollution and air quality.

In order to improve our understanding of the impact of  $\text{RONO}_2$  on atmospheric chemistry, particularly on the global and regional  $\text{NO}_x$  and  $\text{HO}_x$  budgets, laboratory studies on the formation of  $\text{RONO}_2$  (particularly for biogenic species other than isoprene),

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oxidation, physical loss, and oxidation products are necessary. These measurements must be supplemented by field measurements spanning  $\text{NO}_x$  concentrations from near zero to a few ppbv. In one such analysis, we use measurements from the ARCTAS campaign (Browne et al., 2012). However, a thorough understanding will require measurements in environments with different classes of BVOC emissions (e.g., pine forests which are dominated by monoterpenes ( $\alpha \sim 18\%$ ) and oak forests which are dominated by isoprene ( $\alpha \sim 10\%$ )). These field measurements will provide constraints on how the importance of  $\text{RONO}_2$  versus nitric acid changes as a function of  $\text{NO}_x$  and will test the representation of  $\text{RONO}_2$  chemistry in reduced chemical mechanisms.

## 8 Conclusions

Recent field measurements have indicated that low  $\text{NO}_x$ , high BVOC chemistry is significantly more complex than the textbook view of low  $\text{NO}_x$  chemistry being controlled by methane and carbon monoxide. Most of the work on low  $\text{NO}_x$ , high BVOC chemistry has focused on the implications for the  $\text{HO}_x$  budget. In this paper we analyze how the  $\text{NO}_x$  lifetime responds to changes in  $\text{RONO}_2$  production under these conditions. We find that production of  $\text{RONO}_2$  accounts for the majority of the instantaneous  $\text{NO}_x$  sink in low  $\text{NO}_x$ , high BVOC environments in both a steady-state model and a 3-D chemical transport model. Furthermore, the  $\text{NO}_x$  lifetime and OPE are highly sensitive to  $\text{RONO}_2$  production. These findings suggest that proper representation of  $\text{RONO}_2$  formation and  $\text{NO}_x$  recycling are necessary for accurate calculation of past, present, and future ozone concentrations and the corresponding climate effects.

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## Appendix A

### Effective branching ratio

The effective branching ratio is a measure of the average branching ratio for the VOC composition contributing to ozone production. For the steady state model, we calculate the effective  $\alpha$  value using Eq. (A1):

$$\alpha_{\text{eff}} = \frac{\alpha k_{\text{RO}_2+\text{NO}}[\text{RO}_2]}{k_{\text{CH}_3\text{O}_2+\text{NO}}[\text{CH}_3\text{O}_2] + k_{\text{RO}_2+\text{NO}}[\text{RO}_2]} \quad (\text{A1})$$

Here  $\text{RO}_2$  refers to the lumped peroxy radical from Table 1. This is equivalent to

$$\alpha_{\text{eff}} = \frac{P(\text{RONO}_2)}{P(\text{O}_3) + P(\text{RONO}_2) - k_{\text{HO}_2+\text{NO}}[\text{HO}_2][\text{NO}]} \quad (\text{A2})$$

where

$$P(\text{O}_3) = k_{\text{HO}_2+\text{NO}}[\text{HO}_2][\text{NO}] + \sum_i (1 - \alpha_i) k_{\text{RO}_{2_i}+\text{NO}}[\text{RO}_{2_i}][\text{NO}] + k_{\text{CH}_3\text{O}_2+\text{NO}}[\text{CH}_3\text{O}_2][\text{NO}] \quad (\text{A3})$$

$$P(\text{RONO}_2) = \sum_i \alpha_i k_{\text{RO}_{2_i}+\text{NO}}[\text{RO}_{2_i}][\text{NO}] \quad (\text{A4})$$

Here we have generalized the production of  $\text{O}_3$  and  $\text{RONO}_2$  to account for situations of multiple peroxy radicals with an  $\text{RONO}_2$  formation channel.

Unlike  $\alpha$ ,  $\alpha_{\text{eff}}$  changes as a function of  $\text{NO}_x$  due to the dependence of  $\alpha_{\text{eff}}$  on the ratio of  $\text{RO}_2$  to  $\text{CH}_3\text{O}_2$ . This ratio decreases as  $\text{NO}_x$  decreases because  $\text{RO}_2 + \text{RO}_2$  reactions which form  $\text{CH}_3\text{O}_2$ , the loss of  $\text{RO}_{2b}$  by isomerization, and the importance of  $\text{RO}_2 + \text{HO}_2$  reactions (which are faster for  $\text{RO}_2$  than for  $\text{CH}_3\text{O}_2$ ) all increase in importance at low  $\text{NO}_x$ . As a result,  $\alpha_{\text{eff}}$  decreases as  $\text{NO}_x$  decreases. This decrease is steepest under low  $\text{NO}_x$  conditions where, due to the high  $\text{RO}_2$  concentrations,

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RO<sub>2</sub>+ RO<sub>2</sub> reactions are most important. As shown in Table 3, the increase in  $\alpha_{\text{eff}}$  from 10 pptv to 100 pptv (~ 20–25 % increases) is about twice the increase from 100 pptv to 500 pptv NO<sub>x</sub> (~ 8–12 % increase).

This definition of effective branching ratio differs slightly from that used by elsewhere in the literature (Rosen et al., 2004; Cleary et al., 2005; Perring et al., 2010; Farmer et al., 2011) where the effective branching ratio is approximated as

$$\alpha_{\text{eff}} \approx \frac{2}{P(\text{O}_3)/P(\text{RONO}_2)} \approx \frac{2}{\Delta[\text{O}_x]/\Delta[\Sigma\text{ANs}]} \quad (\text{A5})$$

where  $P(\text{O}_3)$  and  $P(\text{RONO}_2)$  refer to the production rate of ozone and RONO<sub>2</sub> respectively. The second equality using concentrations holds under conditions where loss rates are small. This derivation relies on the assumption that HO<sub>2</sub> and RO<sub>2</sub> radicals are present in near equal concentrations (i.e., that each RO generates a carbonyl and an HO<sub>2</sub>) and is equal to Eq. (A2) when this assumption is valid. This assumption is appropriate under high NO<sub>x</sub> conditions where this derivation has been used previously, but is invalid under low NO<sub>x</sub> conditions where RO<sub>2</sub> concentrations are larger than HO<sub>2</sub> concentrations.

## Appendix B

### WRF-Chem details

#### B1 Domain

We run the WRF-Chem model at 36 km ×36 km resolution with 29 vertical layers for 23 June–13 July 2008 using meteorological data from NARR (North American Regional Reanalysis). Biogenic emissions are from MEGAN (Guenther et al., 2006, available at <http://www.acd.ucar.edu/wrf-chem/>) and anthropogenic emissions are from RETRO and EDGAR using the global emissions preprocessor for WRF-Chem (Freitas et al.,

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2011). Boundary conditions come from the MOZART model (Emmons et al., 2010) using GEOS-5 meteorology (available at <http://www.acd.ucar.edu/wrf-chem/>). Photolysis rates are calculated using the FAST-J scheme (Bian and Prather, 2002). WRF-Chem is described in further detail by Grell et al. (2005).

5 The domain is shown in Fig. B1. We exclude results south of 53° N, over water, and over snow/ice. Additionally, we remove the first five boxes on all sides to allow for relaxation of the boundary conditions which come from the MOZART-4 model using GEOS-5 meteorology (Emmons et al., 2010). For the remainder of the grid boxes, we take a 24 h boundary layer (a median of 8 vertical levels at midday) average for the last  
10 two weeks of the run. When we bin the results by NO<sub>x</sub> for Figs. 6 and 7 (midpoint of the bin shown by the symbols in the figures), we exclude any bin with fewer than five points in the bin. Consequently, all NO<sub>x</sub> concentrations greater than 250 pptv are excluded.

## B2 Chemical mechanism

15 A complete description of the WRF-Chem chemical mechanism can be found in Browne and Cohen (2012). Here we provide a brief overview of the chemical mechanism which is based on RACM2 chemistry (Goliff and Stockwell, 2010; Stockwell et al., 2010) with substantial modifications to the RONO<sub>2</sub> and isoprene chemistry. The isoprene chemistry is based on Paulot et al. (2009a, b) and uses ozonolysis rates of isoprene-derived nitrates from Lockwood et al. (2010). The formation of a hydroperoxyaldehyde (HPALD) from the 1,6 H-shift of isoprene peroxy radicals is included using  
20 the rate constant measured by Crouse et al. (2011). Photolysis of HPALD is the same as assumed in Stavrakou et al. (2010) with the assumption that one OH is generated. Loss of HPALD also occurs through reaction with OH and is assumed to regenerate OH (Peeters and Müller, 2010). When the first generation isoprene-derived nitrates  
25 react with OH between 0 % and 65 % of the nitrogen is returned as NO<sub>x</sub>. The exact amount of NO<sub>x</sub> returned depends on whether the isoprene nitrate peroxy radical reacts with HO<sub>2</sub> (with an assumed 100 % yield of a multi-functional nitrate) or with NO or other peroxy radicals (to return between ~ 34 % and ~ 65 % of the nitrogen as NO<sub>x</sub>).

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Ozonolysis of the first generation nitrates is assumed to return 32.7% (for  $\beta$ -hydroxy isoprene nitrates) or 44.5% (for  $\delta$ -hydroxy isoprene nitrates) of the nitrogen as per MCM v3.2 (Jenkin et al., 1997; Saunders et al., 2003). Based on Geiger et al. (2003) the NO<sub>3</sub>+ isoprene reaction forms an organic nitrate that is oxidized by OH to return 0% of the NO<sub>x</sub>. There are no reactions between NO<sub>3</sub> and the isoprene-derived nitrates in the chemical mechanism. Monoterpene derived nitrates are oxidized to form HNO<sub>3</sub>; all other nitrates are assumed to release NO<sub>2</sub> with 100% efficiency when oxidized by OH.

Photolysis of RONO<sub>2</sub> is assumed to release NO<sub>2</sub> with 100% efficiency except for the photolysis of the peroxide nitrate formed from reaction of an isoprene nitrate peroxy radical with HO<sub>2</sub>. As per MCM v3.2, we assume that photolysis results in OH and an alkoxy radical which then decomposes. We assume that ~ 1/3 of the alkoxy radicals will release NO<sub>2</sub> when they decompose. Photolysis cross-sections of RONO<sub>2</sub> were calculated using FAST-JX 6.5 (Bian and Prather, 2002) and include enhancement from carbonyl groups (Barnes et al., 1993) and reductions from hydroxy groups (Roberts and Fajer, 1989) where appropriate. Dry deposition rates of RONO<sub>2</sub> follow Ito et al. (2007) and there is no wet deposition for any species.

There is no heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub> in the WRF-Chem model, however this should be a small NO<sub>x</sub> sink under low NO<sub>x</sub> conditions and we anticipate no significant change to the results if heterogeneous N<sub>2</sub>O<sub>5</sub> hydrolysis were included.

*Acknowledgements.* We thank Wendy Goliff for providing the RACM2 chemical mechanism and Lukas Valin for helpful discussions regarding the WRF-Chem model. The WRF-Chem model was run on the Mako cluster supported by the UC Shared Research Computing Services and we thank the consultants for their technical help. This work was supported by a NASA Earth Systems Science Fellowship to ECB.

## References

- Alvarado, M. J., Logan, J. A., Mao, J., Apel, E., Riemer, D., Blake, D., Cohen, R. C., Min, K.-E., Perring, A. E., Browne, E. C., Wooldridge, P. J., Diskin, G. S., Sachse, G. W., Fuelberg, H., Sessions, W. R., Harrigan, D. L., Huey, G., Liao, J., Case-Hanks, A., Jimenez, J. L., Cubison, M. J., Vay, S. A., Weinheimer, A. J., Knapp, D. J., Montzka, D. D., Flocke, F. M., Pollack, I. B., Wennberg, P. O., Kurten, A., Crounse, J., Clair, J. M. St., Wisthaler, A., Mikoviny, T., Yantosca, R. M., Carouge, C. C., and Le Sager, P.: Nitrogen oxides and PAN in plumes from boreal fires during ARCTAS-B and their impact on ozone: an integrated analysis of aircraft and satellite observations, *Atmos. Chem. Phys.*, 10, 9739–9760, doi:10.5194/acp-10-9739-2010, 2010.
- Archibald, A. T., Levine, J. G., Abraham, N. L., Cooke, M. C., Edwards, P. M., Heard, D. E., Jenkin, M. E., Karunaharan, A., Pike, R. C., Monks, P. S., Shallcross, D. E., Telford, P. J., Whalley, L. K. and Pyle, J. A.: Impacts of HO<sub>x</sub> regeneration and recycling in the oxidation of isoprene: Consequences for the composition of past, present and future atmospheres, *Geophys. Res. Lett.*, 38, L05804, doi:10.1029/2010GL046520, 2011.
- Arey, J., Aschmann, S. M., Kwok, E. S. C. and Atkinson, R.: Alkyl nitrate, hydroxyalkyl nitrate, and hydroxycarbonyl formation from the NO<sub>x</sub>-air photooxidations of C5-C8 n-alkanes, *J. Phys. Chem. A*, 105, 1020–1027, doi:10.1021/jp003292z, 2001.
- Atkinson, R., Aschmann, S. M., Carter, W. P. L., Winer, A. M. and Pitts, J. N.: Alkyl nitrate formation from the nitrogen oxide (NO<sub>x</sub>)-air photooxidations of C2-C8 n-alkanes, *J. Phys. Chem.*, 86, 4563–4569, doi:10.1021/j100220a022, 1982.
- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of O<sub>x</sub>, HO<sub>x</sub>, NO<sub>x</sub> and SO<sub>x</sub> species, *Atmos. Chem. Phys.*, 4, 1461–1738, doi:10.5194/acp-4-1461-2004, 2004.
- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and IUPAC Subcommittee: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species, *Atmos. Chem. Phys.*, 6, 3625–4055, doi:10.5194/acp-6-3625-2006, 2006.
- Barnes, I., Becker, K. H., and Zhu, T.: Near UV absorption spectra and photolysis products of difunctional organic nitrates: Possible importance as NO<sub>x</sub> reservoirs, *J. Atmos. Chem.*, 17, 353–373, doi:10.1007/BF00696854, 1993.

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- Beaver, M. R., Clair, J. M. St., Paulot, F., Spencer, K. M., Crounse, J. D., LaFranchi, B. W., Min, K. E., Pusede, S. E., Wooldridge, P. J., Schade, G. W., Park, C., Cohen, R. C., and Wennberg, P. O.: Importance of biogenic precursors to the budget of organic nitrates: observations of multifunctional organic nitrates by CIMS and TD-LIF during BEARPEX 2009, *Atmos. Chem. Phys.*, 12, 5773–5785, doi:10.5194/acp-12-5773-2012, 2012.
- Bertram, T. H., Heckel, A., Richter, A., Burrows, J. P., and Cohen, R. C.: Satellite measurements of daily variations in soil NO<sub>x</sub> emissions, *Geophys. Res. Lett.*, 32, L24812, doi:10.1029/2005GL024640, 2005.
- Bian, H. and Prather, M. J.: Fast-J2: Accurate Simulation of Stratospheric Photolysis in Global Chemical Models, *J. Atmos. Chem.*, 41, 281–296, doi:10.1023/A:1014980619462, 2002.
- Bonan, G. B. and Levis, S.: Quantifying carbon-nitrogen feedbacks in the Community Land Model (CLM4), *Geophys. Res. Lett.*, 37, L07401, doi:10.1029/2010GL042430, 2010.
- Browne, E. C. and Cohen, R. C.: Impacts of monoterpene nitrates on NO<sub>x</sub> and NO<sub>y</sub> in the Boreal, forest, *Atmos. Chem. Phys. Discuss.*, in preparation, 2012.
- Browne, E. C., Min, K.-E., Wooldridge, P. J., Apel, E., Blake, D. R., Cantrell, C. A., Cubison, M. J., Jimenez, J. L., Weinheimer, A. J., Wennberg, P. O., Wisthaler, A., and Cohen, R. C.: Observations of total RONO<sub>2</sub> over the Boreal forest: NO<sub>x</sub> sinks and HNO<sub>3</sub> sources, *Atmos. Chem. Phys. Discuss.*, in preparation, 2012.
- Cleary, P. A., Murphy, J. G., Wooldridge, P. J., Day, D. A., Millet, D. B., McKay, M., Goldstein, A. H., and Cohen, R. C.: Observations of total alkyl nitrates within the Sacramento Urban Plume, *Atmos. Chem. Phys. Discuss.*, 5, 4801–4843, doi:10.5194/acpd-5-4801-2005, 2005.
- Crounse, J. D., Knap, H. C., Ørnsø, K. B., Jørgensen, S., Paulot, F., Kjaergaard, H. G., and Wennberg, P. O.: Atmospheric fate of methacrolein. 1. Peroxy radical isomerization following addition of OH and O<sub>2</sub>, *J. Phys. Chem. A*, 116, 5756–5762, doi:10.1021/jp211560u, 2012.
- Crounse, J. D., Paulot, F., Kjaergaard, H. G., and Wennberg, P. O.: Peroxy radical isomerization in the oxidation of isoprene, *Phys. Chem. Chem. Phys.*, 13, 13607, doi:10.1039/c1cp21330j, 2011.
- Dallmann, T. R. and Harley, R. A.: Evaluation of mobile source emission trends in the United States, *J. Geophys. Res.*, 115, D14305, doi:10.1029/2010JD013862, 2010.
- Day, D. A., Farmer, D. K., Goldstein, A. H., Wooldridge, P. J., Minejima, C., and Cohen, R. C.: Observations of NO<sub>x</sub>, ΣPNs, ΣANs, and HNO<sub>3</sub> at a Rural Site in the California Sierra Nevada Mountains: summertime diurnal cycles, *Atmos. Chem. Phys.*, 9, 4879–4896, doi:10.5194/acp-9-4879-2009, 2009.

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- Day, D. A., Wooldridge, P. J., Dillon, M. B., Thornton, J. A., and Cohen, R. C.: A thermal dissociation laser-induced fluorescence instrument for in situ detection of NO<sub>2</sub>, peroxy nitrates, alkyl nitrates, and HNO<sub>3</sub>, *J. Geophys. Res.*, 107, 4046, doi:10.1029/2001JD000779, 2002.
- Derwent, R., Stevenson, D., Doherty, R., Collins, W., Sanderson, M., and Johnson, C.: Radiative forcing from surface NO<sub>x</sub> emissions: spatial and seasonal variations, *Climatic Change*, 88, 385–401, doi:10.1007/s10584-007-9383-8, 2008.
- Emmons, L. K., Walters, S., Hess, P. G., Lamarque, J.-F., Pfister, G. G., Fillmore, D., Granier, C., Guenther, A., Kinnison, D., Laepple, T., Orlando, J., Tie, X., Tyndall, G., Wiedinmyer, C., Baughcum, S. L., and Kloster, S.: Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4), *Geosci. Model Dev.*, 3, 43–67, doi:10.5194/gmd-3-43-2010, 2010.
- Farmer, D. K. and Cohen, R. C.: Observations of HNO<sub>3</sub>, ΣAN, ΣPN and NO<sub>2</sub> fluxes: evidence for rapid HO<sub>x</sub> chemistry within a pine forest canopy, *Atmos. Chem. Phys.*, 8, 3899–3917, doi:10.5194/acp-8-3899-2008, 2008.
- Farmer, D. K., Perring, A. E., Wooldridge, P. J., Blake, D. R., Baker, A., Meinardi, S., Huey, L. G., Tanner, D., Vargas, O., and Cohen, R. C.: Impact of organic nitrates on urban ozone production, *Atmos. Chem. Phys.*, 11, 4085–4094, doi:10.5194/acp-11-4085-2011, 2011.
- Fiore, A. M., Horowitz, L. W., Purves, D. W., II, H. L., Evans, M. J., Wang, Y., Li, Q., and Yantosca, R. M.: Evaluating the contribution of changes in isoprene emissions to surface ozone trends over the eastern United States, *J. Geophys. Res.*, 110, D12303, doi:10.1029/2004JD005485, 2005.
- Freitas, S. R., Longo, K. M., Alonso, M. F., Pirre, M., Marecal, V., Grell, G., Stockler, R., Mello, R. F., and Sánchez Gácita, M.: PREP-CHEM-SRC – 1.0: a preprocessor of trace gas and aerosol emission fields for regional and global atmospheric chemistry models, *Geosci. Model Dev.*, 4, 419–433, doi:10.5194/gmd-4-419-2011, 2011.
- Fry, J. L., Kiendler-Scharr, A., Rollins, A. W., Brauers, T., Brown, S. S., Dorn, H.-P., Dubé, W. P., Fuchs, H., Mensah, A., Rohrer, F., Tillmann, R., Wahner, A., Wooldridge, P. J., and Cohen, R. C.: SOA from limonene: role of NO<sub>3</sub> in its generation and degradation, *Atmos. Chem. Phys.*, 11, 3879–3894, doi:10.5194/acp-11-3879-2011, 2011.
- Fry, J. L., Kiendler-Scharr, A., Rollins, A. W., Wooldridge, P. J., Brown, S. S., Fuchs, H., Dubé, W., Mensah, A., dal Maso, M., Tillmann, R., Dorn, H.-P., Brauers, T., and Cohen, R. C.: Organic nitrate and secondary organic aerosol yield from NO<sub>3</sub> oxidation of β-pinene evaluated



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using a gas-phase kinetics/aerosol partitioning model, *Atmos. Chem. Phys.*, 9, 1431–1449, doi:10.5194/acp-9-1431-2009, 2009.

Fry, M. M., Naik, V., West, J. J., Schwarzkopf, M. D., Fiore, A. M., Collins, W. J., Dentener, F. J., Shindell, D. T., Atherton, C., Bergmann, D., Duncan, B. N., Hess, P., MacKenzie, I. A., Marmar, E., Schultz, M. G., Szopa, S., Wild, O., and Zeng, G.: The influence of ozone precursor emissions from four world regions on tropospheric composition and radiative climate forcing, *J. Geophys. Res.*, 117, D07306, doi:10.1029/2011JD017134, 2012.

Fuglestedt, J. S., Berntsen, T. K., Isaksen, I. S. A., Mao, H. T., Liang, X. Z., and Wang, W. C.: Climatic forcing of nitrogen oxides through changes in tropospheric ozone and methane; global 3D model studies, *Atmos. Environ.*, 33, 961–977, doi:10.1016/S1352-2310(98)00217-9, 1999.

Galloway, J. N., Townsend, A. R., Erisman, J. W., Bekunda, M., Cai, Z., Freney, J. R., Martinelli, L. A., Seitzinger, S. P., and Sutton, M. A.: Transformation of the Nitrogen cycle: Recent trends, questions, and potential solutions, *Science*, 320, 889–892, doi:10.1126/science.1136674, 2008.

Geiger, H., Barnes, I., Bejan, J., Benter, T., and Spittler, M.: The tropospheric degradation of isoprene: an updated module for the regional atmospheric chemistry mechanism, *Atmos. Environ.*, 37, 1503–1519, doi:10.1016/S1352-2310(02)01047-6, 2003.

Ghude, S. D., Lal, D. M., Beig, G., A, R. van der and Sable, D.: Rain-induced soil NO<sub>x</sub> emission from India during the onset of the summer monsoon: A satellite perspective, *J. Geophys. Res.*, 115, D16304, doi:10.1029/2009JD013367, 2010.

Goliff, W. and Stockwell, W. R.: The Regional Atmospheric Chemistry Mechanism, Version 2 – a final frozen version at last, Atmospheric Chemical Mechanisms Conference, Davis, CA, USA, 2010.

Grell, G. A., Peckham, S. E., Schmitz, R., McKeen, S. A., Frost, G., Skamarock, W. C., and Eder, B.: Fully coupled “online” chemistry within the WRF model, *Atmos. Environ.*, 39, 6957–6975, doi:10.1016/j.atmosenv.2005.04.027, 2005.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmos. Chem. Phys.*, 6, 3181–3210, doi:10.5194/acp-6-3181-2006, 2006.

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- Henderson, B. H., Pinder, R. W., Crooks, J., Cohen, R. C., Carlton, A. G., Pye, H. O. T., and Vizuete, W.: Combining Bayesian methods and aircraft observations to constrain the HO<sup>•</sup> + NO<sub>2</sub> reaction rate, *Atmos. Chem. Phys.*, 12, 653–667, doi:10.5194/acp-12-653-2012, 2012.
- Holland, E. A., Braswell, B. H., Lamarque, J.-F., Townsend, A., Sulzman, J., Müller, J.-F., Dentener, F., Brasseur II, G., H. L., Penner, J. E., and Roelofs, G.-J.: Variations in the predicted spatial distribution of atmospheric nitrogen deposition and their impact on carbon uptake by terrestrial ecosystems, *J. Geophys. Res.*, 102, 15849–15866, doi:10.1029/96JD03164, 1997.
- Horowitz, L. W., Fiore, A. M., Milly, G. P., Cohen, R. C., Perring, A., Wooldridge, P. J., Hess, P. G., Emmons, L. K., and Lamarque, J.-F.: Observational constraints on the chemistry of isoprene nitrates over the eastern United States, *J. Geophys. Res.*, 112, D12S08, doi:10.1029/2006JD007747, 2007.
- Horowitz, L. W., Liang, J., Gardner, G. M., and Jacob, D. J.: Export of reactive nitrogen from North America during summertime: Sensitivity to hydrocarbon chemistry, *J. Geophys. Res.*, 103, 13451–13476, doi:10.1029/97JD03142, 1998.
- Hudman, R. C., Jacob, D. J., Turquety, S., Leibensperger, E. M., Murray, L. T., Wu, S., Gilliland, A. B., Avery, M., Bertram, T. H., Brune, W., Cohen, R. C., Dibb, J. E., Flocke, F. M., Fried, A., Holloway, J., Neuman, J. A., Orville, R., Perring, A., Ren, X., Sachse, G. W., Singh, H. B., Swanson, A., and Wooldridge, P. J.: Surface and lightning sources of nitrogen oxides over the United States: Magnitudes, chemical evolution, and outflow, *J. Geophys. Res.*, 112, D12S05, doi:10.1029/2006JD007912, 2007.
- Hudman, R. C., Russell, A. R., Valin, L. C., and Cohen, R. C.: Interannual variability in soil nitric oxide emissions over the United States as viewed from space, *Atmos. Chem. Phys.*, 10, 9943–9952, doi:10.5194/acp-10-9943-2010, 2010.
- Ito, A., Sillman, S., and Penner, J. E.: Effects of additional nonmethane volatile organic compounds, organic nitrates, and direct emissions of oxygenated organic species on global tropospheric chemistry, *J. Geophys. Res.*, 112, D06309, doi:10.1029/2005JD006556, 2007.
- Ito, A., Sillman, S., and Penner, J. E.: Global chemical transport model study of ozone response to changes in chemical kinetics and biogenic volatile organic compounds emissions due to increasing temperatures: Sensitivities to isoprene nitrate chemistry and grid resolution, *J. Geophys. Res.*, 114, D09301, doi:10.1029/2008JD011254, 2009.
- Jacob, D. J., Crawford, J. H., Maring, H., Clarke, A. D., Dibb, J. E., Emmons, L. K., Ferrare, R. A., Hostetler, C. A., Russell, P. B., Singh, H. B., Thompson, A. M., Shaw, G. E., McCauley, E.,

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Pederson, J. R., and Fisher, J. A.: The Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) mission: design, execution, and first results, *Atmos. Chem. Phys.*, 10, 5191–5212, doi:10.5194/acp-10-5191-2010, 2010.

Jaeglé, L., Steinberger, L., Martin, R. V. and Chance, K.: Global partitioning of NO<sub>x</sub> sources using satellite observations: Relative roles of fossil fuel combustion, biomass burning and soil emissions, *Faraday Discuss.*, 130, 407–423, doi:10.1039/b502128f, 2005.

Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: a protocol for mechanism development, *Atmos. Environ.*, 31, 81–104, doi:10.1016/S1352-2310(96)00105-7, 1997.

Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli, D., and Williams, J.: Atmospheric oxidation capacity sustained by a tropical forest, *Nature*, 452, 737–740, doi:10.1038/nature06870, 2008.

Lockwood, A. L., Filley, T. R., Rhodes, D., and Shepson, P. B.: Foliar uptake of atmospheric organic nitrates, *Geophys. Res. Lett.*, 35, L15809, doi:10.1029/2008GL034714, 2008.

Lockwood, A. L., Shepson, P. B., Fiddler, M. N., and Alaghmand, M.: Isoprene nitrates: preparation, separation, identification, yields, and atmospheric chemistry, *Atmos. Chem. Phys.*, 10, 6169–6178, doi:10.5194/acp-10-6169-2010, 2010.

Mao, J., Ren, X., Brune, W. H., Van Duin, D. M., Cohen, R. C., Park, J.-H., Goldstein, A. H., Paulot, F., Beaver, M. R., Crounse, J. D., Wennberg, P. O., DiGangi, J. P., Henry, S. B., Keutsch, F. N., Park, C., Schade, G. W., Wolfe, G. M., and Thornton, J. A.: Insights into hydroxyl measurements and atmospheric oxidation in a California forest, *Atmos. Chem. Phys. Discuss.*, 12, 6715–6744, doi:10.5194/acpd-12-6715-2012, 2012.

Mebust, A. K., Russell, A. R., Hudman, R. C., Valin, L. C., and Cohen, R. C.: Characterization of wildfire NO<sub>x</sub> emissions using MODIS fire radiative power and OMI tropospheric NO<sub>2</sub> columns, *Atmos. Chem. Phys.*, 11, 5839–5851, doi:10.5194/acp-11-5839-2011, 2011.

Mickley, L. J., Jacob, D. J., and Rind, D.: Uncertainty in preindustrial abundance of tropospheric ozone: Implications for radiative forcing calculations, *J. Geophys. Res.*, 106, 3389–3399, 2001.

Murphy, J. G., Day, D. A., Cleary, P. A., Wooldridge, P. J., and Cohen, R. C.: Observations of the diurnal and seasonal trends in nitrogen oxides in the western Sierra Nevada, *Atmos. Chem. Phys.*, 6, 5321–5338, doi:10.5194/acp-6-5321-2006, 2006.

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- Novelli, P. C., Lang, P. M., Masarie, K. A., Hurst, D. F., Myers, R. and Elkins, J. W.: Molecular hydrogen in the troposphere: Global distribution and budget, *J. Geophys. Res.-Atmos.*, 104, 30427–30444, doi:10.1029/1999JD900788, 1999.
- Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kroll, J. H., Seinfeld, J. H., and Wennberg, P. O.: Isoprene photooxidation: new insights into the production of acids and organic nitrates, *Atmos. Chem. Phys.*, 9, 1479–1501, doi:10.5194/acp-9-1479-2009, 2009a.
- Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kürten, A., Clair, S., M, J., Seinfeld, J. H., and Wennberg, P. O.: Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene, *Science*, 325, 730–733, doi:10.1126/science.1172910, 2009b.
- Paulot, F., Henze, D. K., and Wennberg, P. O.: Impact of the isoprene photochemical cascade on tropical ozone, *Atmos. Chem. Phys.*, 12, 1307–1325, doi:10.5194/acp-12-1307-2012, 2012.
- Peeters, J. and Müller, J.-F.: HO<sub>x</sub> radical regeneration in isoprene oxidation via peroxy radical isomerisations. II: experimental evidence and global impact, *Phys. Chem. Chem. Phys.*, 12, 14227, doi:10.1039/c0cp00811g, 2010.
- Peeters, J., Nguyen, T. L., and Vereecken, L.: HO<sub>x</sub> radical regeneration in the oxidation of isoprene, *Phys. Chem. Chem. Phys.*, 11, 5935, doi:10.1039/b908511d, 2009.
- Perring, A. E., Bertram, T. H., Farmer, D. K., Wooldridge, P. J., Dibb, J., Blake, N. J., Blake, D. R., Singh, H. B., Fuelberg, H., Diskin, G., Sachse, G., and Cohen, R. C.: The production and persistence of ΣRONO<sub>2</sub> in the Mexico City plume, *Atmos. Chem. Phys.*, 10, 7215–7229, doi:10.5194/acp-10-7215-2010, 2010.
- Perring, A. E., Bertram, T. H., Wooldridge, P. J., Fried, A., Heikes, B. G., Dibb, J., Crounse, J. D., Wennberg, P. O., Blake, N. J., Blake, D. R., Brune, W. H., Singh, H. B., and Cohen, R. C.: Airborne observations of total RONO<sub>2</sub>: new constraints on the yield and lifetime of isoprene nitrates, *Atmos. Chem. Phys.*, 9, 1451–1463, doi:10.5194/acp-9-1451-2009, 2009a.
- Perring, A. E., Pusede, S. E., and Cohen, R. C.: An observational perspective on the atmospheric impacts of alkyl and multifunctional nitrates on ozone and secondary organic aerosol, *Chem. Rev.*, in preparation, 2012.
- Perring, A. E., Wisthaler, A., Graus, M., Wooldridge, P. J., Lockwood, A. L., Mielke, L. H., Shepson, P. B., Hansel, A., and Cohen, R. C.: A product study of the isoprene+NO<sub>3</sub> reaction, *Atmos. Chem. Phys.*, 9, 4945–4956, doi:10.5194/acp-9-4945-2009, 2009b.
- Roberts, J. M. and Fajer, R. W.: UV absorption cross sections of organic nitrates of potential atmospheric importance and estimation of atmospheric lifetimes, *Environ. Sci. Technol.*, 23, 945–951, doi:10.1021/es00066a003, 1989.

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- Rollins, A. W., Kiendler-Scharr, A., Fry, J. L., Brauers, T., Brown, S. S., Dorn, H.-P., Dubé, W. P., Fuchs, H., Mensah, A., Mentel, T. F., Rohrer, F., Tillmann, R., Wegener, R., Wooldridge, P. J., and Cohen, R. C.: Isoprene oxidation by nitrate radical: alkyl nitrate and secondary organic aerosol yields, *Atmos. Chem. Phys.*, 9, 6685–6703, doi:10.5194/acp-9-6685-2009, 2009.
- 5 Rosen, R. S., Wood, E. C., Wooldridge, P. J., Thornton, J. A., Day, D. A., Kuster, W., Williams, E. J., Jobson, B. T., and Cohen, R. C.: Observations of total alkyl nitrates during Texas Air Quality Study 2000: Implications for O<sub>3</sub> and alkyl nitrate photochemistry, *J. Geophys. Res.*, 109, D07303, doi:10.1029/2003JD004227, 2004.
- 10 Russell, A. R., Valin, L. C., Bucsel, E. J., Wenig, M. O., and Cohen, R. C.: Space-based constraints on spatial and temporal patterns of NO<sub>x</sub> emissions in California, 2005–2008, *Environ. Sci. Technol.*, 44, 3608–3615, doi:10.1021/es903451j, 2010.
- Russell, A. R., Valin, L. C., and Cohen, R. C.: Trends in OMI NO<sub>2</sub> observations over the US: effects of emission control technology and the economic recession, *Atmos. Chem. Phys. Discuss.*, 12, 15419–15452, doi:10.5194/acpd-12-15419-2012, 2012.
- 15 Sander, S. P., Finlayson-Pitts, J., Friedl, R. R., Golden, D. M., Huie, R. E., Keller-Rudek, H., Kolb, C. E., Kurylo, M. J., Molina, M. J., Moortgat, G. K., Orkin, V. L., Ravishankara, A. R., and Wine, P. H.: Chemical kinetics and photochemical data for use in atmospheric studies, Evaluation No. 15, JPL Publication 06-2, Jet Propulsion Laboratory, Pasadena, http://jpldataeval.jpl.nasa.gov, 2006.
- 20 Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, *Atmos. Chem. Phys.*, 3, 161–180, doi:10.5194/acp-3-161-2003, 2003.
- Schumann, U. and Huntrieser, H.: The global lightning-induced nitrogen oxides source, *Atmos. Chem. Phys.*, 7, 3823–3907, doi:10.5194/acp-7-3823-2007, 2007.
- 25 Sillman, S. and Samson, P. J.: Impact of temperature on oxidant photochemistry in urban, polluted rural and remote environments, *J. Geophys. Res.*, 100, 11497–11508, doi:10.1029/94JD02146, 1995.
- St. Clair, J. M., McCabe, D. C., Crouse, J. D., Steiner, U., and Wennberg, P. O.: Chemical ionization tandem mass spectrometer for the in situ measurement of methyl hydrogen peroxide, *Rev. Sci. Instrum.*, 81, 094102, doi:10.1063/1.3480552, 2010.
- 30

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Stavrakou, T., Peeters, J., and Müller, J.-F.: Improved global modelling of HO<sub>x</sub> recycling in isoprene oxidation: evaluation against the GABRIEL and INTEX-A aircraft campaign measurements, *Atmos. Chem. Phys.*, 10, 9863–9878, doi:10.5194/acp-10-9863-2010, 2010.

Stockwell, W. R., Goliff, W. S., and Lawson, C. V.: RACM Developments, Atmospheric Chemical Mechanisms Conference, Davis, CA, USA, 2010.

Stone, D., Evans, M. J., Edwards, P. M., Commane, R., Ingham, T., Rickard, A. R., Brookes, D. M., Hopkins, J., Leigh, R. J., Lewis, A. C., Monks, P. S., Oram, D., Reeves, C. E., Stewart, D., and Heard, D. E.: Isoprene oxidation mechanisms: measurements and modelling of OH and HO<sub>2</sub> over a South-East Asian tropical rainforest during the OP3 field campaign, *Atmos. Chem. Phys.*, 11, 6749–6771, doi:10.5194/acp-11-6749-2011, 2011.

Taraborrelli, D., Lawrence, M. G., Crowley, J. N., Dillon, T. J., Gromov, S., Groß, C. B. M., Vereecken, L., and Lelieveld, J.: Hydroxyl radical buffered by isoprene oxidation over tropical forests, *Nature Geosci.*, 5, 190–193, doi:10.1038/ngeo1405, 2012.

Thornberry, T., Carroll, M. A., Keeler, G. J., Sillman, S., Bertman, S. B., Pippin, M. R., Ostling, K., Grossenbacher, J. W., Shepson, P. B., Cooper, O. R., Moody, J. L., and Stockwell, W. R.: Observations of reactive oxidized nitrogen and speciation of NO<sub>y</sub> during the PROPHET summer 1998 intensive, *J. Geophys. Res.*, 106, 24359–24386, doi:10.1029/2000JD900760, 2001.

Thornton, P. E., Doney, S. C., Lindsay, K., Moore, J. K., Mahowald, N., Randerson, J. T., Fung, I., Lamarque, J.-F., Feddesma, J. J., and Lee, Y.-H.: Carbon-nitrogen interactions regulate climate-carbon cycle feedbacks: results from an atmosphere-ocean general circulation model, *Biogeosciences*, 6, 2099–2120, doi:10.5194/bg-6-2099-2009, 2009.

Thornton, P. E., Lamarque, J.-F., Rosenbloom, N. A., and Mahowald, N. M.: Influence of carbon-nitrogen cycle coupling on land model response to CO<sub>2</sub> fertilization and climate variability, *Global Biogeochem. Cy.*, 21, GB4018, doi:10.1029/2006GB002868, 2007.

Trainer, M., Buhr, M. P., Curran, C. M., Fehsenfeld, F. C., Hsie, E. Y., Liu, S. C., Norton, R. B., Parrish, D. D., Williams, E. J., Gandrud, B. W., Ridley, B. A., Shetter, J. D., Allwine, E. J., and Westberg, H. H.: Observations and modeling of the reactive nitrogen photochemistry at a rural site, *J. Geophys. Res.*, 96, 3045–3063, doi:10.1029/90JD02395, 1991.

Valin, L. C., Russell, A. R., Hudman, R. C., and Cohen, R. C.: Effects of model resolution on the interpretation of satellite NO<sub>2</sub> observations, *Atmos. Chem. Phys.*, 11, 11647–11655, doi:10.5194/acp-11-11647-2011, 2011.

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- van der A, R. J., Eskes, H. J., Boersma, K. F., Noije, T. P. C. van, Roozendael, M. V., Smedt, I. D., Peters, D. H. M. U., and Meijer, E. W.: Trends, seasonal variability and dominant NO<sub>x</sub> source derived from a ten year record of NO<sub>2</sub> measured from space, *J. Geophys. Res.*, 113, D04302, doi:10.1029/2007JD009021, 2008.
- 5 von Kuhlmann, R., Lawrence, M. G., Pöschl, U., and Crutzen, P. J.: Sensitivities in global scale modeling of isoprene, *Atmos. Chem. Phys.*, 4, 1–17, doi:10.5194/acp-4-1-2004, 2004.
- Whalley, L. K., Edwards, P. M., Furneaux, K. L., Goddard, A., Ingham, T., Evans, M. J., Stone, D., Hopkins, J. R., Jones, C. E., Karunaharan, A., Lee, J. D., Lewis, A. C., Monks, P. S., Moller, S. J., and Heard, D. E.: Quantifying the magnitude of a missing hydroxyl radical source in a tropical rainforest, *Atmos. Chem. Phys.*, 11, 7223–7233, doi:10.5194/acp-11-7223-2011, 10 2011.
- Wiedinmyer, C., Quayle, B., Geron, C., Belote, A., McKenzie, D., Zhang, X., O'Neill, S., and Wynne, K. K.: Estimating emissions from fires in North America for air quality modeling, *Atmos. Environ.*, 40, 3419–3432, doi:10.1016/j.atmosenv.2006.02.010, 2006.
- 15 Wild, O., Prather, M. J., and Akimoto, H.: Indirect long-term global radiative cooling from NO<sub>x</sub> emissions, *Geophys. Res. Lett.*, 28, 1719–1722, doi:10.1029/2000GL012573, 2001.
- Wu, S., Mickley, L. J., Jacob, D. J., Logan, J. A., Yantosca, R. M., and Rind, D.: Why are there large differences between models in global budgets of tropospheric ozone?, *J. Geophys. Res.*, 112, D05302, doi:10.1029/2006JD007801, 2007.

**Table 1.** Reactions and rate coefficients used in the steady-state modeling of daytime chemistry.

Reaction	Rate
$\text{CH}_4 + \text{OH} \xrightarrow{\text{O}_2} \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$	$1.85 \times 10^{-12} \exp(-1690/T)^{\text{a}}$
$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{HO}_2 + \text{HCHO}$	$2.8 \times 10^{-12} \exp(300/T)^{\text{b}}$
$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{products}$	$4.1 \times 10^{-13} \exp(750/T)^{\text{b}}$
$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow 0.66\text{HO}_2 + \text{products}$	$9.5 \times 10^{-14} \exp(390/T)^{\text{b}}$
$\text{NMVOC} + \text{OH} \xrightarrow{\text{O}_2} \text{RO}_2$	See Table 2
$\text{RO}_2 + \text{NO} \rightarrow (1 - \alpha)\text{HO}_2 + (1 - \alpha)\text{NO}_2 + \alpha\text{RONO}_2$	$2.7 \times 10^{-12} \exp(360/T)^{\text{c}}$
$\text{RO}_2 + \text{HO}_2 \rightarrow \text{products}$	$2.06 \times 10^{-13} \exp(1300/T)^{\text{d}}$
$\text{RO}_2 + \text{RO}_2 \xrightarrow{2\text{O}_3} 1.2\text{CH}_3\text{O}_2 + \text{products}$	$1.4 \times 10^{-12}^{\text{e}}$
$\text{RO}_2 \rightarrow \text{HO}_2 + \text{OH}$	$4.12 \times 10^8 \exp(-7700/T)^{\text{e}}$
$\text{RO}_2 + \text{CH}_3\text{O}_2 \xrightarrow{2\text{O}_3} 0.6\text{CH}_3\text{O}_2 + 0.6\text{HO}_2 + \text{products}$	$1.4 \times 10^{-12}^{\text{f}}$
$\text{CO} + \text{HO} \xrightarrow{\text{M}, \text{O}_2} \text{HO}_2 + \text{CO}_2$	$k_0 = 1.5 \times 10^{-13} (T/300)^{0.6}$ $k_{\infty} = 2.1 \times 10^9 (T/300)^{6.1\text{b}^*}$
$\text{CO} + \text{OH} \xrightarrow{\text{M}} \text{HOCO} \xrightarrow{\text{O}_2} \text{HO}_2 + \text{CO}_2$	$k_0 = 5.9 \times 10^{-33} (T/300)^{-1.4}$ $k_{\infty} = 1.1 \times 10^{-12} (T/300)^{1.3\text{p}}$
$P(\text{HO}_x) \rightarrow 0.8\text{OH} + 0.2\text{HO}_2$	See Table 2
$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	$1.7 \times 10^{-12} \exp(-940/T)^{\text{a}}$
$\text{OH} + \text{H}_2 \xrightarrow{\text{O}_2} \text{HO}_2 + \text{H}_2\text{O}$	$7.7 \times 10^{-12} \exp(-2100/T)^{\text{a}}$ $\text{H}_2 = 531 \text{ ppb}^{\text{**}}$
$\text{HCHO} + \text{OH} \rightarrow \text{HO}_2 + \text{CO}_2 + \text{H}_2\text{O}$	$5.4 \times 10^{-12} \exp(135/T)^{\text{a}}$
$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	$2.9 \times 10^{-12} \exp(-160/T)^{\text{a}}$
$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	$4.8 \times 10^{-11} \exp(250/T)^{\text{a}}$
$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$	$1.0 \times 10^{-14} \exp(-490/T)^{\text{b}}$
$\text{HO}_2 + \text{HO}_2 \xrightarrow{\text{M}} \text{H}_2\text{O}_2 + \text{H}_2\text{O}$	$(2.1 \times 10^{-33} \times \text{M} \times \exp(920/T) +$ $3.0 \times 10^{-13} \exp(460/T)) \times$ $(1 + [\text{H}_2\text{O}] \times 1.4 \times 10^{-21} \exp(2200/T))^{\text{b}}$
$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$	$3.45 \times 10^{-12} \exp(270/T)^{\text{a}}$
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$1.4 \times 10^{-12} \exp(-1310/T)^{\text{a}}$
$\text{NO}_2 + \text{OH} \xrightarrow{\text{M}} \text{HNO}_3$	$k_0 = 1.49 \times 10^{-30} (T/300)^{-1.8}$ $k_{\infty} = 2.58 \times 10^{-11}^{\text{q}}$
$\text{NO}_2 + h\nu \xrightarrow{\text{O}_2} \text{NO} + \text{O}_3$	See Table 2

<sup>a</sup> IUPAC Atkinson et al. (2004, 2006), <sup>b</sup> JPL 2010 (Sander et al., 2006), <sup>c</sup> MCM v3.2 (Jenkin et al., 1997; Saunders et al., 2003), <sup>d</sup> MCM v3.2  $\text{RO}_2 + \text{HO}_2$  for five carbon  $\text{RO}_2$ , <sup>e</sup> Crounse et al. (2011) using MCM v3.2  $\text{RO}_2 + \text{HO}_2$  reaction rate with a 5 carbon  $\text{RO}_2$  to represent isoprene peroxy +  $\text{HO}_2$ , <sup>f</sup> (Jenkin et al., 1997)  $\text{RO}_2$  reactions secondary  $\text{RO}_2$  with  $\beta\text{-OH}$ , <sup>g</sup> Henderson et al. (2012), <sup>h</sup> Calculated using the JPL 2010 termolecular rate for chemical activation reactions, <sup>\*\*</sup> Novelli et al. (1999).

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**Table 2.** Parameters used in the daytime steady-state model. The value of the parameters (except for NMVOC + OH) are based on the median ARCTAS measurements from less than 2 km pressure altitude and excluding data with recent anthropogenic or biomass burning influence.

Species	Value
Temperature	285 K
Photolysis rate of NO <sub>2</sub>	$6.2 \times 10^{-3} \text{ s}^{-1}$
CH <sub>4</sub>	1865 ppbv
CO	130 ppbv
O <sub>3</sub>	40 ppbv
HO <sub>x</sub> production rate	$4.1 \times 10^6 \text{ molecules cm}^{-3} \text{ s}^{-1}$
HCHO	1.48 ppbv
H <sub>2</sub> O <sub>2</sub>	2.04 ppbv
H <sub>2</sub> O	$1.18 \times 10^4 \text{ ppm}$
NMVOC+OH	$2 \text{ s}^{-1}$

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**Table 3.** Effective  $\alpha$  value at various NO<sub>x</sub> concentrations. These are calculated using Eq. (A2).

$\alpha$	$\alpha_{\text{eff}}$ 10 pptv NO <sub>x</sub>	$\alpha_{\text{eff}}$ 100 pptv NO <sub>x</sub>	$\alpha_{\text{eff}}$ 500 pptv NO <sub>x</sub>
0.1 %	0.06 %	0.08 %	0.09 %
1 %	0.64 %	0.81 %	0.87 %
5 %	3.22 %	4.03 %	4.37 %
10 %	6.43 %	8.06 %	8.74 %

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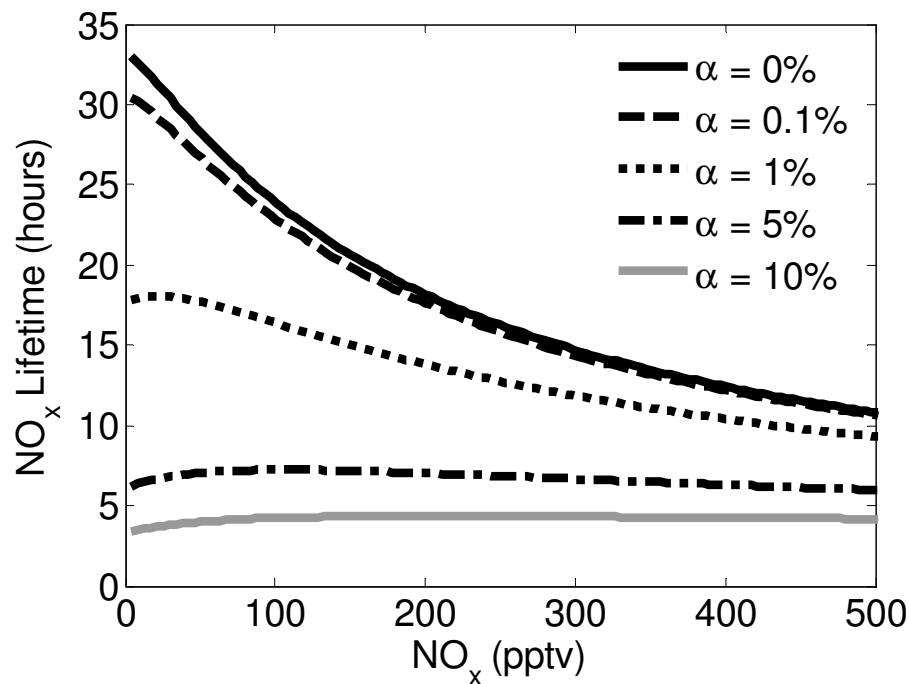
**Table 4.** Reactions and rate coefficients used in the steady-state modeling of nighttime chemistry.

Reaction	Rate
$\text{NO}_2 + \text{O}_3 \longrightarrow \text{NO}_3$	$1.2 \times 10^{-13} \exp(-2450/T)^a$
$\text{NO}_3 + \text{NO}_2 \xrightarrow{\text{M}} \text{N}_2\text{O}_5$	$k_0 = 2.0 \times 10^{-30} (T/300)^{-4.4}$ $k_\infty = 1.4 \times 10^{-12} (T/300)^{-0.7^a}$
$\text{N}_2\text{O}_5 \xrightarrow{\text{M}} \text{NO}_3 + \text{NO}_2$	$K_{\text{eq}} = 2.7 \times 10^{-27} \exp(11\,000/T)^b$
$\alpha\text{-pinene} + \text{NO}_3 \longrightarrow \beta_{\alpha\text{-pinene}} \text{RONO}_2 + \text{products}$	$1.2 \times 10^{-12} \exp(490/T)^c$
$\text{Isoprene} + \text{NO}_3 \longrightarrow \beta_{\text{isoprene}} \text{RONO}_2 + \text{products}$	$3.15 \times 10^{-12} \exp(-450/T)^c$
$\text{Acetaldehyde} + \text{NO}_3 \longrightarrow \text{HNO}_3 + \text{products}$	$1.4 \times 10^{-12} \exp(-1860/T)^c$
$\text{N}_2\text{O}_5 \xrightarrow{\text{H}_2\text{O, surface}} 2\text{HNO}_3$	See Table 5

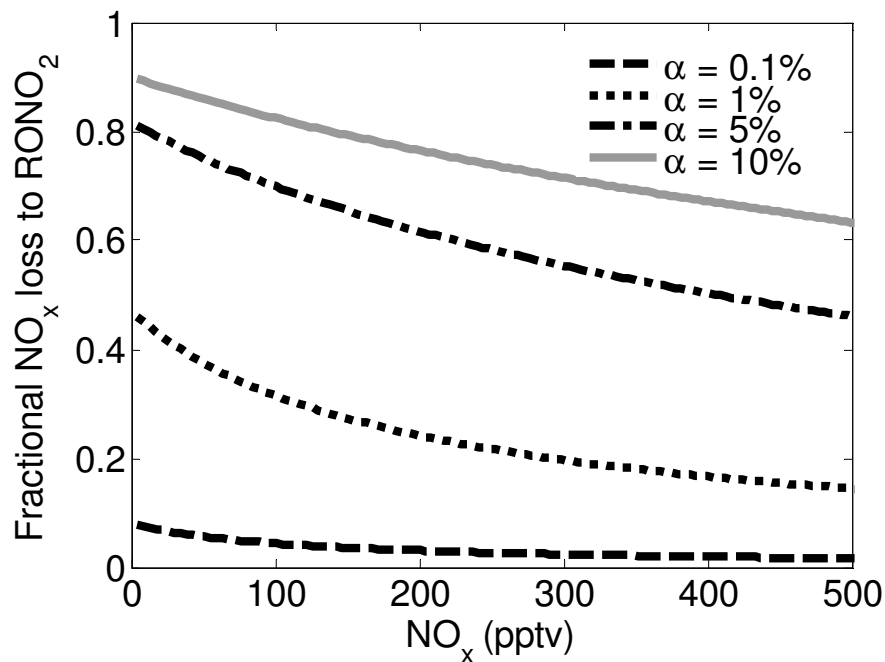
<sup>a</sup> JPL 2010 (Sander et al., 2006) <sup>b</sup> JPL 2010 calculated from  $\frac{k_{\text{NO}_3+\text{NO}_2}}{K_{\text{eq}}}$ . <sup>c</sup> IUPAC (Atkinson et al., 2006).

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R. C. Cohen[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)**Table 5.** Parameters used in the nighttime steady-state model.

Species	Value
Temperature	285 K
O <sub>3</sub>	40 ppbv
$\alpha$ -pinene	200 pptv
isoprene	200 pptv
acetaldehyde	2 ppbv
$\beta$ <sub>isoprene</sub>	0.7
$\beta$ <sub><math>\alpha</math>-pinene</sub>	0.3
N <sub>2</sub> O <sub>5</sub> hydrolysis	$\tau = 180, 120, 60, \text{ or } 10 \text{ min}$

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**Fig. 1.** Steady-state model results of  $\text{NO}_x$  lifetime to chemical loss versus  $\text{NO}_x$  concentration for  $\alpha = 0\%$  (solid black line),  $\alpha = 0.1\%$  (dashed black line),  $\alpha = 1\%$  (dotted black line),  $\alpha = 5\%$  (dash-dot black line), and  $\alpha = 10\%$  (grey solid line).

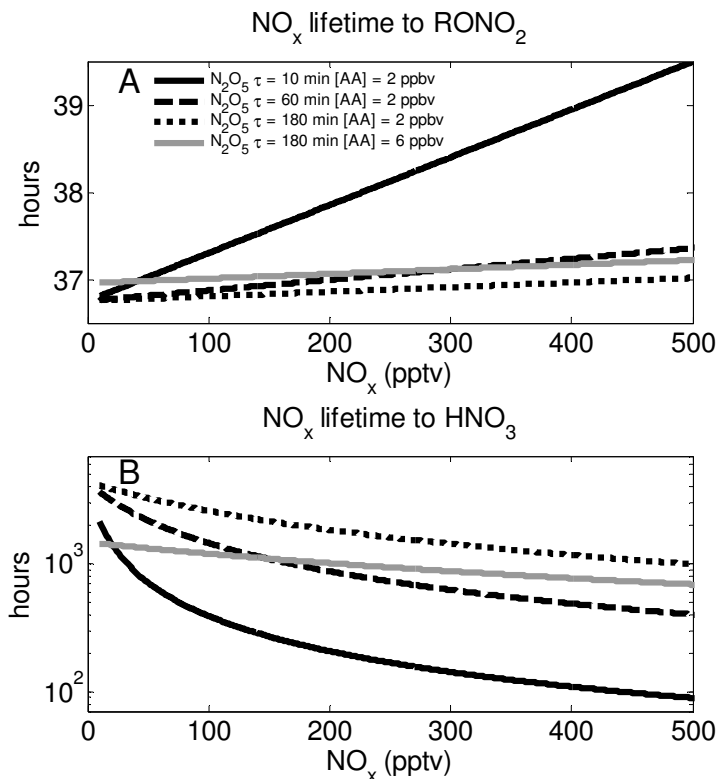
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**Fig. 2.** Steady-state model results of fractional chemical  $\text{NO}_x$  loss to  $\text{RONO}_2$  versus  $\text{NO}_x$  concentration for  $\alpha = 0.1\%$  (dashed black line),  $\alpha = 1\%$  (dotted black line),  $\alpha = 5\%$  (dash-dot black line), and  $\alpha = 10\%$  (grey solid line).  $\text{HNO}_3$  production accounts for the remainder of the  $\text{NO}_x$  loss.

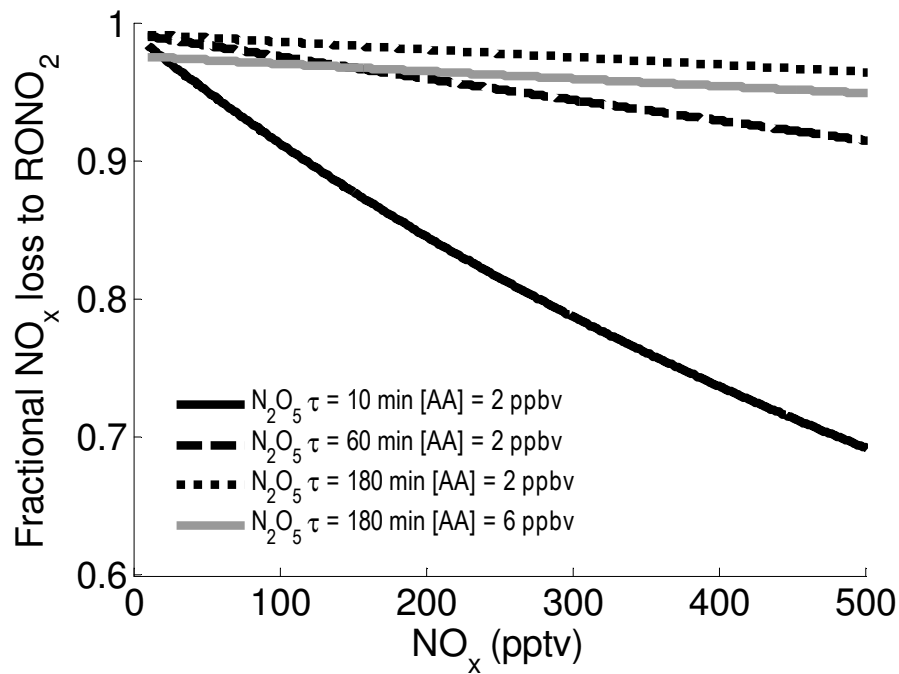
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**Fig. 3.** Steady state model calculation of  $\text{NO}_x$  lifetime at night to **(A)** organic nitrate formation and **(B)** to nitric acid formation through both  $\text{NO}_3$  reaction with aldehydes and  $\text{N}_2\text{O}_5$  hydrolysis. The solid black line is for an  $\text{N}_2\text{O}_5$  hydrolysis lifetime ( $\tau$ ) of 10 min with 2 ppbv of acetaldehyde (AA), the dashed black line for an  $\text{N}_2\text{O}_5$  hydrolysis lifetime of 60 min with 2 ppbv of acetaldehyde, the dotted black line for an  $\text{N}_2\text{O}_5$  hydrolysis lifetime of 180 min with 2 ppbv of acetaldehyde, and the solid grey line for an  $\text{N}_2\text{O}_5$  hydrolysis lifetime of 180 min with 6 ppbv of acetaldehyde.



**Fig. 4.** Fractional NO<sub>x</sub> loss to RONO<sub>2</sub> at night in the steady-state model for an N<sub>2</sub>O<sub>5</sub> hydrolysis lifetime of 10 min with 2 ppbv of acetaldehyde (solid black line), N<sub>2</sub>O<sub>5</sub> hydrolysis lifetime of 60 min with 2 ppbv of acetaldehyde (dashed black line), N<sub>2</sub>O<sub>5</sub> hydrolysis lifetime of 180 min with 2 ppbv of acetaldehyde (dotted black line), and an N<sub>2</sub>O<sub>5</sub> hydrolysis lifetime of 180 min with 6 ppbv of acetaldehyde (solid grey line). HNO<sub>3</sub> production accounts for the remainder of the NO<sub>x</sub> loss.

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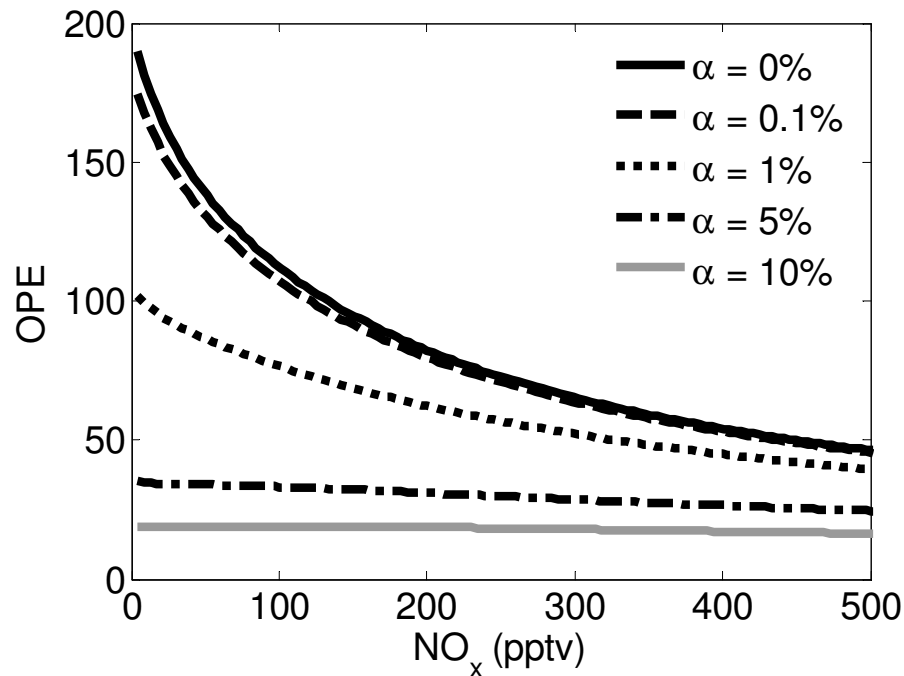
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**Fig. 5.** Steady-state model results for ozone production efficiency (OPE) versus NO<sub>x</sub> concentration for  $\alpha = 0\%$  (solid black line),  $\alpha = 0.1\%$  (dashed black line),  $\alpha = 1\%$  (dotted black line),  $\alpha = 5\%$  (dash-dot black line), and  $\alpha = 10\%$  (grey solid line).

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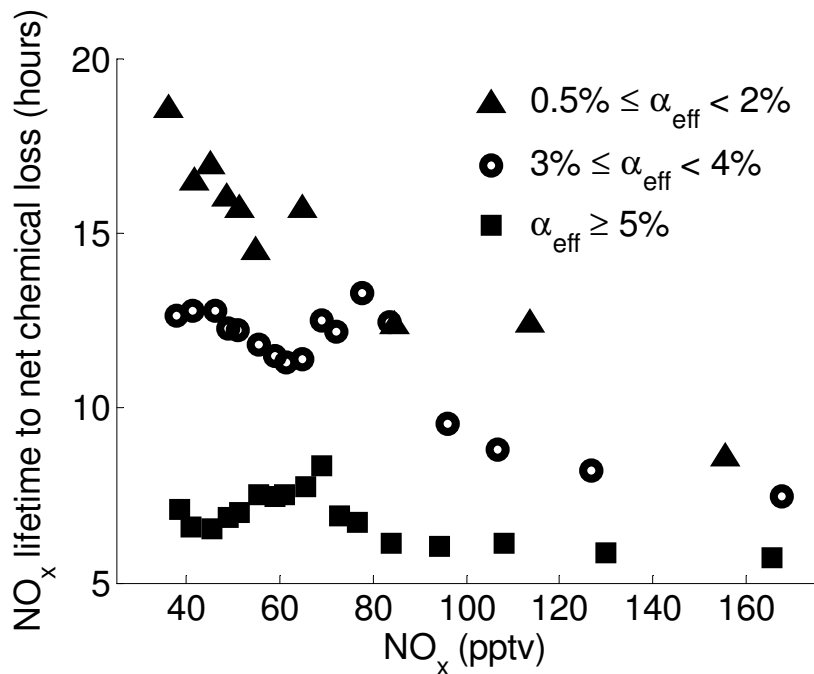
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**Fig. 6.** WRF-Chem prediction of the  $\text{NO}_x$  lifetime to net chemical loss over Canada (north of  $53^\circ \text{N}$ ) averaged over two weeks in July. The net chemical loss is defined as the sum of the net chemical loss to different classes of  $\text{NO}_y$  including  $\text{RONO}_2$ ,  $\text{RO}_2\text{NO}_2$ , and  $\text{HNO}_3$  (full details can be found in Appendix B). If the net chemical loss is less than zero for any particular class, the net loss is set to zero. The results are sorted by the effective  $\alpha_{\text{eff}}$  value as calculated using Eq. (A2). The triangles represent  $0.5\% \leq \alpha_{\text{eff}} < 2\%$ , the open circles are  $3\% \leq \alpha_{\text{eff}} < 4\%$ , and the squares are  $\alpha_{\text{eff}} \geq 5\%$ .

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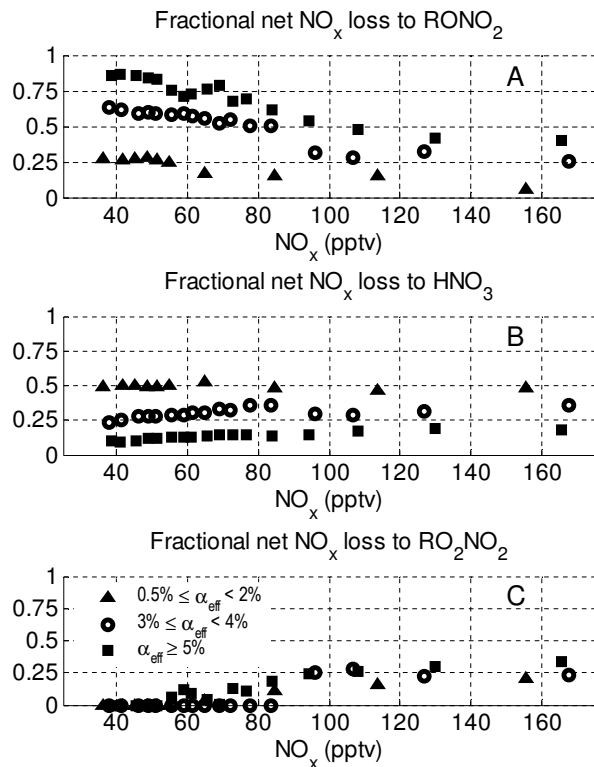
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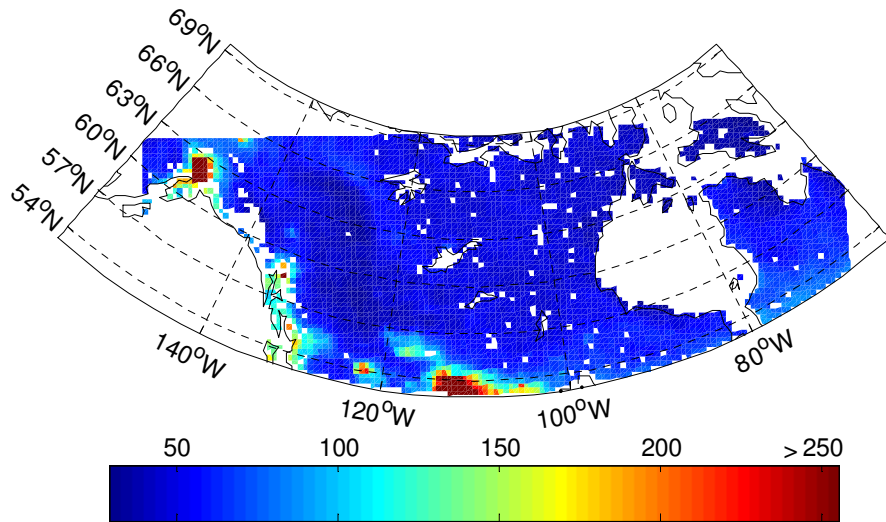


## Effects of biogenic nitrate chemistry on the $\text{NO}_x$ lifetime

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**Fig. 7.** WRF-Chem results for **(A)** fractional net  $\text{NO}_x$  loss to organic nitrates, **(B)** fractional net  $\text{NO}_x$  loss to  $\text{HNO}_3$ , and **(C)** fractional net  $\text{NO}_x$  loss to peroxy nitrates. The net chemical loss is defined as the sum of the net chemical loss to different classes of  $\text{NO}_y$  including organic nitrates, peroxy nitrates, and nitric acid (full details can be found in Appendix B). If the net chemical loss is less than zero for any particular class, the net loss is set to zero. The results are sorted by the effective  $\alpha_{\text{eff}}$  value as calculated using Eq. (A2). The triangles represent  $0.5\% \leq \alpha_{\text{eff}} < 2\%$ , the open circles are  $3\% \leq \alpha_{\text{eff}} < 4\%$ , and the squares are  $\alpha_{\text{eff}} \geq 5\%$ .



**Fig. B1.**  $\text{NO}_x$  ( $=\text{NO}+\text{NO}_2+\text{NO}_3+2*\text{N}_2\text{O}_5$ ) concentration (pptv) over the WRF-Chem domain. This concentration represents the boundary layer average over two weeks of simulation.

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