

**We thank the referees for their helpful comments. Below we have responded to each comment individually. Responses to each comment are in bold.**

Comments from Anonymous Referee #1

1. p 20680 line 17

have the nighttime performance of WRF been evaluated? If so provide a reference.

**We are unaware of an evaluation of the nighttime performance of WRF in a remote, forested environment.**

2. p 20681 line 9

the major role of RONO<sub>2</sub> at low NO<sub>x</sub> is partly driven by the decrease in OH. There is a lot of uncertainty regarding OH concentrations under low NO<sub>x</sub> conditions, especially in the biogenic rich environments the authors focus on. Could the authors comment on the sensitivity of their results to OH concentrations under low NO<sub>x</sub>? How does the use of a faster isomerization rate for isoprene peroxy radicals affect their results (e.g., [3]). One would expect a much more limited influence of organic nitrate (greater OH concentrations, smaller fraction of RO<sub>2</sub> reacting with NO).

**Since both HNO<sub>3</sub> and RONO<sub>2</sub> production are a function of OH (Rosen et al., 2004), uncertainty in the OH concentration stemming from isomerization reactions only affects our results insofar as the concentration of RO<sub>2</sub> that reacts with RO<sub>2</sub> is lower (as noted by the referee). If we increase the isomerization rate by an order of magnitude, the fractional loss of NO<sub>x</sub> to RONO<sub>2</sub> approaches 80%, rather than 90%) for the  $\alpha=10\%$  case. Although this changes the absolute numbers, it does not affect any of our conclusions that for the branching ratios expected for remote continental regions ( $\alpha=5-10\%$ ), that NO<sub>x</sub> loss is dominated by the formation of organic nitrates. We have addressed this in the last sentence of section 4.1 by including the isomerization rate as a parameter we have investigated.**

3. p 20682 line 22

I was expecting HNO<sub>3</sub> production to be very sensitivity to P(HO<sub>x</sub>) under low NO<sub>x</sub> conditions, yet the authors suggest it is not. Could the authors clarify the mechanism at play?

**As P(HO<sub>x</sub>) increases so does the absolute production rate of both HNO<sub>3</sub> and RONO<sub>2</sub>. The production rate of HNO<sub>3</sub> is slightly more sensitive to P(HO<sub>x</sub>); increasing P(HO<sub>x</sub>) to  $1 \times 10^7$  molecules cm<sup>-3</sup> s<sup>-1</sup> (From  $4.6 \times 10^6$  molecules cm<sup>-3</sup> s<sup>-1</sup>) causes the fraction NO<sub>x</sub> loss to RONO<sub>2</sub> at  $\alpha=10\%$  to approach ~84% rather than ~90%. This change is small enough that there is no change to our conclusion that RONO<sub>2</sub> formation is an important NO<sub>x</sub> loss process under low NO<sub>x</sub> conditions. We have clarified this by changing the last sentence of 4.1 to read:**

**We find that the basic conclusion of our results, that organic nitrate formation is an important NO<sub>x</sub> loss under low NO<sub>x</sub> conditions, is insensitive to wide variations in the assumed parameters.**

4. p 20684 eq. 5

(a) It seems to me the  $\alpha$  in eq. 5 is different from  $\alpha$  in R3a. This is because  $\text{RONO}_2$  is considered a terminal  $\text{NO}_x$  sink in the chemical mechanism used in the steady state mechanism, while (as noted by the authors later), there are evidence many  $\text{RONO}_2$  can be photooxidized quickly. Hence, I believe  $\alpha$  (eq. 5) represents the overall loss of  $\text{NO}_x$  following  $\text{RONO}_2$  formation. This should be clarified.

**The  $\alpha$  values in Eq. 5 and R3a are the same as defined in the steady-state model. In a model that takes into account transport then we agree with the referee that the denominator of Eq. 5 should reflect the instantaneous net  $\text{NO}_x$  loss to organic nitrates. We believe that it is incorrect to reflect the instantaneous  $\text{NO}_x$  loss to  $\text{RONO}_2$  simply by changing the  $\alpha$  value. The  $\text{NO}_x$  source from organic nitrates will depend on the history of the airmass and not (necessarily) on the local chemistry. Therefore, when transport is included the appropriate denominator in Eq. 5 would be:**

$$k_{\text{OH}+\text{NO}_2}[\text{NO}_2][\text{OH}] + \alpha k_{\text{RO}_2+\text{NO}}[\text{RO}_2][\text{NO}] - \delta k_{\text{RONO}_2 \text{ loss}}[\text{RONO}_2]$$

**where  $k_{\text{RONO}_2 \text{ loss}}$  represents the total effective first order loss rate of  $\text{RONO}_2$  and  $\delta$  represents the fraction of this loss that returns  $\text{NO}_x$  to the atmosphere (rather than removing it - e.g., deposition).**

**We have added a brief discussion of this to section 5.**

(b) Following on the previous comment, the steady state model does not represent the dependence of  $\alpha$  (eq. 5) on OH (and other oxidants): under low OH,  $\text{RONO}_2$  behaves like a terminal sink, while under higher OH, it can be seen as a temporary reservoir (thus reducing  $\alpha$ ). This effect may account for some of the differences between the steady state and WRF-Chem results.

**As per the answer to the previous comment, we disagree that  $\alpha$  has an OH dependence. The  $\alpha$  value is representative of the VOCs present and should not be manipulated to account for the  $\text{NO}_x$  recycling from  $\text{RONO}_2$  oxidation which depends on the history of the airmass. Furthermore, it is likely that some fraction of the  $\text{RONO}_2$  is removed from the atmosphere via processes such as deposition and thus is a permanent sink of  $\text{NO}_x$ . Complex processes such as that cannot be represented by changing the local chemistry. We agree with the referee that the  $\text{NO}_x$  recycling from  $\text{RONO}_2$  is important and that is why we used the WRF-Chem model to investigate how that process could affect our results (see p. 20685 line 27).**

5. Section 6 The authors use a 3D model to illustrate the applicability of the conclusions derived from the steady state model. I think this study would greatly benefit from a more thorough discussion of the results of the 3D model.

(a) to my knowledge, WRF-Chem has not been evaluated in boreal regions. The authors should present a short comparison between models and observations (ozone, alkyl nitrate), to convince

the reader the model performs reasonably well and then illustrate the sensitivity of boreal ozone to the treatment of alkyl nitrates (cf. point (c))

**This comparison is available in Browne (2012). Our main goal in this manuscript (as stated in the introduction) is to present a straight-forward guide for thinking about the first order impacts of RONO<sub>2</sub> chemistry on NO<sub>x</sub> and ozone production. Incorporating detailed CTM runs is beyond the scope of this goal as it will introduce added complexity due to changes (for instance) in peroxy nitrates and OH. Some of these effects have been investigated by others previously (e.g., Ito et al., 2007)).**

(b) many chemical transport models do not include a specific treatment of terpenes and it would be of interest to show how sensitive boreal ozone is to their chemistry. How does the OPE change when terpene chemistry is included? Can this change be attributed to changes in the local removal of NO<sub>x</sub> (through RONO<sub>2</sub>), the local production of O<sub>3</sub> (through increase in P(RO<sub>2</sub>)), and the long-range of transport of organic nitrate (including PAN)? How sensitive are those conclusions to uncertainties in chemical mechanisms, e.g., terpene chemistry, OH concentration under low NO<sub>x</sub>?

**We agree with the referee that these are interesting questions and should be explored in detail. We do not believe any of them will change the core conclusions of the present paper and answering these questions will require at least another manuscript if not several.**

(c) a new detailed mechanism of isoprene/terpene chemistry is used. It is essential that this mechanism be properly documented. This is especially critical for terpene chemistry, where this study relies on unpublished work (RACM2, future work by the authors). Alternatively and keeping with the mechanistic focus of this study, I would suggest to use an already published simplified treatment of terpene chemistry (e.g., from [1]).

**The detailed chemistry is extensively documented in Browne (2012). We have added a brief overview of the monoterpene chemistry in Appendix B2. We note that both RACM2 and the mechanism used by Ito et al. (2007) are based off of the RACM parameterization (Stockwell et al., 1997).**

6. p 20688 line 9

I am not convinced by the importance of NO<sub>x</sub> removal by organic nitrates to reconcile measured and simulated preindustrial ozone (a) the largest discrepancy is in the winter, when biogenic VOCs are low

**We have shown that under these low NO<sub>x</sub> conditions, OPE is very sensitive to changes in the assumed NO<sub>x</sub> loss. Therefore, even if the change in NO<sub>x</sub> loss from including RONO<sub>2</sub> is small, it may have a large integrated effect. We also note that the production of HNO<sub>3</sub> is lower during the winter due to lower OH concentrations (which will also affect RONO<sub>2</sub> production). It is possible that a small increase to this already small NO<sub>x</sub> loss may have important integrated effects. Therefore, we do not think the winter data is necessarily incompatible with the important role of RONO<sub>2</sub> as a NO<sub>x</sub> loss. We are not suggesting that organic nitrate chemistry is the only reason for the discrepancy (we acknowledge other**

**possibilities in the manuscript). Rather, we are saying that RONO<sub>2</sub> chemistry plays an important role in the NO<sub>x</sub> and O<sub>3</sub> budgets. Since many current condensed chemical mechanisms contain an unsatisfactory parameterization of biogenic RONO<sub>2</sub> chemistry, model results using these mechanisms will not correctly predict ozone (or if they do, it will be for the wrong reasons).**

(b) Mickley et al. [2] did include isoprene and terpene nitrates. Could the authors elaborate on the differences between their mechanisms and that of Mickley et al.? I would actually expect the discrepancy between model and measurements to be larger with the authors' more realistic treatment of BVOC chemistry.

**The monoterpene chemistry reference in Mickley et al. (2001) is a Ph.D. dissertation which we are unable to access, and we are unable find the monoterpene chemistry in other publications. Therefore we cannot comment on the differences. It is likely however that the use of different biogenic emission inventories will likely affect results such as this (as we mentioned in the manuscript). We also note that our isoprene chemistry is substantially different than that used in Mickley et al. (2001) due to the recent developments in our understanding of our chemistry.**

## **Anonymous Referee #2**

Specific comments

Abstract

The implications of these findings for representation of BVOC chemistry in CTMs and the resulting uncertainty in NO<sub>x</sub>/O<sub>3</sub> chemistry should be mentioned here. How do issues of RONO<sub>2</sub> destruction pathways (NO<sub>x</sub> recycling) influence the interpretation of the findings of this study? Also, what about implications for OPE?

**We have expanded the abstract.**

1. Introduction

p.20674 – The first paragraph of this section has insufficient references. For instance, the statement that anthropogenic NO<sub>x</sub> emissions "contribute directly to ... secondary organic aerosol" needs a reference. So too should the statement about "increasing global background ozone concentration ... making it more difficult for individual cities to reduce ozone".

**We have added references for these statements.**

p.20674, line 20 – Delete "thus".

**We have reworded this sentence.**

p.20675, l.10 – Define "lifetime of NO<sub>x</sub>" as used in this study.

**Done.**

## 2. Background

p.20676, 1.5 – Do you include loss of HO<sub>x</sub> through other NO<sub>x</sub>-related reactions (e.g., organic nitrate production) as part of the "high-NO<sub>x</sub>" criteria?

**Here we are talking in general about the broad textbook definitions of high and low NO<sub>x</sub> chemistry. Since we only examine cases where NO<sub>x</sub> is less than 500 pptv, we don't ever have a high NO<sub>x</sub> regime to define. To make our meaning clearer we changed it from:**

***in which HO<sub>x</sub> (HO<sub>x</sub> = OH + HO<sub>2</sub> + RO<sub>2</sub>) self reactions (e.g., HO<sub>2</sub> + RO<sub>2</sub>) dominate HO<sub>x</sub> loss processes***

**to**

***in which HO<sub>x</sub> (HO<sub>x</sub> = OH + HO<sub>2</sub> + RO<sub>2</sub>) self reactions (e.g., HO<sub>2</sub> + RO<sub>2</sub>) dominate radical loss processes***

### 3.1 Daytime

p.20679 – Comment on the length of NO<sub>x</sub> lifetime versus the length of daytime (or nighttime, in section 3.2), and implications for the validity of the steady-state day/night assumptions.

**We have expanded the beginning of section 3 to discuss this.**

### 3.2 Nighttime

p.20680, 1. 19 – Explain the rationale for splitting alkenes evenly between isoprene (not emitted at night) and alpha-pinene (emitted during day and night).

**In this calculation we are only attempting to approximate the BVOC composition; we do not believe that this is the actual distribution. Rather we wanted to use compounds with different nitrate yields and reaction rates. We do note that although isoprene is not emitted at night, it can persist throughout the night due to emissions in the late evening when OH is low and a decrease in boundary layer height (e.g., Brown et al., 2009). Therefore, it is not unreasonable to assume that there is some isoprene at night. If we instead assume all 400 pptv of BVOC reacts like our  $\alpha$ -pinene like species, we find that the NO<sub>x</sub> lifetime to RONO<sub>2</sub> approaches ~41 h at low NO<sub>x</sub> concentrations rather than ~37 h. This minor change has no influence on any conclusions that we make in the paper. We have added a brief discussion clarifying this choice to Sect. 3.2**

p.20680, 1. 20-21 – Explain what aerosol conditions these N<sub>2</sub>O<sub>5</sub> hydrolysis rates would correspond to.

**We have added the following:**

***Assuming a reactive uptake coefficient of 0.01, these lifetimes correspond to aerosol surface areas of approximately 2600, 433, and 144  $\mu\text{m}^2 \text{cm}^{-3}$  for the lifetimes of 10, 60, and 180 min, respectively. We note that both these surface areas and the reactive uptake coefficient are likely much larger than expected for a remote environment. Consequently, loss through the N<sub>2</sub>O<sub>5</sub> reaction should be considered an upper limit.***

### 4.1 Daytime

p.20681, 1.24 – Delete "(solid lines) and to HNO<sub>3</sub> (dashed lines)".

**Done.**

4.2 Nighttime

p.20684, 1.1 – Delete "HNO<sub>3</sub> and".

**Done.**

4.3 Twenty-four hour average lifetime

p.20684, 1.12-13 – Do you mean that the diurnal average lifetime will be similar to the daytime lifetime \*times two\* (to account for "much longer" lifetime night)?

**We have re-written this section to make our meaning more clear.**

p.20684 – How would the added complexity of a realistic diurnal cycle (e.g., driven by constant NO<sub>x</sub> emissions, resulting in accumulation of NO<sub>x</sub> to higher concentrations at night) change this estimate of 24-hr average lifetime? Would only a small fraction of RONO<sub>2</sub> production occur at night?

**Given the small variance of the nighttime lifetime as a function of NO<sub>x</sub>, higher NO<sub>x</sub> concentrations at night due to emissions into a smaller volume should have little influence on any of our conclusions. Furthermore, the WRF-Chem calculations address this added complexity and suggest that this analysis is appropriate. We have not presented any results showing the relative contributions of daytime and nighttime production to RONO<sub>2</sub> since our focus here is to discuss the factors controlling NO<sub>x</sub> and not NO<sub>y</sub>.**

5. Ozone production efficiency

p.20684, 1.22 – Change "and ozone loss" to "and NO<sub>x</sub> loss".

**Done.**

p.20685, 1. 3-9 – Do alkyl nitrates serve the same reservoir role as peroxy nitrates, or should they be considered as "terminal" sinks for NO<sub>x</sub> in this context? What are the implications for OPE? (This issue is touched on somewhat in the Discussion section.)

**We have elaborated more on this (see response to Referee 1 #4).**

6. Boreal forest

p.20687 – This "net loss" formulation is very sensitive to local conditions, in particular to the local supply of NO<sub>x</sub> emissions versus the transport of organic nitrates (alkyl and peroxy) from upwind regions.

**We agree with the referee that this formulation is sensitive to the local conditions. However, we believe that this is the correct formulation of the NO<sub>x</sub> loss for calculating properties such as OPE (see response to Referee 1 #4). We have emphasized this at the top of p 20686.**

## 7. Discussion

p.20689 – What are the key uncertainties in RONO<sub>2</sub> chemistry (and biogenic RO<sub>2</sub> in general) and how sensitive would the NO<sub>x</sub> lifetime and OPE results presented here be to these uncertainties? Do the ranges of possibilities considered here (alpha parameter, etc.) span much of the uncertainty in biogenic RO<sub>2</sub> chemistry, or are there other significant uncertainties (e.g., current competing understandings of isoprene chemical mechanisms under low-NO<sub>x</sub> conditions [Peeters et al., Paulot et al., etc.])?

**We have expanded and re-structured our discussion to touch on some of these concerns.**

Table 1 – Table footnote "e" seems to be incorrect.

**Fixed.**

## References

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