Reply to Referee #1

We are grateful to Referee #1 for the insightful comments which we believe have improved the manuscript. Detailed responses are provided below.

Review of Pratt et al. (2012), *Contributions of individual reactive biogenic volatile organic compounds to organic nitrates above a mixed forest*

8/24/2012

Summary

This paper utilizes a simplified 1-D chemical-transport model to estimate the diurnal cycle and vertical profile of speciated BVOC-derived organic nitrates over a rural mixed deciduous forest during summertime. The model is constrained to some extent by previous observations of branch-level BVOC emissions and canopy-level trace gas concentrations and meteorology. Much of the specific reaction parameters (rates and yields) are unknown and must be estimated; indeed, this fact is one of the main messages of the paper. Model results demonstrate (perhaps not surprisingly) that isoprene and monoterpenes are the dominant BVOCs during day and night, respectively. One interesting result is the importance of daytime NO3-isoprene chemistry. The study concludes with a number of recommendations for future research efforts and a reminder of the role of RONO2 as a reactive nitrogen reservoir.

This paper will be suitable for publication in ACP after consideration of the following.

General Comments

1. It is somewhat curious that the authors elect to build their own simplified 1-D model, despite the growing abundance of more sophisticated (though not necessarily better) 1-D models described in the literature (CACHE, CAFE, etc.). While I do not think this greatly affects the results of this paper, more could be gleaned from a model with a more resolved canopy – for example, the gradient in OH vs. NO3-driven chemistry driven by light attenuation inside the canopy, or the role of soil NOx vs. advected NOx. I would just like to know why the authors chose to not use something like CACHE, especially given that they use this model to constrain diffusion. Perhaps those building the fancy models need make such tools more accessible to the broader community.

   The model began as a box model, similar to the previous work of Giacopelli et al. (2005), and evolved into a 1-D model when it became apparent that it would benefit from consideration of vertical transport. The unique aspect of this model is that it tracks primary and secondary $RONO_2$ formation from 57 individual BVOCs with speciation of many isoprene nitrates based on recent laboratory studies. We are not aware of any other currently-available model with this level of explicit BVOC-$RONO_2$ photochemistry. However, we are interested in incorporating this $RONO_2$ chemistry into more complex 1-D models in the future.

2. Parts of the model description are somewhat ambiguous or lacking in detail. I will try to point these out in specific comments below.

   Thank you for these comments. As noted in the responses below, we have addressed these specific comments to improve the model description.

3. My biggest concern is that emissions alone are not sufficient to account for the measurement BVOC, leading to under-predictions of isoprene at night and MT, MVK and MACR throughout the diel cycle. It is stated on p. 17047-17048 that these concentrations are "within the range of measured variability," which is true, but there is clearly a systematic bias. Moreover, it is stated multiple times throughout the manuscript that these under-predictions directly affect calculated RONO2 concentrations and partitioning. This is likely due to a combination of issues with emissions and advection. Arguably, a more appropriate "base" scenario would constrain BVOC directly to observations in the appropriate model layer and use the observed relative emission rates of individual MT to speciate these compounds; emissions could then be included for the remaining compounds for which ambient measurements are not available. At the very least, a more quantitative assessment of how the under-prediction of MT, MVK and MACR propagates into RONO2 results is warranted.

   We chose to simulate the emissions based on branch-level emissions measurements to ensure that, for example, we capture the distribution of highly reactive BVOCs that react, and possibly form $RONO_2$ species, prior to arrival at 12 m above the forest canopy. In this regard, a prior reviewer insisted that it was best to not fully constrain the BVOC emissions based on the measurements. The minimum, base, and maximum emissions scenarios show the large uncertainty and variability associated with branch-level emissions measurements and how these relate to modeled BVOC and oxidation product concentrations (e.g., Figures 1, 2, and 6, as well as discussion throughout). This examination is valuable because it is often not included in models, and it is important to advance our understanding of speciated BVOC emissions and possible impacts of BVOC emissions variability on BVOCs and oxidation products.

   With these emissions scenarios, we can examine the range in the predicted $RONO_2$ concentrations due to these emissions uncertainties and variability, as previously stated on p.17050 of the original manuscript. Additional statements of the predicted $RONO_2$ concentrations for the minimum and maximum emissions scenarios have also been added to the discussion to emphasize this point further. In particular, it is now noted in the monoterpene nitrate section that the maximum emissions scenario, which showed improved agreement with the measured MT concentration, is likely more representative of the monoterpene nitrate concentrations during the nighttime maximum. In addition, since the maximum MT scenario likely better represents the $RONO_2$ produced from these species, the MT $RONO_2$ figure has been changed to show the results of the maximum MT scenario, rather than the base case. This information also provides important feedback to those modeling monoterpene emissions.

Specific Comments

P. 17034, l.10 and p. 17035, l.5: Regarding the effect of RONO2 on ozone production, you might also reference these two papers: (Farmer et al., 2011; Paulot et al., 2012).

> *These references have been added.*

P. 17035, l.29: You might also site (Rinne et al., 2012).

> *This reference has been added.*

P.17037, l.25: Any particular reason for choosing 4 km as the top of the model? Is something gained by having a few boxes in the free troposphere?

> *Sensitivity tests with the 1-D model described by Bryan et al. (2012) found that a higher model height provided a better description of boundary layer* K_h*. However, given the very low modeled BVOC and* $RONO_2$ *concentrations at this height, it did not significantly change, or negatively impact, the results discussed, as this reviewer suggests.*

P17038: Please provide more details regarding how the model is run (time step/intervals, spin-up time, etc.).

> *This information has been moved to the beginning of section 2.2, as suggested.*

P. 17038, l.4: I think it would be better to define D(z,t) as the rate and incorporate hz inside the definition of D later on.

> *Good point. This has been changed as suggested.*

P. 17038, l.7: “bin height” is a little ambiguous, as this could be taken as referring to the height above the ground. Better to call it “bin width.”

> *This is a good point. The text has been changed throughout the model description, as suggested.*

Also, strictly speaking, I believe the flux should be divided by the difference between the centers of two adjacent boxes that are mixing ($\Delta z = z2 - z1$), but this is a minor issue if your bin width is not changing dramatically from one point to the next.

> *Yes, indeed, in the model, the flux is calculated using the centers of the adjacent bins. This has been clarified in the model description*

P.17039, l.24: again, it might be better to say “width” rather than “height.” Also, you should explicitly state that all of the leaf biomass is assumed to exist in the lowermost bin.

> *We assume that the reviewer is referring to pg. 17040 and have changed “height” to “width” there. As suggested, this assumption is also now restated at this point in the text.*

P. 17042, l.1: it would also be useful to see a nighttime KH profile in Fig. S1, as this quantifies the inhibition of nighttime mixing that is stated to be important later on.

> *The K_H profile from 04:15 EST has now been added to Fig. S1 to provide a day vs. night mixing comparison.*

p. 17042, l.4: Please provide plots of the diurnal cycles of OH, O3 and NO3 in the supplement.

> *These are now included in the supplement (now Figure S2).*

p.17042, l.25: Given that L is defined as a rate in Eq. (1), _t should not be included in this equation.

> *This has been corrected.*

p.17042, l.26: the model time step should be stated at the beginning of Sec. 2.2.

> *As suggested, the time step is now stated in section 2.2.*

p.17044, l.3: remove _t.

> *Done.*

p.17044, l.5: “Low NOx” is an increasingly dangerous term to use. What was the range of NO concentrations? What is the range/typical values of beta?

> *This is a good point. The term “low NO_x” has been removed. A diurnal plot of β has been added to the supplemental information (Figure S3). In addition, the average diurnal ranges in [NO] and β are now discussed in this section (2.2.4).*

p.17044, l.19: Can you estimate how much this uncertainty would affect beta and thus nitrate abundance/partitioning?

> *It was stated in the manuscript that the result of the uncertainty associated with the HO_2 measurements is that the calculated β and organic nitrate production represent lower limits. We now elaborate on this further in the supplemental information, where it is shown that if actual HO_2 concentrations were half the measured values due to an interference from isoprene RO_2, this translates to an average diurnal increase in β of*

0.12 (range of 0.02-0.17). As shown in the added figure of the diurnal cycle of β, the primary effect would be to increase $RONO_2$ production in the mid-day and nighttime.

p.17046, l.8: It seems better to define these by their bin-center rather than starting heights.

The bin mid-point was used previously, but this was not stated clearly in the text. It has been clarified in section 2.2.5.

p. 17047, l.10: remove _t. Also, to keep consistent with my recommendation for Eq. (1), you could divide vd by hz here.

Done.

p.17048: Section 3.2 seems a little out of place relative to the rest of the manuscript, though it is still important. Perhaps you can tie this more to RONO2; for example, how much do you think the missing reactivity would alter your RONO2 abundance if it was isoprene-like versus monoterpene-like?

To place further emphasis on the main focus of the manuscript ($RONO_2$ species), the OH reactivity section has been removed from the manuscript.

p.17050, l.14-16: How do you distinguish RONO2 "transported upwards" from RONO2 that is produced aloft after precursors are transported upwards?

This is a good point. The sentence has been reworded: "In the morning hours, enhanced vertical mixing led to increased simulated [$RONO_2$] aloft…".

p. 17050, l.23: Why is there not a more thorough comparison with measured RONO2? This seems odd, if the observations are available. Also, the modeled values of 4 – 137 pptv encompass the range of 10-40 pptv reported by (Thornberry et al., 2001), seemingly at odds with your value of 2-48%.

In Thornberry et al. (2001), $\Sigma RONO_2$ refers to the sum of individually measured C_3-C_5 alkyl nitrates, rather than the now often measured total $RONO_2$ via thermal dissociation-laser induced fluorescence. As previously noted in the text, unfortunately, only 7 data points of concurrently measured $RONO_2$ and NO_y data were available for sunny/partly-sunny days in the summer of 2008. Considering the uncertainty associated with so few data points, we have removed this data from the manuscript and revised the section.

It is an excellent point that we can do additional comparisons with $RONO_2$ measured in other years. Therefore, we have added a figure and corresponding discussion comparing the sum of the concentrations of the two most abundant modeled (~12 m above forest canopy) isoprene nitrate isomers ($RONO_2$-4,3 and $RONO_2$-1,2) with the two most abundant isoprene nitrate isomers measured (~10 m above the forest canopy) at UMBS (Ford, 2001; Giacopelli et al., 2005), which are believed to be these species.

p.17052, l.17: I am not clear on what is meant by this statement. Perhaps you could rephrase or expound.

> *Since the soil NO_x flux is ~24% of the simulated local $RONO_2$ production rate, this suggests significant local organic nitrate formation involving locally-emitted NO_x. This has been clarified in the manuscript.*

p.17052, l.18: Given that advection is such a substantial sink and that it is quite uncertain (e.g. looking at MVK and MACR), it could be useful to do a sensitivity study where advection is decreased by e.g. a factor of 2. Just to see how much RONO2 concentrations increase. The applied sensitivity factor could be chosen to optimize agreement of modeled and measured MVK and MACR, if in fact these are mainly lost via advection.

> *As stated in the original manuscript (p.17047, l.23-26), the underprediction of MVK and MACR is likely due to the fact that the model does not include species advected to the measurement site. Instead, it concentrates on the oxidation of locally emitted BVOCs; thus, an underprediction of MVK and MACR is expected. Also, as suggested, a sensitivity study was completed to examine the effects of decreasing advection by a factor of 2. The impact of this was to increase MVK+MACR concentrations by a factor of 2 on average; however, [MVK+MACR] was still underestimated compared to measured, particularly in the morning, when isoprene concentrations were also under-predicted. This result is now noted in the main text in section 3.1. The effects on total locally-produced biogenic $RONO_2$ were similar with concentrations increased by a factor of 1.7 on average.*

p.17053, l.25-28: This list of percentages is not particularly helpful; I think the previous and subsequent sentences convey the point sufficiently well.

> *We appreciate this suggestion and have removed the sentence.*

p.17056: The changes in RONO2 levels could be more succinctly illustrated with a few pie charts.

> *Thank you for the suggestion. We have added a figure (Figure S9) showing the contributions of different BVOC classes to $RONO_2$ concentrations for the base scenario compared to the future forest scenarios.*

p.17059, l.28: this information on NOx levels should appear much earlier (see above comments).

> *The range of the diurnal average [NO] is now given in section 2.2.4.*

Table 1 – Given the larger number of compounds listed here, would it be possible to list them in order of decreasing importance for the RONO2 budget? This would help the reader easily identify the key compounds mentioned in the conclusions.

> *This is an excellent suggestion. We have reordered the BVOCs based on* $RONO_2$ *concentrations and moved species contributing <0.5 ppt, at any time at ~12 m above the forest canopy, to a table in the supplemental information.*

Figs. 1,2,5: missing borders

> *Missing borders have been added.*

Fig. 4 caption: The middle two sentences are a little confusing and seem unnecessary, or at least more appropriate for the text than a caption.

> *These sentences were previously added since it is difficult to discern the sesquiterpene and other BVOC nitrates in the plot at very low concentrations. These sentences have been revised so that this point is clearer.*

Supplement, p.3: the description of how emissions were scaled seems ambiguous. Are scaling factors applied to all emission parameterizations for the base scenario? This seems to be the case for isoprene (-30%), but is this also the case for MT and SQT (e.g. lines 64 and 68)?

> *Yes, as stated, MTs and SQTs were also scaled, by +107% and +130%, for the base emission scenario. The wording of this section has been revised to make this clearer.*

Technical Comments

P. 17040, l.1: 95,000

> *Thank you for pointing out this typo. This has been fixed.*

P.17041, l.9: delete up arrow

> *Done.*

p.17043, l.6 and l9: Table S4

> *Corrected.*

p.17043, l.7: “The reaction parameters for isoprene…”

> *This sentence has been modified for clarity.*

p.17044, l.23: do you mean to site Tables 2-3?

> *Yes, thank you. This has been corrected.*

p.17051, l.17: This looks more like ~550m than 200m to me.

This is correct and has been changed from ~200 m to ~500 m.

p.17055, l.5: Section

Corrected.

p.17056,l.24: base emission scenarios

Corrected.

Supplement p.2, l.45: scenarios were based

Corrected.

Supplement p.2, l.50: (0.14 K-1) was used.

Corrected.

Supplement p.4, l.84: NO + O2

Corrected.

Supplement p.4, l.85: Table S3

Corrected.

References:

Bryan, A. M., Bertman, S. B., Carroll, M. A., Dusanter, S., Edwards, G. D., Forkel, R., Griffith, S., Guenther, A. B., Hansen, R. F., Helmig, D., Jobson, B. T., Keutsch, F. N., Lefer, B. L., Pressley, S. N., Shepson, P. B., Stevens, P. S., and Steiner, A. L.: In-canopy gas-phase chemistry during CABINEX 2009: sensitivity of a 1-D canopy model to vertical mixing and isoprene chemistry, Atmos. Chem. Phys. Discuss., 12, 12801-12852, 2012.

Ford, K. M.: The study of organic nitrates in the field and in the laboratory, M.S., Purdue University, West Lafayette, IN, 85 pp., 2001.

Giacopelli, P., Ford, K., Espada, C., and Shepson, P. B.: Comparison of the measured and simulated isoprene nitrate distributions above a forest canopy, J. Geophys. Res., 110, doi:10.1029/2004JD005123, 2005.

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_y during the PROPHET summer 1998 intensive, Journal of Geophysical Research, 106, 24359-24386, 2001.