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.

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

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.

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).

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

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?

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

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

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.” Also, strictly speaking, I believe the flux should be divided by the difference between the centers of two adjacent boxes that are mixing ($\Delta z = z_2 - z_1$), but this is a minor issue if your bin width is not changing dramatically from one point to the next.

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.

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

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

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

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

p.17044, l.3: remove Δt.

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?

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

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

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

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?

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

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%.

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

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.

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.

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

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

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.

Figs. 1,2,5: missing borders

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.

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)?

Technical Comments

P. 17040, l.1: 95,000

P.17041, l.9: delete up arrow

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

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

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

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

p.17055, l.5: Section

p.17056,l.24: base emission scenarios

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

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

Supplement p.4, l.84: NO + O_2

Supplement p.4, l.85: Table S3

References

Farmer, D. K., Perring, A. E., Wooldridge, P. J., Blake, D. R., Baker, A., Meinardi, S., Huey, L. G., Tanner, D., O.Vargas, and Cohen, R. C.: Impact of organic nitrates on urban ozone production, Atmos. Chem. Phys., 11, 4085-4094, 2011.

Paulot, F., Henze, D. K., and Wennberg, P. O.: Impact of the isoprene photochemical cascade on tropical ozone, Atmos. Chem. Phys., 12, 1307-1325, 2012.

Rinne, J., Markkanen, T., Ruuskanen, T. M., Petaja, T., Keronene, P., Tange, M. J., Crowley, J. N., Rannik, U., and Vesala, T.: Effect of chemical degradation on fluxes of reactive compounds - a study with a stochastic Lagrangian transport model, Atmos. Chem. Phys., 12, 4843-4854, 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_y during the PROPHET summer 1998 intensive, J. Geophys. Res., 106, 24359-24386, 2001.