

We thank the two reviewers for their careful reading of the manuscript and their detailed comments. Our responses are shown below in green, with quoted text indented and new text in **bold**.

Anonymous Referee #1

This paper advances our understanding of isoprene and monoterpene degradation chemistry in a regional modelling framework. It specifically implements a range of updates to the isoprene and monoterpenes derived nitrates and compares the model results to those observed by field campaigns in the southern US. These observational datasets provide a uniquely comprehensive assessment of the species produced through this chemistry. The paper shows the role of a range of new processes notably the heterogeneous processing of RONO₂ species.

This paper is comprehensive, well written and advances our understanding of this important area of atmospheric chemistry. My suggestion is that the paper is published but have one potential addition to the paper and a couple of minor comments below.

My major difficulty reading the paper is that there is little discussion of the impact of the addition of all of this chemistry on the wider composition of the atmosphere. How different are the North American concentrations of NO_x, O₃, PM, OH etc after all of this new chemistry has been added? How much difference does this make overall to the chemistry of the atmosphere? Should this chemistry be included in all modelling or is it of niche interest? This final summing up seems to be missing from the paper which makes it a little dissatisfying overall. The authors presumably have simulations with the old chemistry and the new chemistry or could readily perform a calculation with the isoprene / monoterpene nitrate chemistry switched off etc and a new section which provides some details of the overall impact would give the reader some sense of how important this is and whether they should care or not about the chemical detail described in the paper.

We agree with the reviewer that quantifying the impacts of the chemistry changes on the wider atmospheric composition would be of great interest – and this will be the topic of a follow-up paper. We would like to separate this analysis from the current paper because it is already very long and is thematically focused on the organic nitrates, so introducing additional analysis of NO_x, O₃, OH, etc. would weaken the overall focus, increase the length, and decrease the readability.

In addition, testing the old vs. new chemistry will require significant additional computational burden, as our model development tests were all performed at coarse resolution and each change was added linearly. A thorough accounting of the impacts will require multiple additional simulations, ideally with each change tested independently and at a finer resolution than used for our test simulations. We prefer to leave this more systematic analysis to a subsequent paper.

The authors gloss over a few of their mechanistic choices. They should put the chemical mechanism used in the work into supplementary material for both the gas, heterogeneous and aerosol phase chemistry and include more details of how they have changed absorption cross-sections from the IUPAC recommendation (presumably the quantum yield is 1?).

Updates to the isoprene oxidation mechanism are provided in the Supplement to Travis et al. (2016), and we now state this in the text at the start of Section 2.1:

All updates to the isoprene oxidation mechanism are provided in Travis et al. (2016) Tables S1 and S2.

We now provide the monoterpene nitrate scheme in the Supplement, and state this in the text at the start of Section 2.2:

Our implementation is summarized in Fig. 3 and described briefly below, with the full mechanism available **in the Supplement (Tables S1-S3) and at** http://wiki.seas.harvard.edu/geos-chem/index.php/Monoterpene_nitrate_scheme.

We now provide the aerosol uptake coefficients in the Supplement (as well as in the text), and state this in the text in Section 2.3:

We assume an uptake coefficient of $\gamma=0.005$ for isoprene nitrates (from both daytime and nighttime chemistry) and $\gamma=0.01$ for all monoterpene nitrates (**Table S4**).

We now provide more details of the change to absorption cross sections in Section 2.2 and Table S5. We also clarify in the text that the IUPAC recommendation used previously was not for the carbonyl nitrates but for their monofunctional analogues.

Here we increase the absorption cross sections of the carbonyl INs **following the methodology of Müller et al. (2014, Sect. 2)**. Briefly, we first use the PROPNN cross section measured by Barnes et al. (1993) to calculate a wavelength-dependent cross section enhancement ratio (r_{nk}), defined as the ratio of the measured cross section to the sum of the IUPAC-recommended cross sections for associated monofunctional nitrates and ketones. We then calculate new cross sections for ETHLN, MVKN, and MACRN by multiplying r_{nk} by the sum of cross sections from appropriate monofunctional analogues (Table S5). The new cross sections are 5-15 times larger than in the original model, which used the IUPAC-recommended cross section of the monofunctional analogue tert-butyl nitrate for all carbonyl nitrates (Roberts and Fajer, 1989). **For all species, we calculate photolysis rates assuming unity quantum yields, whereby the weak O–NO₂ bond dissociates upon a rearrangement after photon absorption to the carbonyl chromophore (Müller et al., 2014).**

In a couple of places we are re-assured that the kinetic choices provide the best fit to the observational data (“Although simplified, we find this parameterization improves the model fit relative to the SEAC4RS and SOAS”, “In any case, the choice of hydrolysis lifetime does not affect the concentration of gas-phase RONO₂ species (because pRONO₂ cannot re-partition to the gas phase in the model), and we find this value provides a reasonable match to AMS measurements of total pRONO₂ at the surface during SOAS and SEAC4RS”). Could these results in the supplementary material so that the readers can judge these for themselves.

As described above, changes to the model chemistry were added linearly and tested at coarse resolution, so we are unable to add a figure showing “before and after” results for each of these changes. We have edited the text to more clearly reflect that our choices are not necessarily a “best” fit but rather a reasonable fit:

Although simplified, we find this parameterization **provides a reasonable fit** to the SEAC⁴RS and SOAS observations. . . .”

In both cases, we have added reference to Sect. 3 and 4 where figures showing the fit of the model to observations are shown and results discussed in more detail.

I found sections 3,4,5 rather long for my taste. Would it be possible to put in some sub-section headings to help split those up and allow the reader to find specific bits of information more easily?

We have now split Section 3 into four subsections:

- 3.1 Isoprene and monoterpenes**
- 3.2 First generation RONO₂**
- 3.3 Second generation RONO₂ and pRONO₂**
- 3.4 RONO₂-HCHO relationship**

We have now split Section 4 into two subsections:

- 4.1 Speciated versus total RONO₂**
- 4.2 RONO₂ composition**

Section 5 is less than 2 pages in length, and does not neatly divide into separate sections, so we have left it as is without subsections.

Anonymous Referee #2

Hydrolysis is receiving increased attention in chemical transport models as a way to remove organic nitrate (thus NO_x) from the atmosphere by converting it to nitric acid. Hydrolysis that has been implemented in (CTMs) chemical transport models thus far (CAMx: Hildebrandt Ruiz and Yarwood 2013, CMAQ: Pye et al. 2015) assumes that hydrolysis occurs after semivolatile organics partition to an organic-rich particle. The process of semivolatile organics (monoterpene-derived) undergoing hydrolysis has been demonstrated in laboratory work (e.g. Boyd et al. 2015, Bean and Hildebrandt Ruiz 2016). The timescales for hydrolysis used in CTMs ranges from 3 to 6 hours or longer. Thus, the work of Fisher et al., with a 1 hour hydrolysis represents a significantly faster rate of hydrolysis. Indeed, more than half of the organic nitrates in table 1 have a sub 2-hour lifetime. The irreversible reactive uptake formulation used by Fisher et al. also differs from the equilibrium vapor-pressure based approach. As a result, the Fisher et al. work represents a significantly different approach than has been used thus far for hydrolysis and creation of particulate organic nitrate. The implications for ozone and aerosol may motivate future work to adopt similar formulations and parameter choices should be fully justified.

My main question is whether or not another set of parameters than those examined here would provide equally good model performance. For example, there are no sensitivity simulations to indicate if the 1 hour hydrolysis is significantly better than say a 6 hour hydrolysis. It would be useful to know if another set of conditions (specifically lower BVOC emissions, higher NO_x emissions, slower hydrolysis, slower uptake of organic nitrates) also leads to a consistent picture of southeast chemistry. More detailed comments follow.

Throughout our model development and testing, we were unable to find another set of conditions that was consistent with the ensemble of measurements (although that does not mean they do not exist).

With respect to the specific set of conditions mentioned:

- Higher NO_x emissions are not consistent with the SEAC⁴RS data, as shown in detail in Travis et al. (2016) and discussed below in response to the more detailed comments regarding NO_x.
- Lower BVOC emissions would not be consistent with the SEAC⁴RS or SOAS observations, as shown in this paper (see also point 6 below regarding BVOC biases). In particular, lower isoprene emissions (already reduced by 15%) would be inconsistent with observed HCHO as described by

Zhu et al. (2016; now available in ACPD), who show a small negative bias of -3% in mixed layer HCHO and an overall negative bias of -10% in total column HCHO.

- Slower (or in some cases, reversible) uptake of organic nitrates is plausible, and we have now made this explicit (see point 4 below). However, slower uptake would significantly degrade model agreement with gas-phase organic nitrates that are currently well represented (e.g., ISOPN, MVKN+MACRN), and this would need to be paired with strengthening (or adding) alternative sinks for these species. The uncertainty of these sinks is already discussed in the context of the ISOPN yield in Section 3.2 (“Including both faster ISOPN photolysis and uptake to the aerosol phase could be a means to accommodate a higher initial ISOPN yield... although both sinks remain unverified. The nature of the sink has implications for NO_x recycling from isoprene nitrates (photolysis recycles NO_x while uptake removes it), and this remains a source of uncertainty in our estimates of the impacts of RONO₂ on the NO_x budget.”)
 - Slower hydrolysis is also plausible. In our current simulation, this would only impact pRONO₂ (the additional HNO₃ source is minor, as detailed in points 5 and 12 below). We already discuss the implications for pRONO₂ in Section 4.2 (“...it is also likely that simulated pRONO₂ is underestimated because of our assumption that all pRONO₂ species undergo rapid hydrolysis...”)
- More details on several of these points are provided in response to the detailed comments that follow.

We also note that the short lifetimes of organic nitrates in Table 1 are consistent with an independent analysis of SOAS data by Romer et al. (currently in ACPD), that finds an average lifetime for reactive RONO₂ of less than 2 hours. We now cite this work in Section 5.

Travis et al. is referenced as the basis for the gas-phase oxidant chemistry in this work. In that work, they indicate NO_x emissions from the EPA NEI are too high by 50%. I assume the simulations in this work (Fisher et al.) reduce NO_x emissions consistent with Travis et al.

The reviewer is correct. We now clearly specify this in Section 2 (before 2.1):

Our simulation is identical to that used in Travis et al. (2016), Yu et al. (2016), and Zhu et al. (2016).

Given the suspected importance of reduced NO_x emissions, I provide some comments on the Travis et al. paper (available at: http://acmg.seas.harvard.edu/publications/2016/Travis_ACPD_2016.pdf). Reducing the NEI NO_x by ~50% may imply a larger hydrolysis sink is needed in the model than is actually necessary. Comments on the Travis et al. paper:

While we are unable to make changes to the Travis et al. (2016) paper – now available at <http://www.atmos-chem-phys-discuss.net/acp-2016-110/> – the 50% decrease in NEI NO_x applied in that work is well constrained by their observations, and in any case does not inflate the hydrolysis sink used in our work. More details of both points follow.

Travis et al. decrease NEI NO_x on the basis of 2 independent data sets: the SEAC⁴RS airborne data and the NADP nitrate wet deposition fluxes (note that OMI NO₂ is not used for this purpose; see below). As stated in their paper (pg. 5, lines 23-24 and pg. 7, lines 2-4 & 13-15):

“Initial implementation of this [NEI11] inventory in GEOS-Chem resulted in a 60% overestimate of SEAC⁴RS DC-8 observations for NO_x and HNO₃, and a 71% overestimate of nitrate (NO₃⁻) wet deposition fluxes measured by the National Acid Deposition Program (NADP) across the Southeast US... Decreasing [NEI11] emissions corrects the model bias for

NO_x and also largely corrects the bias for inorganic nitrate... the model with decreased NO_x emissions reproduces the spatial variability in the [NADP] observations with minimal bias across the US. In comparison, the model with original emissions had a 60% overestimate of the nitrate wet deposition flux nationally and a 71% overestimate in the Southeast.”

These results are further supported by their Fig. 2 and Fig. 3. They also find that the change to NEI emissions removes a 12 ppb bias in boundary layer ozone relative to the SEAC⁴RS data. Combined, these datasets provide strong evidence for the validity of the NEI decrease applied in the model. The decrease is also consistent with several other studies cited in Travis et al. that find NEI NO_x emissions are too high (Fujita et al., 2012; Brioude et al., 2013; Anderson et al., 2014) .

pRONO₂ is positively dependent on surface NO_x emissions, and decreases by ~15% at the surface when NEI emissions are decreased. In other words, with the original NEI emissions, we would require a *faster* hydrolysis sink to maintain the same atmospheric concentration of pRONO₂ as in our current model. Note that we determined the most appropriate hydrolysis lifetime on the basis of the pRONO₂ concentrations, and impacts on HNO₃ are small as described in points 5 and 12 below.

1. Given the missing free tropospheric NO₂ in GEOS-Chem and the fact that boundary layer NO₂ is less than 30% of the column, how quantitative can the NO₂ column evaluation be? What is the error associated with the BEHR and NASA columns? It seems like the GEOS-Chem shape factors may not be a good representation of the NO₂ profile given the lack of NO₂ aloft. What is the detection limit/precision for surface NO₂ from OMI?

Travis et al. use OMI NO₂ only to confirm consistency with other evidence, and not as the basis for their NEI emissions reductions. Within the large uncertainties of the satellite retrievals, the OMI data do not cast doubt on the NEI NO_x emissions reductions, and further details of the retrievals are not relevant to our work in this paper.

2. The ratio of ISOPOOH to ISOPN seems degraded with the NO_x emission reduction compared to the base indicating too much RO₂+HO₂ vs RO₂+NO. Are there additional later generation products that can be examined to justify proper branching?

We find that the ISOPOOH to ISOPN ratio is not an ideal metric for testing the branching ratio because so many factors besides the branching influence each species, and the uncertainties on the measurements are large (30% for ISOPN, 40% for ISOPOOH).

The NO_x emission decrease improves simulation of isoprene nitrates, with NMB decreasing from +8% to -0.6% for ISOPN and from +23% to -10% for MVKN+MACRN (in both cases, still within the uncertainties).

We note that the ISOPOOH overestimate in the final simulation is paired with an HPALD underestimate, which could indicate that the problems in first-stage isoprene oxidation lie within the low-NO_x pathway rather than the partitioning between low-NO_x and high-NO_x pathways. Both the HPALD underestimate and the ISOPOOH overestimate may be due to kinetic uncertainties, as discussed in Travis et al. (pg. 10, lines 9-16):

“The bias for HPALD is within the uncertainty of the kinetics and measurement. Our HPALD source is based on the ISOPO₂ isomerization rate constant from Crouse et al. (2011). A

theoretical calculation by Peeters et al. (2014) suggests a rate constant that is 1.8× higher, which would reduce the model bias for HPALD and ISOPOOH and increase boundary layer OH by 8%. GEOS-Chem overestimates ISOPOOH by 74% below 1.5 km. Recent work by St Clair et al. (2015) found that the reaction rate of ISOPOOH + OH to form IEPOX is approximately 10% faster than the rate given by Paulot et al. (2009b), which would further reduce the model overestimate. It is likely that after these changes the GEOS-Chem overestimate of ISOPOOH would be within measurement uncertainty.”

For all three species, GEOS-Chem generally captures the spatial variability ($r = 0.8$ for ISOPOOH, $r=0.7$ for HPALD, $r=0.6$ for ISOPN).

3. How does the magnitude of the soil NO_x emission predicted in GEOS-Chem compare to other estimates? Does the NEI provide a comparable estimate?

Detailed discussion of the soil NO_x emission is left to the Travis et al. paper. We note that our results are not particularly sensitive to this change. As described in point 12 below, we now include a section in the supplement evaluating the sensitivity of the organic nitrates to the changes in NO_x emissions, including both NEI11 and soil NO_x reductions.

Fisher et al. (this work) comments:

4. Figure S3 indicates too many pRONO₂ compared to the AMS data during the day, particularly 13-17 local time. The diurnal profile of the model pRONO₂ (relatively flat with peak around 15 local time) also doesn't match the observed AMS profile (peak at night around 3-4 am with minimum around 15 local time). Are the isoprene nitrates too aggressively put in the particle?

This is a plausible explanation, and we have added it to the text at the end of Section 3.3:

Afternoon overestimates of pRONO₂ relative to the AMS observations (Fig. S3) are coincident with the peak in isoprene nitrates (Fig. 6), suggesting overly strong partitioning to the aerosol phase likely due to our assumption of irreversibility (Sect. 2.3).

5. I recommend performing a total NO_y and total inorganic nitrate (HNO₃ + NO₃⁻) evaluation. I didn't see a total NO_y evaluation in either Travis et al. or Fisher et al. It was a little unclear if Travis et al. included all the updates (ie monoterpenes) of Fisher et al. In any case, Travis shows that HNO₃ is high in the base. If the base includes hydrolysis, that may explain why. Furthermore, total RONO₂ is underestimated by ~50% according to Figure 10. This implies there are missing NO_x sinks (or sources) in the model.

As we now specify in Section 2 (see above), the model runs in this paper and in Travis et al. are identical, and Travis et al. include all the updates from this work.

Travis et al. evaluate total inorganic nitrate (gas HNO₃ + aerosol NO₃⁻) in their Figure 2 (top middle panel, mislabeled as HNO₃). The HNO₃ increase associated with hydrolysis (~20 ppt) is 20x smaller than the decrease associated with the reduction in NO_x emissions (~400 ppt; see Travis et al. Fig 2). We

now state at the end of Section 2.3 that hydrolysis has minimal impact on simulation of HNO_3 :

Impacts on HNO_3 are minor: compared to a simulation without hydrolysis, our simulation with a 1 hr lifetime against hydrolysis increased boundary layer HNO_3 by 20 ppt, or 2.4%.

We have not used total NO_y or inorganic nitrate to constrain our simulation because the measurements are inconsistent with one another. Depending which datasets are used, ΣNO_y as measured by the NOAA NO_yO_3 chemiluminescence instrument differs from the sum of the measured components by as much as 35% (based on median values for surface air over the Southeast US). The experimenters responsible for these measurements have yet to reconcile the differences. Until they do, we do not consider these datasets as appropriate constraints on our simulation of RONO_2 .

Similarly, measurements of total RONO_2 differ by $\sim 50\%$ between ΣANs as measured by TD-LIF and the total of the speciated components as measured by CIT-ToF-CIMS, WAS, and AMS. This is shown in Figure 10a and discussed in the text in Section 4.1. Although we offer some possible explanations in Section 4.1, we cannot arbitrate between the different measurements. Total RONO_2 in the model is underestimated relative to the TD-LIF, but not relative to the sum of the speciated measurements, and without further reconciliation of the datasets by the experimenters, we cannot use total RONO_2 as a constraint on NO_x .

6. Figure 12 shows that as the ratio of BVOC to NO_x emissions increases, the fraction of NO_x lost to RONO_2 (vs HNO_3) increases. If BVOC emissions are biased high (Fig 4 shows a NMB of 58% for isoprene and 18% for monoterpenes compared to DC8 flights) and NO_x emissions are biased low (2011 NEI is reduced $\sim 50\%$) then the model will predict too much NO_x lost to RONO_2 vs HNO_3 . Hydrolysis converts RONO_2 to HNO_3 . Another set of BVOC and NO_x emission levels and their evaluation would be useful.

It would be nice to see analysis examining the possibility of lower BVOC emissions, higher NO_x emissions, slower hydrolysis, and slower uptake of organic nitrates leading to a consistent picture of southeast chemistry.

Upon reading this comment, we realised that the normalised mean bias (NMB) values given in Fig. 4 were misleading. The NMB was calculated from all data below 1 km, but as seen in Fig. 5 there are discrepancies in the simulated profile shape above 500 m that inflate the bias at the surface. The NMB for data below 500 m is more representative for the purpose of evaluating emissions, and we now provide this instead. Because the figure shows data below 1 km but the NMB is calculated for data below 500 m, we have removed the NMB from the figure itself and instead state it in the caption:

The normalized mean bias of the simulation relative to the PTR-MS measurements in the lowest 500 m is +34% for isoprene and +3% for monoterpenes.

We have similarly updated Fig. 7.

Although there is still a positive bias for isoprene, we have already decreased isoprene emissions by 15% relative to the standard MEGAN model and it is not clear that even lower emissions would be consistent with the ensemble of measurements. We show in Fig. 6 that isoprene is biased low relative to the SOAS data, and Zhu et al. (2016) show that mixed layer HCHO currently has a very small negative bias ($-3\% \pm 2\%$) relative to the aircraft observations. The justification for the reduction in NEI 2011 NO_x emissions is discussed above. We do not feel that another set of emissions is justified.

In any case, our finding that NO_x loss to RONO_2 increases with lower NO_x emissions is consistent with the findings of Browne and Cohen (2012). They analysed an environment with different BVOC and NO_x emissions (boreal Canada) and did not include aerosol uptake or subsequent hydrolysis in their model – suggesting this result is not particularly sensitive to these uncertainties.

7. Page 7, line 32: The yield of organic nitrates from $\text{API} + \text{NO}_3$ is set to 10%. This seems to be on the low end considering the values tabulated in Fry et al. 2014 which range from 11-29% for a-pinene and 40-74% for b-pinene. Is there a specific RO_2 fate assumed for these yields?

We applied the yield from the RACM-2 mechanism on which our mechanism was built (Goliff et al., 2013; Browne et al., 2014). As the resultant MONIT was already higher than observed, we did not update this value. We have now clarified in Section 2.3 that this should be considered a lower bound: The branching ratio between these two fates is 50% nitrate-retaining for $\text{LIM} + \text{NO}_3$ (Fry et al., 2014) and 10% nitrate-retaining for $\text{API} + \text{NO}_3$ (Browne et al., 2014). **The 10% nitrate yield from $\text{API} + \text{NO}_3$ is on the low end of the observed range (Fry et al., 2014), so simulated pinene-derived MONIT should be considered a lower bound.**

Relevant reactions including rates and products are now shown in the Supplement.

8. Page 8, line 33: Is there a figure that can be referenced to show good RONO_2 performance?

As described in the response to Reviewer 1, changes to the model chemistry were added linearly and tested at coarse resolution, so we are unable to add a figure showing “before and after” results for this change. We have edited the text to more clearly state this:

Although simplified, we find this parameterization **provides a reasonable fit** to the SEAC^4RS and SOAS observations...”

We have also added a reference to Sect. 3 and 4 where figures showing the fit of the model to observations are shown and results discussed in more detail.

9. Page 9, near line 7, how was the specific lifetime of 1 hour against hydrolysis chosen? Were other values used in preliminary simulations? For the isoprene system, what is the fraction of tertiary vs. non-tertiary nitrates?

We now specify in Section 2.3:

We assume here a bulk lifetime against hydrolysis of 1 hr, which we found in preliminary simulations to provide a better simulation of pRONO_2 than longer lifetimes.

We were unable to find estimates of the fraction of tertiary vs. non-tertiary nitrates under atmospheric conditions. For first generation isoprene nitrates, the tertiary $\beta(1,2)$ isomer accounts for ~23% of the yield at the time of formation (Paulot et al., 2009). For second generation isoprene nitrates, the SEAC^4RS observations (Fig. 5) indicate a dominant contribution from MVKN (non-tertiary) + MACRN (tertiary), but cannot distinguish between the two. At this stage, for isoprene nitrates we expect the uncertainty in the uptake parameterization (see point 4 above) has a larger impact on the simulation than our choice of hydrolysis lifetime (which would change with a different uptake parameterization).

10. Page 9, line 16, in reality, the hydrolysis lifetime should affect gas-phase RONO₂. In the reactive uptake formulation of Marais et al. the uptake coefficient depends on the rate of particle-phase reaction (here hydrolysis). Faster reaction increases the uptake coefficient. It should be pointed out that this dependence of γ on hydrolysis is not captured by the model.

We now state this in Section 2.3:

In other words, our implementation of aerosol partitioning involves a two-step process of (1) uptake of gas-phase RONO₂ to form a simplified non-volatile pRONO₂ species, with rate determined by γ , followed by (2) hydrolysis of the simplified pRONO₂ species to form HNO₃, with rate determined by the lifetime against hydrolysis. **These steps are de-coupled, and we do not include any dependence of γ on the hydrolysis rate (unlike the more detailed formulation of Marais et al. (2016)).**

11. Page 13: Are the TD-LIF measurements of total ANs consistent with the SEARCH network measurements during SOAS?

We now include the following at the end of the first paragraph in Section 4.1:

An independent thermal dissociation instrument operated by the SouthEastern Aerosol Research and Characterization (SEARCH) Network also measured Σ ANs at the SOAS site and showed values that were 80 ppt higher than measured by the TD-LIF (but generally well correlated, with slope close to 1 and $r \sim 0.8$).

12. A few things indicate the NO_x emissions may have been reduced too much:

- o the total ANs are low by $\sim 50\%$ (Figure 10)
- o The ratio of ISOPOOH to ISOPN seems degraded (too high) with the NO_x emission reduction compared to the base (Travis et al. Figure 2)
- o The NO₂ columns are low compared to observations (Travis et al.) and the ability of the satellite products to determine the magnitude of a given error in surface NO₂ is unclear
- o A source of HNO₃ (hydrolysis) must be added to the model

The points relating to ISOPOOH/ISOPN and NO₂ columns are addressed above.

With respect to the total ANs underestimate, in addition to existing text discussing the discrepancy (Section 4.1, see above) we now include a new section in the Supplement:

S1. RONO₂ sensitivity to NO_x emissions reductions

We use the same simulation as Travis et al. (2016), who reduced NO_x emissions in the NEI11v1 inventory by 60% for all anthropogenic sources except power plants (equivalent to a 53% decrease in total annual NEI11v1 emissions) and also reduced soil NO_x emissions in the Midwest US by 50% (Vinken et al., 2014). Figure S5 compares model results during SEAC⁴RS before and after applying these NO_x emissions decrease. As seen in the figure, the change to NO_x emissions cannot explain the model underestimate in Σ ANs relative to the SEAC⁴RS TD-LIF measurement (-46% with original NO_x, -57% with reduced NO_x). The figure also shows that the change to NO_x emissions does not have an appreciable effect on simulation of individual RONO₂ species, which fall within the experimental uncertainties of the CIT-ToF-CIMS instrument in both versions of the model.

The new Figure S5 can be found at the end of this document.

With respect to HNO_3 , the hydrolysis was added to provide a sink for pRONO_2 rather than to provide a source of HNO_3 . In fact, hydrolysis has no appreciable impact on HNO_3 , and we now state this at the end of Section 2.3:

Impacts on HNO_3 are minor: compared to a simulation without hydrolysis, our simulation with a 1 hr lifetime against hydrolysis increased boundary layer HNO_3 by 20 ppt, or 2.4%.

13. In addition to posting the mechanism online, can full details be provided in the supporting material for future reference?

As detailed in the response to Reviewer 1, we now provide the full monoterpene nitrate mechanism in the Supplement. Updates to the isoprene oxidation mechanisms are provided in the Supplement to Travis et al.

14. While I am aware of studies of isoprene nitrates undergoing hydrolysis in bulk systems (e.g. Jacobs et al. 2014 ACP), what studies explore the interaction of gas-phase isoprene nitrates and aerosol-phase hydrolysis products for the isoprene system?

As far as we are aware the only study that begins to address these questions for the isoprene nitrates is Lee et al. (2016) – not yet published when we were developing our model. This is why many of our parameters (e.g., uptake coefficients, hydrolysis lifetimes) were selected as best guesses to fit the species for which we did have observational constraints.

References

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Hildebrandt Ruiz, L.; Yarwood, G. Interactions between organic aerosol and NO_y : influence on oxidant production, AQRP Project 12–012; Report, 2013, aqrp.ceer.utexas.edu/projectinfoFY12_13/12-012/12-012%20Final%20Report.pdf.

Jacobs, M. I., Burke, W. J., and Elrod, M. J.: Kinetics of the reactions of isoprene- derived hydroxynitrates: gas phase epoxide formation and solution phase hydrolysis, *Atmos. Chem. Phys.*, 14, 8933-8946, doi:10.5194/acp-14-8933-2014, 2014.

New Figures

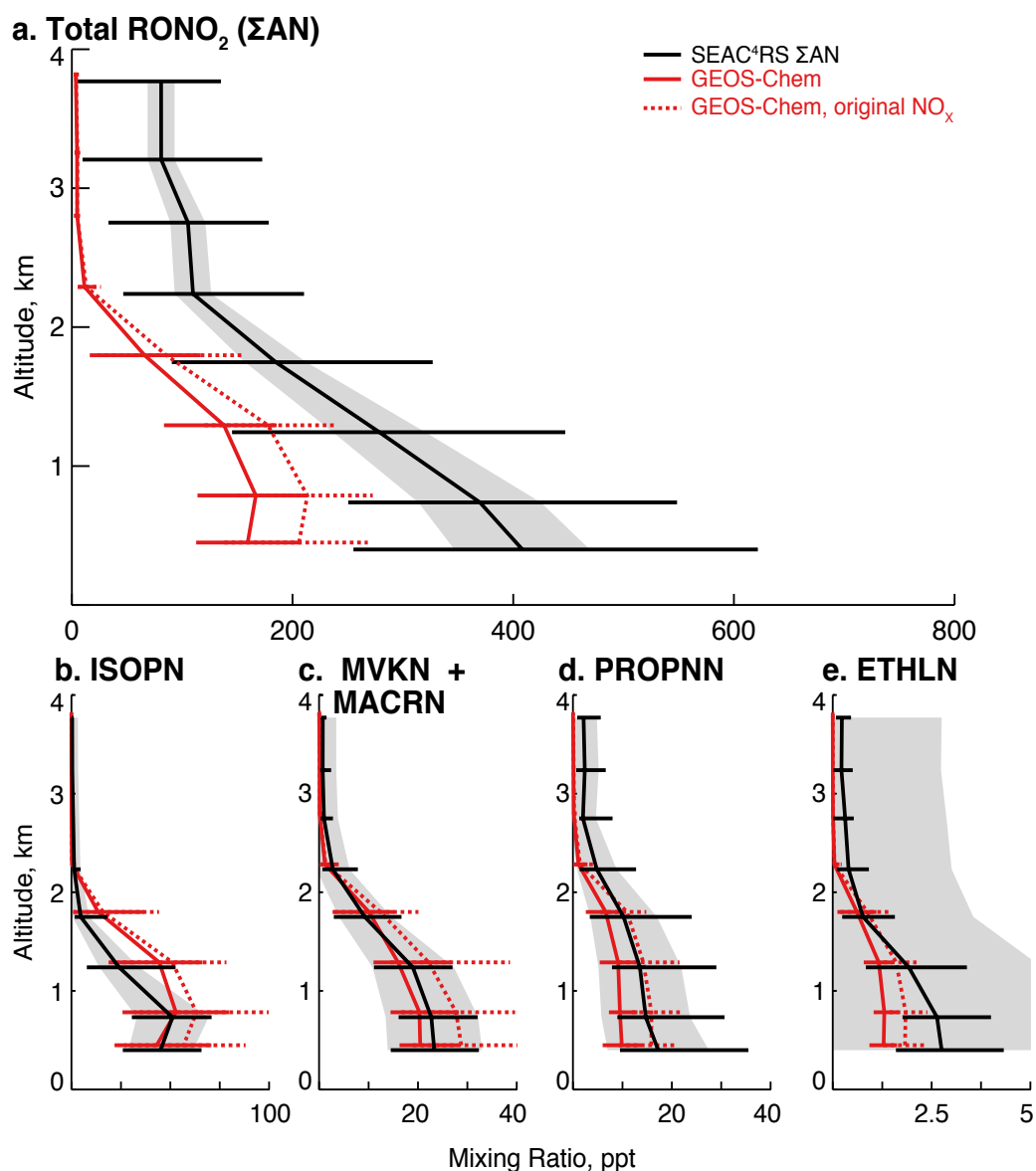


Figure S5. Observed (black) and modeled (red) median 0-4 km profiles of RONO₂ over the Southeast US during SEAC⁴RS. The dotted red line shows model results before scaling non-power plant NO_x emissions from the NEI11v1 inventory and soil NO_x in the Midwest US.

References (only those not in original manuscript or updated since submission)

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Organic nitrate chemistry and its implications for nitrogen budgets in an isoprene- and monoterpene-rich atmosphere: constraints from aircraft (SEAC⁴RS) and ground-based (SOAS) observations in the Southeast US

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Abstract. Formation of organic nitrates (RONO_2) during oxidation of biogenic volatile organic compounds (BVOCs: isoprene, monoterpenes) is a significant loss pathway for atmospheric nitrogen oxide radicals (NO_x), but the chemistry of RONO_2 formation and degradation remains uncertain. Here we implement a new BVOC oxidation mechanism (including updated isoprene chemistry, new monoterpene chemistry, and particle uptake of RONO_2) in the GEOS-Chem global chemical transport model with $\sim 25 \times 25 \text{ km}^2$ resolution over North America. We evaluate the model using aircraft (SEAC⁴RS) and ground-based (SOAS) observations of NO_x , BVOCs, and RONO_2 from the Southeast US in summer 2013. The updated simulation successfully reproduces the concentrations of individual gas- and particle-phase RONO_2 species measured during the campaigns. Gas-phase isoprene nitrates account for 25-50% of observed RONO_2 in surface air, and we find that another 10% is contributed by gas-phase monoterpene nitrates. Observations in the free troposphere show an important contribution from long-lived nitrates derived from anthropogenic VOCs. During both campaigns, at least 10% of observed boundary layer RONO_2 were in the particle phase. We find that aerosol uptake followed by hydrolysis to HNO_3 accounts for 60% of simulated gas-phase RONO_2 loss in the boundary layer. Other losses are 20% by photolysis to recycle NO_x and 15% by dry deposition. RONO_2 production accounts for 20% of the net regional NO_x sink in the Southeast US in summer, limited by the spatial segregation between BVOC and NO_x emissions. This segregation implies that RONO_2 production will remain a minor sink for NO_x in the Southeast US in the future even as NO_x emissions continue to decline.

1 Introduction

Nitrogen oxide radicals ($\text{NO}_x \equiv \text{NO} + \text{NO}_2$) are critical in controlling tropospheric ozone production (Monks et al., 2015, and references therein) and influencing aerosol formation (Rollins et al., 2012; Ayres et al., 2015; Xu et al., 2015), with indirect impacts on atmospheric oxidation capacity, air quality, climate forcing, and ecosystem health. The ability of NO_x to influence ozone and aerosol budgets is tied to its atmospheric fate. In continental regions, a significant loss pathway for NO_x is reaction with peroxy radicals derived from biogenic volatile organic compounds (BVOCs) to form organic nitrates (Liang et al., 1998; Browne and Cohen, 2012). NO_x loss to organic nitrate formation is predicted to become increasingly important as NO_x abundance declines (Browne and Cohen, 2012), as has occurred in the US over the past two decades (Hidy et al., 2014; Simon et al., 2015). Despite this increasing influence on the NO_x budget, the chemistry of organic nitrates remains the subject of debate, with key uncertainties surrounding the organic nitrate yield from BVOC oxidation, the recycling of NO_x from organic nitrate degradation, and the role of organic nitrates in secondary organic aerosol formation (Paulot et al., 2012; Perring et al., 2013). Two campaigns in the Southeast US in summer 2013 provided datasets of unprecedented chemical detail for addressing these uncertainties: the airborne NASA SEAC⁴RS (Studies of Emissions and Atmospheric Composition, Clouds, and Climate Coupling by Regional Surveys; Toon et al., 2016) and the ground-based SOAS (Southern Oxidants and Aerosols Study). Here we use a $\sim 25 \times 25 \text{ km}^2$ resolution 3-D chemical transport model (GEOS-Chem) to interpret organic nitrate observations from both campaigns, with focus on their impacts on atmospheric nitrogen (N) budgets.

Nitrogen oxides are emitted from natural and anthropogenic sources primarily as NO, which rapidly achieves steady state with NO_2 . Globally, the dominant loss pathway for NO_x is reaction with the hydroxyl radical (OH) to form nitric acid (HNO_3).

In the presence of VOCs, NO_x can also be lost by reaction with organic peroxy radicals (RO_2) to form peroxy nitrates (RO_2NO_2) and alkyl and multifunctional nitrates (RONO_2) (O'Brien et al., 1995). Their daytime formation temporarily sequesters NO_x , facilitating its export to more remote environments (Horowitz et al., 1998; Paulot et al., 2012; Mao et al., 2013). RO_2NO_2 species are thermally unstable at boundary layer temperatures and decompose back to NO_x on a time scale of minutes, except for the longer-lived peroxyacylnitrates (PANs) (Singh and Hanst, 1981). RONO_2 species can dominate NO_x loss when BVOC emissions are high and NO_x emissions are low (Browne and Cohen, 2012; Paulot et al., 2012; Browne et al., 2014) and may be more efficient for reactive N export than PANs (Mao et al., 2013). The amount of NO_x sequestered by RONO_2 depends on the interplay between BVOC and NO_x emissions, the RONO_2 yield from BVOC oxidation, and the eventual RONO_2 fate. ~~In industrialized regions, BVOC and sources tend to be spatially segregated, limiting the impact of production on loss (Yu et al., 2016). However, the BVOC emission flux can be much larger than the emission flux, so even with small yields may significantly impact the budget (Browne and Cohen, 2012).~~

RONO_2 chemistry and impacts are illustrated schematically in Fig. 1, starting from reaction of NO_x with BVOCs (mainly isoprene and monoterpenes) to form RONO_2 . The RONO_2 yield (α) from isoprene oxidation by OH has been inferred from laboratory and field experiments to be 4-15% (Tuazon and Atkinson, 1990; Chen et al., 1998; Sprengnether et al., 2002; Patchen et al., 2007; Perring et al., 2009a; Paulot et al., 2009; Nguyen et al., 2014; Xiong et al., 2015). Models have shown nearly this full range of yields to be compatible with RONO_2 observations, depending on the chemical mechanism assumed. For example, two models using different isoprene reaction schemes both successfully reproduced observations from a 2004 aircraft campaign (ICARTT) - one assuming a 4% molar yield (Horowitz et al., 2007) and the other assuming an 11.7% molar yield (Mao et al., 2013). The RONO_2 yield from monoterpene oxidation by OH is even more uncertain. Laboratory measurements exist only for α -pinene, and these show divergent results: 26% (Rindelaub et al., 2015), 18% (Nozière et al., 1999), and 1% (Aschmann et al., 2002, a lower limit due to significant wall losses). RONO_2 yields remain a significant uncertainty in BVOC oxidation schemes, with implications for their impacts on NO_x sequestration.

The fate of RONO_2 is of central importance in determining whether sequestered NO_x is returned to the atmosphere or removed irreversibly. Many first generation RONO_2 (i.e., those formed from NO reaction with BVOC-derived peroxy radicals) have a short lifetime against further oxidation to form a suite of second generation RONO_2 (Beaver et al., 2012; Mao et al., 2013; Browne et al., 2014), especially if they are produced from di-olefins such as isoprene or limonene. Laboratory studies indicate little NO_x release during this process (Lee et al., 2014); however, NO_x can be recycled by subsequent oxidation and photolysis of second generation species (Müller et al., 2014). Estimates of the NO_x recycling efficiency, defined as the mean molar percentage of RONO_2 loss that releases NO_x , range from <5% to >50% for isoprene nitrates (INs) (Horowitz et al., 2007; Paulot et al., 2009), and best estimates depend on assumptions about the IN yield (Perring et al., 2009a). NO_x recycling efficiencies from monoterpene nitrates (MTNs) have not been observed experimentally, but model sensitivity studies have shown a 14% difference in boundary layer NO_x between scenarios assuming 0% versus 100% recycling (assuming an initial 18% MTN yield, Browne et al., 2014). Uncertainty in the NO_x recycling efficiency has a bigger impact on simulation of NO_x and ozone than uncertainty in the RONO_2 yield (Xie et al., 2013).

Organic nitrates are typically more functionalized and less volatile than their BVOC precursors and are therefore more likely to partition to the particle phase. In the Southeast US, Xu et al. (2015) recently showed that particulate RONO_2 (pRONO_2) make an important contribution to total organic aerosol (5-12%), consistent with in situ observations from other environments (Brown et al., 2009, 2013; Fry et al., 2013; Rollins et al., 2012, 2013). Chamber experiments have shown high mass yields of aerosol from NO_3 -initiated oxidation of isoprene (15-25%; Ng et al., 2008; Rollins et al., 2009) and some monoterpenes (33-65%; Fry et al., 2014). There is evidence that RONO_2 from OH-initiated oxidation also form aerosol, although with lower yields, possibly via multi-functionalized oxidation products (Kim et al., 2012; Lin et al., 2012; Rollins et al., 2012; Lee et al., 2014). pRONO_2 are removed either by deposition or by hydrolysis to form HNO_3 (Jacobs et al., 2014; Rindelaub et al., 2015). Both losses augment N deposition to ecosystems (Lockwood et al., 2008). Aerosol partitioning competes with photochemistry as a loss for gas-phase RONO_2 with impacts for NO_x recycling. Partitioning also competes with gas-phase deposition, and because lifetimes against deposition are much longer for organic aerosols than for gas-phase precursors (Wainwright et al., 2012; Knote et al., 2015), this process may shift the enhanced N deposition associated with RONO_2 (Zhang et al., 2012; Nguyen et al., 2015) to ecosystems further downwind of sources.

The 2013 SEAC⁴RS and SOAS campaigns provide a unique resource for evaluating the impact of BVOC-derived organic nitrates on atmospheric NO_x . Both campaigns provided datasets of unprecedented chemical detail, including isoprene, monoterpenes, total and particle-phase RONO_2 , and speciated INs; during SOAS these were further augmented by measurements of MTNs. Continuous measurements from the SOAS ground site provide high temporal resolution and constraints on diurnal variability (e.g., Nguyen et al., 2015; Xiong et al., 2015). These are complemented by extensive boundary layer profiling across a range of chemical environments from the SEAC⁴RS airborne measurements (Toon et al., 2016). Combined, the campaigns covered the summer period when BVOC emissions in the Southeast US are at a maximum (Palmer et al., 2006). These data offer new constraints for testing models of organic nitrate chemistry, with implications for our understanding of NO_x , ozone, and aerosol budgets in BVOC-dominated environments worldwide.

We examine here the impact of BVOC oxidation on atmospheric NO_x , using the 2013 campaign data combined with the GEOS-Chem model. The version of GEOS-Chem used in this work represents a significant advance over previous studies, with higher spatial resolution ($\sim 25 \times 25 \text{ km}^2$) that better captures the spatial segregation of BVOC and NO_x emissions (Yu et al., 2016); updated isoprene nitrate chemistry incorporating new experimental and theoretical findings (e.g., Lee et al., 2014; Müller et al., 2014; Peeters et al., 2014; Xiong et al., 2015); addition of monoterpene nitrate chemistry (Browne et al., 2014; Pye et al., 2015); and consideration of particle uptake of gas-phase isoprene and monoterpene nitrates. We first evaluate the updated GEOS-Chem simulation using SOAS and SEAC⁴RS observations of BVOCs, organic nitrates, and related species. We then use GEOS-Chem to quantify the fates of BVOC-derived organic nitrates in the Southeast US. Finally, we investigate the impacts of organic nitrate formation on the NO_x budget.

2 Updates to GEOS-Chem simulation of organic nitrates

We use a new high resolution version of the GEOS-Chem CTM (www.geos-chem.org) v9-02, driven by assimilated meteorology from the NASA Global Modeling and Assimilation Office (GMAO) Goddard Earth Observing System Forward Processing (GEOS-FP) product. The model is run in a nested configuration (Wang et al., 2004), with native GEOS-FP horizontal resolution of 0.25° latitude by 0.3125° longitude over North America ($130\text{-}60^\circ\text{W}$, $9.75\text{-}60^\circ\text{N}$). Boundary conditions are provided from a $4^\circ \times 5^\circ$ global simulation, also using GEOS-Chem. The native GEOS-FP product includes 72 vertical layers of which ~ 38 are in the troposphere. Temporal resolution of GEOS-FP is hourly for surface variables and 3-hourly for all others. Our simulations use a time step of 5 minutes for transport and 10 minutes for emissions and chemistry.

GEOS-Chem has been applied previously to simulation of organic nitrates in the Southeast US (e.g., Fiore et al., 2005; Zhang et al., 2011; Mao et al., 2013). Mao et al. (2013) recently updated the GEOS-Chem isoprene oxidation mechanism to include explicit production and loss of a suite of second generation isoprene nitrates and nighttime oxidation by nitrate radicals. While their updated simulation showed good agreement with aircraft observations from the 2004 ICARTT campaign over the eastern US, we find that the more detailed chemical payloads available during SOAS and SEAC⁴RS highlight deficiencies in that mechanism, resulting in large model biases in RONO_2 .

A major component of this work is modification of the organic nitrate simulation in GEOS-Chem. Our focus here is on the BVOC-derived nitrates for which field measurements are newly available. GEOS-Chem simulation of PANs was recently updated by Fischer et al. (2014) and is not discussed here. Our improvements to the RONO_2 simulation are detailed below and include updates to isoprene oxidation chemistry, addition of monoterpene oxidation chemistry, and inclusion of aerosol uptake of RONO_2 followed by particle-phase hydrolysis. Other updates from GEOS-Chem v9-02 and comparison to Southeast US observations are presented in several companion papers. Kim et al. (2015) describe the aerosol simulation and Travis et al. (2016) the gas-phase oxidant chemistry. Constraints on isoprene emissions from satellite formaldehyde observations are described by Zhu et al. (2016). The low- NO_x isoprene oxidation pathway and implications for organic aerosols are described by Marais et al. (2016). Finally, Yu et al. (2016) evaluate the impact of model resolution and spatial segregation of NO_x and BVOC emissions on isoprene oxidation. [Our simulation is identical to that used in Travis et al. \(2016\), Yu et al. \(2016\), and Zhu et al. \(2016\).](#)

2.1 Isoprene oxidation chemical mechanism

The basic structure of the GEOS-Chem isoprene oxidation mechanism is described by Mao et al. (2013), with updates to low- NO_x pathways described and validated by Travis et al. (2016). [All updates to the isoprene oxidation mechanism are provided in Travis et al. \(2016\) Tables S1 and S2.](#) Figure 2 shows our updated implementation of OH-initiated isoprene oxidation in the presence of NO_x leading to isoprene nitrate (IN) formation. Isoprene oxidation by OH produces isoprene peroxy radicals (ISOPO_2) in either β - or δ -hydroxy peroxy configurations depending on the location of OH addition. In the presence of NO_x , ISOPO_2 reacts with NO to either produce NO_2 (the dominant fate; Perring et al., 2013) or form INs, with the yield of INs (α) defined as the branching ratio between these two channels. Early laboratory measurements of α suggested an IN yield

between 4.4 ~~-12~~ and 12% (Tuazon and Atkinson, 1990; Chen et al., 1998; Sprengnether et al., 2002; Patchen et al., 2007; Paulot et al., 2009; Lockwood et al., 2010). More recent experiments indicate continuing uncertainty in α , with a measured yield of $\alpha = 9 \pm 4\%$ from the Purdue Chemical Ionization Mass Spectrometer (CIMS; Xiong et al., 2015) and $\alpha = 13 \pm 2\%$ from the Caltech CF_3O^- Time-of-Flight CIMS (CIT-ToF-CIMS; Teng et al., in preparation), despite excellent agreement

5 during calibrated intercomparison exercises using one isoprene nitrate isomer (4,3 ISOPN). The sensitivity of the CIT-ToF-CIMS is similar for all isomers of ISOPN (Lee et al., 2014), while the Purdue instrument is less sensitive to the major isomer (1,2 ISOPN) (Xiong et al., 2015). Here, we use a first generation IN yield of $\alpha = 9\%$, which we find provides a reasonable simulation of the SOAS observations and is also consistent with the SOAS box model simulations of Xiong et al. (2015). We discuss the model sensitivity to the choice of α in Sect. 3.

10 For the oxidation of isoprene by OH, the mechanism described in Mao et al. (2013) assumed a first generation IN composition of 40% β -hydroxyl INs (β -ISOPN) and 60% δ -hydroxyl INs (δ -ISOPN). However, new theoretical constraints show that under atmospheric conditions, δ -channel peroxy radicals are only a small fraction of the total due to fast redissociation of peroxy radicals that fosters interconversion between isomers and tends towards an equilibrium population with more than 95% β -isomers (Peeters et al., 2014). Using a simplified box model based on the extended Leuven Isoprene Mechanism LIM1, we

15 found δ -isomers were 4-8% of the total peroxy pool in representative Southeast US boundary layer conditions (temperature ~ 295 -300 K, ISOPNO_2 lifetime ~ 20 -60 seconds). In what follows, we use an IN distribution of 90% β -ISOPN and 10% δ -ISOPN. Our box modeling suggests 10% is an upper limit for the δ -ISOPN pool; however, we maintain this value as ~~we find it necessary for it allows improved~~ simulation of species with predominantly δ -pathway origins, including glyoxal and the second generation INs propylene nitrate (PROPNN) and ethanal nitrate (ETHLN).

20 First generation ISOPN isomers formed via OH oxidation of isoprene have a short photochemical lifetime against atmospheric oxidation (Paulot et al., 2009; Lockwood et al., 2010; Lee et al., 2014). Here we use updated reaction rate constants and products from Lee et al. (2014) that increase the β -ISOPN+OH reaction by roughly a factor of two and decrease ozonolysis by three orders of magnitude (relative to the previous mechanism based on Lockwood et al., 2010; Paulot et al., 2009). Changes in δ -ISOPN reaction rate constants are more modest but in the same direction. For both isomers, reaction with OH

25 forms a peroxy radical (ISOPNO_2) along with a small (10%) yield of isoprene epoxy diols (Jacobs et al., 2014). Rate constants and products of the subsequent oxidation of ISOPNO_2 to form a suite of second generation INs follow the Lee et al. (2014) mechanism. We explicitly simulate methylvinylketone nitrate (MVKN) and methacrolein nitrate (MACRN), which are primarily from the β -pathway; PROPNN and ETHLN, which are primarily from the δ -pathway (and NO_3 -initiated oxidation); and C_5 dihydroxy dinitrate (DHDN), formed from both isomers (Lee et al., 2014).

30 Isoprene reaction with NO_3 is the dominant isoprene sink at night and can also be significant during the day (Ayres et al., 2015), producing INs with high yield (Perring et al., 2009b; Rollins et al., 2009). This reaction can account for more than 20% of isoprene loss in some environments (Brown et al., 2009) and may explain 40-50% of total RONO_2 in the Southeast (Mao et al., 2013; Xie et al., 2013). The mechanism used here is identical to that described by Mao et al. (2013). Reaction of isoprene with NO_3 forms a nitrooxy peroxy radical (INO_2). Subsequent reaction of INO_2 with NO , NO_3 , itself, or other

35 peroxy radicals forms a first generation C_5 carbonyl nitrate (ISN1) with 70% yield, while reaction with HO_2 forms a C_5

nitrooxy hydroperoxide (INPN) with 100% yield. In this simplified scheme, we do not distinguish between β - and δ - isomers for ISN1 and INPN, nor do we include the C_5 hydroxy nitrate species recently identified in chamber experiments (Schwantes et al., 2015). Mao et al. (2013) lumped all second generation nitrates derived from ISN1 and INPN into a single species (R_4N_2), but here we assume that the lumped species is PROPNN on the basis of recent chamber experiments that show PROPNN to be a high-yield photooxidation product of INs from NO_3 -initiated oxidation (Schwantes et al., 2015). This effectively assumes instantaneous conversion of INs to PROPNN, a simplification that results in a shift in the simulated diurnal cycle of PROPNN (see Sect. 3). We do not include here the nitrooxy hydroxyepoxide product recently identified by Schwantes et al. (2015).

Possible fates for second generation INs include further oxidation, photolysis, uptake to the aerosol phase followed by hydrolysis (Sect. 2.3), and removal via wet and dry deposition. Müller et al. (2014) show that photolysis is likely significantly faster than reaction with OH for carbonyl nitrates (e.g., MVKN, MACRN, ETHLN, PROPNN) due to enhanced absorption cross sections and high quantum yields caused by the proximity of the carbonyl group (a strongly absorbing chromophore) to the weakly-bound nitrate group. Here we ~~followed the methodology of Müller et al. (2014) to~~ increase the absorption cross sections of the carbonyl INs ~~following the methodology of Müller et al. (2014, Sect. 2).~~ Briefly, we first use the PROPNN cross section measured by Barnes et al. (1993) to calculate a wavelength-dependent cross section enhancement ratio (r_{nk}), defined as the ratio of the measured cross section to the sum of the IUPAC-recommended cross sections for associated monofunctional nitrates and ketones. We then calculate new cross sections for ETHLN, MVKN, and MACRN by multiplying r_{nk} by the sum of cross sections from appropriate monofunctional analogues (Table S5). The new cross sections are 5-15 times larger than in the original model, which used the IUPAC-recommended cross section of the monofunctional analogue tert-butyl nitrate cross section-nitrate for all carbonyl nitrates (Roberts and Fajer, 1989). For all species, we calculate photolysis rates assuming unity quantum yields, whereby the weak O- NO_2 bond dissociates upon a rearrangement after photon absorption to the carbonyl chromophore (Müller et al., 2014). Peak midday photolysis rates now range from $\sim 3 \times 10^{-5} s^{-1}$ (PROPNN) to $\sim 3 \times 10^{-4} s^{-1}$ (MACRN).

Removal by dry deposition has been updated based on new observations from the SOAS ground site. The dry deposition calculation is now constrained to match observed deposition velocities for ISOPN, MVKN, MACRN, and PROPNN (Nguyen et al., 2015; Travis et al., 2016), with all other $RONO_2$ deposition velocities scaled to that of ISOPN. Wet scavenging of gases is described in Amos et al. (2012) and has been modified here to use the same Henry's Law coefficients as for dry deposition. Aerosol partitioning is described in Sect. 2.3 below.

2.2 Monoterpene oxidation chemical mechanism

Monoterpene chemistry is not included in the standard GEOS-Chem gas-phase chemical mechanism. Here we implement a monoterpene nitrate scheme developed by Browne et al. (2014) that was built on the RACM2 chemical mechanism (Goliff et al., 2013) and evaluated using aircraft observations over the Canadian boreal forest (Browne et al., 2014). Our implementation is summarized in Fig. 3 and described briefly below, with the full mechanism available [in the Supplement \(Tables S1-S3\)](http://wiki.seas.harvard.edu/geos-chem/index.php/Monoterpene_nitrate_scheme) and at http://wiki.seas.harvard.edu/geos-chem/index.php/Monoterpene_nitrate_scheme. We include two lumped monoterpene tracers: API representing monoterpenes with one double bond (α -pinene, β -pinene, sabinene, and Δ -3-carene) and LIM repre-

5 sending monoterpenes with two double bonds (limonene, myrcene, and ocimene). Combined, these species account for roughly 90% of all monoterpene emissions (Guenther et al., 2012), and we neglect other terpenes here. During the day, LIM and API are oxidized by OH to form peroxy radicals. Subsequent reaction with NO forms first generation monoterpene nitrates with a yield of 18% (Nozière et al., 1999). These can be either saturated (MONITS) or unsaturated (MONITU), with precursor-dependent partitioning as shown in Fig. 3. For all subsequent discussion, we refer to their sum MONIT = MONITU + MONITS.

At night, both LIM and API react with NO₃ to form a nitrooxy peroxy radical that either decomposes to release NO₂ or retains the nitrate functionality to form MONIT. The branching ratio between these two fates is ~~40~~50% nitrate-retaining for ~~API~~ LIM + NO₃ (Browne et al., 2014) and ~~50~~50% nitrate-retaining for ~~LIM-API + NO₃~~ (Fry et al., 2014) (Browne et al., 2014). The 10% nitrate yield from API + NO₃ is on the low end of the observed range (Fry et al., 2014), so simulated pinene-derived MONIT should be considered a lower bound. In Browne et al. (2014), the API + NO₃ reaction used the α-pinene + NO₃ rate constant from the Master Chemical Mechanisms (MCMv3.2). We have updated this rate constant to $k_{API+NO_3} = 8.33 \times 10^{-13} e^{490/T}$, a rough average of the MCMv3.3 α- and β-pinene values, as API comprises both α- and β-pinenes (the dominant API components, present in roughly equal amounts during both SEAC⁴RS and SOAS). API and LIM also react with O₃, but this reaction does not lead to RONO₂ formation.

15 We do not distinguish between OH-derived and NO₃-derived MTN species. MONIT are subject to removal via wet and dry scavenging, aerosol uptake, photolysis, ozonolysis (MONITU only) and oxidation by OH. Here, we also add MONIT reaction with NO₃ with the same rate constant as used for nighttime isoprene nitrates. The products of MONIT oxidation are currently unknown; here we follow Browne et al. (2014) and assume oxidation produces a second generation monoterpene nitrate (HONIT) that undergoes dry deposition, photolysis, and oxidative loss. In our simulation, HONIT is also removed via
20 aerosol uptake (Sect. 2.3).

2.3 Aerosol partitioning of RONO₂

Evidence from laboratory and field studies suggests aerosol uptake is a potentially significant loss pathway for gas-phase RONO₂ (e.g., Day et al., 2010; Rollins et al., 2010; Darer et al., 2011; Fry et al., 2013, 2014). In particular, BVOC oxidation by NO₃ radicals has been shown to result in high organic aerosol yields (Ng et al., 2008; Fry et al., 2009; Rollins et al., 2012).
25 Recent work from SOAS highlighted the role of the monoterpenes + NO₃ reaction, with an estimated 23-44% yield of organic nitrate aerosol (Ayres et al., 2015) that can explain roughly half of nighttime secondary organic aerosol production (Xu et al., 2014). Isoprene + NO₃ results in smaller but still significant yields; Xu et al. (2014) estimate that isoprene was responsible for 20% of nighttime NO₃-derived organic aerosol observed during SOAS. Organic nitrate aerosol yields from daytime oxidation by OH are lower but non-negligible. At Bakersfield, for example, Rollins et al. (2013) found 21% of RONO₂ partitioned to
30 the aerosol phase during the day, and that these could explain 5% of the total daytime organic aerosol mass.

Aerosol partitioning of RONO₂ has not previously been considered in GEOS-Chem. Here we add this process using a reactive uptake coefficient (γ) parameterization. Our parameterization was designed to provide a necessary sink for gas-phase RONO₂ species (overestimated in earlier iterations of our model), and therefore makes a number of simplifying assumptions. In particular, we do not allow pRONO₂ to re-partition to the gas phase (likely to impact the more volatile isoprene-derived

5 nitrates), and uptake coefficients are defined to fit the measurements of gas-phase species. More accurate simulation of organic nitrate aerosols would require additional updates that take into account vapor pressure differences between species (as done recently by Pye et al., 2015) and incorporate new findings from SOAS (Ayres et al., 2015; Lee et al., 2016). For our simulation, we apply reactive uptake to all BVOC-derived RONO₂ except PROPNN and ETHLN, which lack hydroxyl groups and are
10 therefore expected to be significantly less soluble. We assume an uptake coefficient of $\gamma=0.005$ for isoprene nitrates (from both daytime and nighttime chemistry) and $\gamma=0.01$ for all monoterpene nitrates (Table S4). Our isoprene nitrate uptake coefficient is in the middle of the range predicted by Marais et al. (2016) using a mechanistic formulation, and is a factor of 4 lower than the upper limit for ISOPN inferred by Wolfe et al. (2015) using SEAC⁴RS flux measurements. Although simplified, we find this parameterization ~~improves the model fit relative~~ provides a reasonable fit to the SEAC⁴RS and SOAS observations
15 of individual gas-phase RONO₂ species measured by the CIT-ToF-CIMS and total pRONO₂ measured by an Aerosol Mass Spectrometer (AMS) ~~-(see Sect. 3 and 4).~~

After partitioning to the aerosol, laboratory experiments have shown that pRONO₂ can hydrolyze to form alcohols and nitric acid via $\text{pRONO}_2 + \text{H}_2\text{O} \rightarrow \text{ROH} + \text{HNO}_3$. Some pRONO₂ species hydrolyze rapidly under atmospherically-relevant conditions, while others are stable against hydrolysis over timescales significantly longer than the organic aerosol lifetime against
20 deposition (Darer et al., 2011; Hu et al., 2011; Liu et al., 2012; Jacobs et al., 2014; Rindelaub et al., 2015). Lifetimes against hydrolysis inferred from bulk aqueous and reaction chamber studies range widely from minutes (Darer et al., 2011; Rindelaub et al., 2015) to a few hours (Liu et al., 2012; Lee et al., 2016) to nearly a day (Jacobs et al., 2014). Here we apply a bulk lifetime ~~of 1 hr~~ against hydrolysis for the entire population of pRONO₂ ~~(similar to Pye et al., 2015, who used a 3 hr bulk lifetime)~~ (similar to Pye et al., 2015).
In other words, our implementation of aerosol partitioning involves a two-step process of (1) uptake of gas-phase RONO₂ to
25 form a simplified non-volatile pRONO₂ species, with rate determined by γ , followed by (2) hydrolysis of the simplified pRONO₂ species to form HNO₃, with rate determined by the lifetime against hydrolysis. These steps are de-coupled, and we do not include any dependence of γ on the hydrolysis rate (unlike the more detailed formulation of Marais et al. (2016)).
In subsequent sections, we compare the simplified pRONO₂ formed as an intermediate during this process to total pRONO₂ derived from observations. The assumption of a single hydrolysis lifetime overestimates the loss rate of non-tertiary nitrates
30 (Darer et al., 2011; Hu et al., 2011) and may lead to model bias in total pRONO₂, particularly in the free troposphere where the longer-lived species would be more prevalent (see Sect. 4).

We assume here a bulk lifetime against hydrolysis of 1 h, which we found in preliminary simulations to provide a better simulation of pRONO₂ than longer lifetimes. Our 1 ~~hr~~ h bulk hydrolysis lifetime is shorter than the 2-4 ~~hr~~ h lifetime found in recent analysis of SOAS data ~~(Lee et al., 2016; Pye et al., 2015)~~ and laboratory experiments (Boyd et al., 2015; Lee et al., 2016; Pye et al., 2015).
35 likely reflecting the simplifying assumptions of our uptake parameterization. In any case, the choice of hydrolysis lifetime does not affect the concentration of gas-phase RONO₂ species (because pRONO₂ cannot re-partition to the gas phase in the model), and we find this value provides a reasonable match to AMS measurements of total pRONO₂ at the surface during SOAS and SEAC⁴RS ~~-(see Sect. 3 and 4). Impacts on HNO₃ are minor: compared to a simulation without hydrolysis, our simulation with a 1 h lifetime against hydrolysis increased boundary layer HNO₃ by 20 ppt, or 2.4%.~~

3 BVOCs and organic nitrates in the Southeast US

We evaluate the updated GEOS-Chem simulation using Southeast US measurements of isoprene, monoterpenes, and a suite of oxidation products from two field campaigns in summer 2013. SEAC⁴RS was a NASA aircraft campaign that took place in August-September 2013 (Toon et al., 2016). All observations discussed in this work were taken onboard the NASA DC-8 (data doi: 10.5067/Aircraft/SEAC⁴RS/Aerosol-TraceGas-Cloud), which was based in Houston, Texas with an ~8-hour flight range. SOAS was a ground-based campaign that took place in June-July 2013 at the Centreville monitoring site near Brent, Alabama (32.903°N, 87.250°W).

3.1 Isoprene and monoterpenes

Understanding BVOC sources and chemistry was a primary goal of SEAC⁴RS, resulting in a large number of boundary layer flights over regions of enhanced biogenic emissions (Kim et al., 2015). Isoprene and monoterpene distributions in Southeast US surface air (80-94.5°W, 29.5-40°N, and below 1 km) measured by PTR-MS are shown in Fig. 4, and their campaign-median vertical profiles are shown in Fig. 5(b,c). Whole Air Sampler (WAS) measurements of isoprene and α -pinene + β -pinene (Fig. S1) are similar, but with more limited sampling than the PTR-MS. All observations have been averaged to the spatial and temporal resolution of the model.

SOAS was a ground-based campaign that took place in June-July 2013 at the Centreville monitoring site near Brent, Alabama (32.903°N, 87.250°W). The site The SOAS site is located at the edge of a mixed coniferous and deciduous forest (Nguyen et al., 2015). Observations SOAS observations of isoprene and monoterpenes, measured by PTR-ToF-MS and averaged to hourly mean values, are shown in Fig. 6. Both species display a clear diurnal cycle with peak isoprene during day, reflecting the light- and temperature-dependent source, and peak monoterpenes at night. For monoterpenes, the figure also shows the sum of α -pinene + β -pinene as measured by 2D-GC-FID, which indicates that these are the dominant monoterpenes.

Figures 4, 5, and 6 compare observed BVOCs from both campaigns to the GEOS-Chem simulation, sampled to match the observations. Similar figures for NO_x can be found in Travis et al. (2016) and in Fig. S2. Model bias relative to observations is quantified using the normalized mean bias $NMB = 100\% \times [\sum_i (M_i - O_i) / \sum_i (O_i)]$, where O_i and M_i are the observed and modeled values and the summation is over all hours (SOAS) or unique gridbox-timestep combinations along the flight tracks (SEAC⁴RS). BVOC emissions are from MEGANv2.1 (Guenther et al., 2012) and have been decreased by 15% for isoprene and doubled for monoterpenes to better match aircraft (isoprene, monoterpene) and satellite (formaldehyde) observations (Kim et al., 2015; Zhu et al., 2016). With these scalings applied, simulated surface isoprene and monoterpenes overestimate somewhat the SEAC⁴RS data (Fig. 4, mainly due to a few simulated high-BVOC events), but the medians are well within the observed variability (Fig. 5). Model high bias above 500 m is likely caused by excessive vertical mixing through the simulated boundary layer (Travis et al., 2016). Relative to the SOAS data, simulated monoterpenes are biased low by a factor of two, while isoprene falls within the interquartile range of the measurements. The opposite sign of the SOAS monoterpene bias relative to the more spatially representative SEAC⁴RS data suggests a low bias in MEGANv2.1 monoterpene emissions that is unique to

the Centreville gridbox; errors in vertical mixing may also contribute. For isoprene, the model reproduces both the observed nighttime decline and the subsequent morning growth with a small delay (~ 1 hour).

The observed declines in isoprene at night (Fig. 6) and above the boundary layer (Fig. 5) reflect its short lifetime against oxidation. We find in the model that OH oxidation accounts for 90% of isoprene loss (Marais et al., 2016), but only 65% of monoterpenes loss (with NO_3 responsible for most of the rest). For isoprene, the subsequent fate of the peroxy radicals (ISOP O_2) has been evaluated in detail by Travis et al. (2016), who also present an in-depth analysis of the NO_x budget and impacts on ozone. They show that on average 56% of ISOP O_2 reaction during SEAC 4 RS is with NO, and that there is large spatial variability in this term that is accurately reproduced by the high-resolution GEOS-Chem simulation. Here we focus exclusively on this pathway and the resultant formation of RONO $_2$ from both isoprene and monoterpenes.

10 3.2 First generation RONO $_2$

Observed near-surface mixing ratios of first generation isoprene nitrates (ISOPN) during SEAC 4 RS are shown in Fig. 7 and are generally well represented by GEOS-Chem ($r = 0.61$; NMB = -1.2 – 0.6%). ISOPN vertical profiles in Fig. 5e indicate a rapid decline from the boundary layer to the free troposphere, reflecting the short atmospheric lifetime (2–4 hrs in our simulation; Table 1). Comparing the lowest altitude SEAC 4 RS observations to the SOAS median from the CIT-ToF-CIMS (black triangle) indicates an apparent vertical gradient from the surface to ~ 500 m. This could be caused by spatial variability between the campaigns, or could reflect rapid dry deposition of ISOPN with limited vertical mixing. GEOS-Chem does not simulate this SOAS-SEAC 4 RS difference, possibly due to overly strong vertical mixing through the modeled boundary layer as identified by Travis et al. (2016) from model comparison to SEACIONS ozonesonde observations.

During SOAS, ISOPN was measured simultaneously by the CIT-ToF-CIMS (Crouse et al., 2006; Nguyen et al., 2015) and the Purdue CIMS (Xiong et al., 2015), and Fig. 6 shows the diurnal cycles from both. Median ISOPN from the Purdue CIMS is a factor of two higher than that from the CIT-ToF-CIMS during daylight hours, with the most significant differences in mid-late morning. In both datasets, ISOPN peaks around 10:00 am local time, is elevated until early evening, and declines to a pre-dawn minimum. Simulated ISOPN from GEOS-Chem is in good agreement with the Purdue CIMS measurements except in the afternoon when modeled ISOPN shows a broad peak (rather than the observed decline) coincident with simulated peak isoprene (Fig. 6). After $\sim 7:00$ pm, the model captures the observed timing of the nighttime ISOPN decline seen in both datasets, as well as the rapid morning growth seen in the Purdue CIMS measurements.

As described in Sect. 2.1, there is considerable uncertainty in the ISOPN yield. We find here that a 9% yield provides the best simulation of the ensemble of SEAC 4 RS and SOAS observations, given experimental constraints on oxidative loss rates (Lee et al., 2014) and dry deposition fluxes (Nguyen et al., 2015). Using model sensitivity studies, we found that applying a lower yield of 7% improved the agreement with the CIT-ToF-CIMS during SOAS, but worsened agreement with the other datasets and is inconsistent with the yields from laboratory experiments (Teng et al., in preparation). We also tested a higher yield of 12%, and found the model overestimated observed SEAC 4 RS and SOAS ISOPN (from both instruments) unless we invoked much larger aerosol uptake and/or added another ISOPN sink. ISOPN sinks (especially aerosol uptake) remain

poorly constrained, and the uncertain parameter space describing these processes likely contains multiple solutions that fit the observations equally well (i.e., a higher yield could be accommodated by faster ISOPN loss to aerosol).

Our finding that GEOS-Chem can reproduce the Purdue CIMS ISOPN observations using a 9% ISOPN yield is consistent with the box model of Xiong et al. (2015). The chemical mechanisms used in both studies are similar. In both simulations, modeled ISOPN was overestimated unless an extra sink was included (also consistent with Wolfe et al., 2015, who inferred a missing sink based on SEAC⁴RS flux measurements). While we assumed this sink was due to aerosol uptake, Xiong et al. (2015) invoked enhanced ISOPN photolysis. They argued that models typically underestimate the ISOPN absorption cross section by not taking into account the combined influence of the double bond and hydroxyl group in the ISOPN structure (Fig. 2). Xiong et al. (2015) were better able to reproduce the observed ISOPN morning peak and afternoon decline when they increased the MCMv3.2 photolysis rate constant by a factor of 5. Including both faster ISOPN photolysis and uptake to the aerosol phase could be a means to accommodate a higher initial ISOPN yield, such as the 12-14% yield inferred from laboratory experiments with the CIT-ToF-CIMS (Teng et al., in preparation), although both sinks remain unverified. The nature of the sink has implications for NO_x recycling from isoprene nitrates (photolysis recycles NO_x while uptake removes it), and this remains a source of uncertainty in our estimates of the impacts of RONO₂ on the NO_x budget.

Even more uncertain than ISOPN are the first generation monoterpene nitrates (MONIT). MONIT in GEOS-Chem is a lumped species that represents the sum of monoterpene nitrates from both daytime OH-initiated and nighttime NO₃-initiated oxidation (Sect. 2.2). The nighttime oxidation cascade involves a diversity of reactants (including NO, HO₂, NO₃, and other peroxy radicals) and produces a diversity of monoterpene nitrate species (Lee et al., 2016) that we do not distinguish here. In the model, most MONIT is produced from the NO₃-initiated chemistry, resulting in mean MONIT concentrations of 30-60 ppt at night and ~10-20 ppt during the day.

During SOAS, two monoterpene nitrates were measured by the CIT-ToF-CIMS: C₁₀H₁₇NO₄ and C₁₀H₁₇NO₅. We find that simulated MONIT shows the same diurnal pattern as the sum of the two measured species (with peak concentrations at night) but is a factor of 2-3 higher (Fig. S3). Pye et al. (2015) similarly found simulated MONIT was a factor of 7 higher than observations using a version of the CMAQ model with explicit MONIT chemistry. The higher modeled values in both studies presumably reflect inclusion in modeled MONIT of many species that were not measured by CIT-ToF-CIMS (including several identified during SOAS by Lee et al., 2016), as well as biases in the model mechanisms (most of the rate constants and products have not been measured). NO₃-initiated monoterpene oxidation is particularly uncertain and is likely too strong in GEOS-Chem, as indicated by large nighttime MONIT overestimates (Fig. S3) combined with monoterpene underestimates (Fig. 6). Simulated nighttime peak values of NO₃-derived isoprene nitrates (ISN1) during SOAS are also up to a factor of 2 higher than the observations reported by Schwantes et al. (2015). This suggests that model biases in nighttime PBL heights and associated vertical mixing may also contribute to simulated nighttime overestimates for some RONO₂ species.

3.3 Second generation RONO₂ and pRONO₂

First generation ISOPN and MONIT undergo further oxidation to form a suite of second generation RONO₂ species that retain the nitrate functionality (Figs. 2, 3). Four of these species (MVKN, MACRN, PROPNN, and ETHLN) were measured by the

CIT-ToF-CIMS, with vertical profiles shown in Fig. 5 (f-h) and spatial distribution shown in Fig. 7. The model provides a good simulation of SEAC⁴RS MVKN+MACRN but underestimates the variability of PROPNN and ETHLN. In contrast, all three species show positive mean model biases relative to the SOAS surface observations. The model tends to overestimate PROPNN and ETHLN at night but underestimate them during the day (Fig. S3), reflecting the assumption in our mechanism that PROPNN is produced at night during NO₃-initiated isoprene oxidation. In reality, the nighttime chemistry produces INs that only photo-oxidize to PROPNN after sunrise (Schwantes et al., 2015). This missing delay between nighttime NO₃ addition and subsequent daytime photo-oxidation likely also explains the model bias relative to the SEAC⁴RS observations, which mostly took place during daytime. Additional simplifications in the NO₃-initiated chemistry could also contribute to the biases, and preliminary simulations conducted with the AM3 model show that including more details of this chemistry improves model ability to match observed PROPNN (Li et al., in preparation). Some of the bias may also be due to error in the assumed distribution between β - and δ -channel OH-initiated oxidation, as both PROPNN and ETHLN are produced by the latter channel only.

The full time series of first and second generation INs measured at Centreville during SOAS are shown in Fig. 8. We also include the time series of observed particulate RONO₂ (pRONO₂) estimated from AMS measurements (Fry et al., 2013; Ayres et al., 2015; Lee et al., 2016; Day et al., in preparation) and of Σ ANs, the sum of all RONO₂ species (including pRONO₂) as measured by thermal dissociation laser-induced fluorescence (TD-LIF; Day et al., 2002). Despite the biases identified above, the simulation captures the temporal variability in gas-phase, particulate, and total RONO₂ observed over the 6-week campaign, with correlation coefficients of $r \sim 0.6-0.7$. Low observed and modeled values for all species in early July (days 185-189) indicate suppressed BVOC emissions caused by low temperatures (Marais et al., 2016). The model underestimates both pRONO₂ and Σ ANs at night (Fig. S3), suggesting that hydrolysis of particulate monoterpene nitrates should be slower than assumed here (Sect. 2.3). Afternoon overestimates of pRONO₂ relative to the AMS observations (Fig. S3) are coincident with the peak in isoprene nitrates (Fig. 6), suggesting overly strong partitioning to the aerosol phase likely due to our assumption of irreversibility (Sect. 2.3).

3.4 RONO₂-HCHO relationship

The relationship between organic nitrates and formaldehyde (HCHO), a high-yield product of the ISOPO₂ + NO reaction, provides an additional test of the model chemistry and in particular the IN yield. Daytime isoprene oxidation in the presence of NO_x co-produces HCHO and INs, resulting in an expected strong correlation between these species (Perring et al., 2009a). When INs dominate total RONO₂, the correlation should also be strong between HCHO and Σ ANs, and this relationship has previously been used to constrain the IN yield when IN measurements were not available. For example, HCHO and Σ ANs measurements from the 2004 ICARTT aircraft campaign showed moderate correlation with $r \sim 0.4-0.6$ (Perring et al., 2009a; Mao et al., 2013). However, linking the HCHO- Σ ANs correlation to the IN yield is complicated by the contribution to Σ ANs from other RONO₂ sources (e.g., monoterpene nitrates, anthropogenic nitrates, etc.). During SEAC⁴RS, a better constraint can be obtained directly from the HCHO-IN relationship. Figure 9 shows the correlation between HCHO and the sum of ISOPN, MVKN, and MACRN (we exclude PROPNN and ETHLN to avoid the biases identified previously). The figure shows the

observed slope of $0.027 \text{ (ppt IN) (ppt HCHO)}^{-1}$ is reproduced by the model but with more scatter in the simulation ($r \sim 0.5$) than in the observations ($r \sim 0.7$). The similarity of the observed and simulated relationships in Fig. 9 lends confidence to the IN mechanism used here, at least for the β -peroxy channel.

4 Total alkyl and multifunctional nitrates (Σ ANs) and speciation

5 4.1 Speciated versus total RONO₂

SEAC⁴RS represents one of the first airborne campaigns to make measurements of individual BVOC-derived RONO₂ species. Without these speciated measurements, previous model evaluations of isoprene nitrate chemistry have relied on TD-LIF observations of Σ ANs (total RONO₂), with the assumption that gas-phase INs account for the majority of Σ ANs (Horowitz et al., 2007; Perring et al., 2009a; Mao et al., 2013; Xie et al., 2013). Figure 10a compares the TD-LIF Σ ANs measurement (solid line) to the sum of explicitly measured gas-phase RONO₂ species and total pRONO₂ (dashed line, combined CIT-ToF-CIMS, WAS, and AMS measurements) during SEAC⁴RS. The figure shows a large gap between measured Σ ANs and the total of speciated RONO₂ (including both gas-phase and aerosol contributions), especially near the surface (Σ ANs = 409 ppt, total speciated RONO₂ = 198 ppt). Figure 10a also shows the median surface Σ ANs measured during SOAS (198 ppt; black triangle). As for SEAC⁴RS, SOAS total speciated RONO₂ is much lower (82 ppt) when calculated from the CIT-ToF-CIMS and AMS measurements. The gap is smaller, but still exists, when calculated using ISOPN from the Purdue CIMS (total RONO₂ = 102 ppt) or pRONO₂ from the TD-LIF (total RONO₂ = 139 ppt). An independent thermal dissociation instrument operated by the SouthEastern Aerosol Research and Characterization (SEARCH) Network also measured Σ ANs at the SOAS site and showed values that were 80 ppt higher than measured by the TD-LIF (but generally well correlated, with slope close to 1 and $r \sim 0.8$).

20 Some of the difference between the total speciated RONO₂ and Σ ANs measurements can be attributed to gas-phase nitrates not measured by CIT-ToF-CIMS or WAS. A number of these were identified during SOAS using a second ToF-CIMS operated by the University of Washington (Lee et al., 2016). In addition, SEAC⁴RS observations of total NO_y (\equiv NO_x+HNO₃+PAN+RONO₂, including pRONO₂) are better balanced by including the Σ ANs than the speciated RONO₂ components ($\approx 81\%$ vs. 70% of surface NO_y, compared to 56% with no RONO₂ contribution). Also contributing to the discrepancy are the large uncertainties still associated with RONO₂ measurement techniques. Lee et al. (2016) found that SOAS measurements of pRONO₂ differ by factors of 2-4, as also shown in Fig. S3, with the AMS lower than TD-LIF. Similarly, we showed in Sect. 3 that the two SOAS measurements of ISOPN differ by up to a factor of 2 (CIT-ToF-CIMS lower than Purdue CIMS, for reasons that remain unclear). Assuming similar uncertainties characterize the SEAC⁴RS RONO₂ measurements, these could readily explain some of the inability of the speciated measurements to close the Σ ANs budget in Fig. 10a.

30 Comparison of GEOS-Chem to the two total RONO₂ estimates in Fig. 10a shows that the model greatly underestimates SEAC⁴RS Σ ANs relative to the TD-LIF measurement, with a much smaller underestimate relative to the speciated sum. The better fit to the speciated measurements than to the Σ ANs is consistent with the model's ability to match both individual gas-

phase RONO₂ species measured by the CIT-ToF-CIMS and total pRONO₂ measured by the AMS (Sect. 3). During SOAS, Fig. 8 shows that GEOS-Chem can reproduce much of the temporal variability in the Σ ANs ($r = 0.57$) with little bias.

4.2 RONO₂ composition

Figure 10b compares the observed and simulated RONO₂ composition in the Southeast US during SEAC⁴RS. For clarity, only the speciated measurements are shown in the figure. The observations show a constant 20-30 ppt background at all altitudes from small (C₁-C₃) RONO₂ produced from anthropogenic VOCs. The contributions of these small nitrates are consistent with the observed concentrations of their parent VOCs and with known reaction rate constants (Atkinson and Arey, 2003), RONO₂ yields (Perring et al., 2013), and RONO₂ lifetimes (Talukdar et al., 1997; Dahl et al., 2005; Worton et al., 2010) assuming steady state. GEOS-Chem does not simulate these nitrates under the assumption that their contributions to total NO_y are insignificant. The SEAC⁴RS data clearly show that this assumption is not valid, at least for the US where natural gas production is a large alkane source, and is contributing to model bias in both RONO₂ and NO_y. Given the long lifetimes (weeks-months) of the small nitrates, the bias is particularly acute in the free troposphere and has implications for global N export.

In both observations and model, gas-phase INs (orange) account for half of speciated RONO₂ (25% of Σ ANs), split roughly equally between 1st and 2nd generation species. The model underestimates somewhat the 2nd generation INs, as seen previously in Figs. 5 and 7. In the model, gas-phase MTNs from monoterpenes (blue; not measured during SEAC⁴RS) account for an additional 10% of simulated RONO₂ (~5% relative to Σ ANs). Previous studies during ICARTT also found a 10% MTN contribution to RONO₂ (Horowitz et al., 2007; Perring et al., 2009a), although MTNs have been neglected in more recent simulations (e.g., Mao et al., 2013; Xie et al., 2013). Other C₄-C₅ nitrates (yellow, including alkyl nitrates from WAS and alkene hydroxynitrates from CIT-ToF-CIMS) similarly contribute 5-10% of observed RONO₂; these are underestimated by 50% in GEOS-Chem because the model does not include nitrate formation from anthropogenic alkenes.

A significant fraction (10-20%) of RONO₂ was in the aerosol phase during SEAC⁴RS. The model underestimates the observed pRONO₂ contribution in the free troposphere; however, some caution should be used when interpreting these data. Observed pRONO₂ is the product of measured total aerosol nitrate and the measured organic fraction of the nitrate aerosol, but during SEAC⁴RS the organic fraction was often not reported in the free troposphere due to interference from dust layers and instrumental issues. In these instances, the organic fraction of measured nitrate is assumed to be 0.8, based largely on surface measurements from multiple campaigns (Day et al., in preparation). In the free troposphere (>1.5 km), this assumption is applied to 85% of the SEAC⁴RS 1-minute data, and could lead to a high bias in the pRONO₂ observations. Nonetheless, it is also likely that simulated pRONO₂ is underestimated because of our assumption that all pRONO₂ species undergo rapid hydrolysis. In fact, many of the nitrates produced from BVOC oxidation are not expected to hydrolyze at all (Boyd et al., 2015; Pye et al., 2015) and so would have lifetimes sufficiently long for export out of the boundary layer.

Our simulated RONO₂ composition in Fig. 10b suggests a less important role for INs than identified from recent simulations of the ICARTT data. In an earlier version of GEOS-Chem, INs alone could explain all measured Σ ANs during ICARTT (~200 ppt at the surface; Mao et al., 2013), and both that model and a CMAQ simulation (Xie et al., 2013) suggested INs were

dominated by 2nd generation species (70-90% of total INs). These earlier simulations did not account for either aerosol uptake and possible hydrolysis (Darer et al., 2011; Jacobs et al., 2014) or fast photolysis (Müller et al., 2014) of 2nd generation INs, and so lifetimes were significantly longer than in our simulation. We performed sensitivity simulations without these additional IN sinks and found that the model overestimated observed 2nd generation INs by a factor of 3-5 during SEAC⁴RS.

5 It seems likely that 2nd generation IN overestimates in previous work were compensated for by omitting the contributions from MTNs and pRONO₂. Here, we find MTN and pRONO₂ combined contribute as much to total RONO₂ as either 1st or 2nd generation INs alone, and that excluding them would lead to major model shortcomings. The pRONO₂ contribution is especially important as different removal processes for gas-phase versus particulate species would have different implications for NO_x budgets and N deposition.

10 **5 Fate of organic nitrates and implications for nitrogen budgets**

Table 1 summarizes the dominant fates and lifetimes of individual gas-phase RONO₂ in the Southeast US boundary layer during the SEAC⁴RS campaign (12 Aug - 23 Sep) as calculated from GEOS-Chem. The contribution of different fates to total gas-phase RONO₂ loss is illustrated in Fig. 11a. Loss processes that recycle RONO₂ by converting between RONO₂ species (e.g., from first to second generation) are not included. Total simulated RONO₂ loss is dominated by aerosol hydrolysis, with
15 an additional large loss to deposition that is consistent with the rapid deposition fluxes of both INs and MTNs observed during SOAS (Nguyen et al., 2015). The large predicted losses to aerosol influence simulation of both pRONO₂ (for which uptake is the only source in the model) and HNO₃ (which is produced during pRONO₂ hydrolysis). We find here that our simulation including a large sink to aerosol is consistent with observed surface pRONO₂ concentrations and variability (Figs. 8 and 10), HNO₃ concentrations (Travis et al., 2016, Fig. 2), and nitrate wet deposition fluxes (Travis et al., 2016, Fig. 3) during
20 SEAC⁴RS and SOAS.

Overall, more than 80% of simulated gas-phase RONO₂ are lost via processes that irreversibly remove nitrogen from the atmosphere (deposition, aerosol hydrolysis). The remainder is primarily lost via photolysis, driven largely by the fast photolysis of 2nd generation carbonyl INs (Müller et al., 2014). [Romer et al. \(2016\) similarly found that terminal NO_x sinks dominated RONO₂ loss processes during SOAS, responsible for 55% ± 20% of total loss, primarily due to aerosol hydrolysis.](#) RONO₂
25 lifetimes are too short (~~minutes-hours, Table 1~~) ([minutes-hours, Table 1 and Romer et al., 2016](#)) for significant transport to occur, and simulated RONO₂ loss typically occurs only a short distance from sources. Summed over the Southeast US domain, we find gross RONO₂ production and loss are roughly balanced (640 Mg N ~~day~~^d⁻¹). This balance implies that BVOC-derived gas-phase RONO₂ are not generally exported from the Southeast US, in agreement with earlier work (Horowitz et al., 2007; Hudman et al., 2007; Fang et al., 2010; Mao et al., 2013). However, this calculation excludes the longer-lived small alkyl
30 nitrates and non-hydrolyzing particulate nitrates not simulated in GEOS-Chem (Sect. 4). These may be an important source of exported reactive nitrogen, and their inclusion should be a priority for future model development.

The impacts of RONO₂ production and other loss processes on the NO_x budget are shown in Fig. 11b for the Southeast US boundary layer in August-September 2013. Non-RONO₂ losses in the figure are mainly HNO₃ formation, with an additional

contribution from PANs (relevant in regions with elevated NO_x ; Browne and Cohen, 2012). We find in the model that gross NO_x loss due to RONO_2 production is 35 Gg N over this period. As shown in Fig. 11a, only 23% of this RONO_2 (8 Gg N) goes on to recycle NO_x . We therefore find that RONO_2 production serves as a net NO_x sink of 27 Gg N in the Southeast US in summer, equivalent to 21% of NO_x emitted in this region and season.

5 These regional-scale averages conceal important spatial variability. Figure 12 shows how the NO_x sink due to RONO_2 production varies spatially across the Southeast US in summer, and how this depends on the ratio between BVOC and NO_x emissions ($E_{\text{BVOC}}/E_{\text{NO}_x}$). The fractional NO_x sink to RONO_2 is strongly correlated ($r = 0.90$) to the $E_{\text{BVOC}}/E_{\text{NO}_x}$ ratio. Our finding that RONO_2 production dominates NO_x loss in very low NO_x environments is consistent with an earlier analysis for boreal Canada (Browne and Cohen, 2012), which found the fractional sink to RONO_2 approached unity for $[\text{NO}_x] < 50$
10 ppt, and with analysis of a subset of the SEAC⁴RS data from the low- NO_x Ozarks Mountains (Wolfe et al., 2015).

Figure 12c shows how the fractional NO_x sink to RONO_2 (blue) and the $E_{\text{BVOC}}/E_{\text{NO}_x}$ emission ratio (red) vary as a function of NO_x emissions (gray, shown as their cumulative distribution binned into 5% quantiles). Both are inversely related to NO_x emissions. We see from the figure that RONO_2 production is the dominant NO_x sink for regions that account for the lowest 5% of total Southeast US NO_x emissions (leftmost bar in Fig. 12c), but the importance of the sink drops off rapidly as
15 NO_x emissions increase. By the time 30% of the regional NO_x emissions are accounted for, the fractional sink has dropped to 0.2, and from there continues to decline to a minimum of 0.03 in the highest-emitting regions.

The mean $E_{\text{BVOC}}/E_{\text{NO}_x}$ ratio averaged over the Southeast US is 5.3 and is highlighted as the white point in Fig. 12c. The figure shows that most Southeast US NO_x emission ($\sim 65\%$) occurs at $E_{\text{BVOC}}/E_{\text{NO}_x}$ ratios that are significantly lower than the regional mean, highlighting the significant spatial segregation between NO_x and BVOC emissions in this region (Yu et al.,
20 2016).

Emissions projections for the Southeast US anticipate continued decreases in NO_x emissions (and concomitant increases in the $E_{\text{BVOC}}/E_{\text{NO}_x}$ ratio). While these changes should increase the importance of RONO_2 for the NO_x budget, the relationship shown in Fig. 12c suggests very large emissions decreases will be necessary before RONO_2 becomes a major regional sink for NO_x . The figure shows that the sink to RONO_2 is only sensitive to NO_x emissions in regions where they are already
25 low: a 10% decrease in total Southeast US NO_x emissions (e.g., a leftward shift by two bars in the figure) would increase the importance of the sink by less than 0.5%. The actual rate at which NO_x emissions in the Southeast US will decrease varies widely among different projections. Under the Representative Concentration Pathway 8.5 (RCP8.5), for example, the Southeast US would see a decrease (relative to 2013 emissions) of 45% by 2050 to $\sim 1300 \text{ Mg N day}^{-1}$; according to Fig. 12, the RONO_2 sink would still only account for about 10% of the loss in the highest emitting regions. Under the more aggressive
30 RCP4.5, emissions would decline by 65% to $\sim 800 \text{ Mg N day}^{-1}$ in 2050. At this stage, the RONO_2 sink would become significant ($>20\%$) throughout the region.

6 Conclusions

We have used airborne and ground-based observations from two summer 2013 campaigns in the Southeast US (SEAC⁴RS, SOAS) to better understand the chemistry and impacts of alkyl and multi-functional organic nitrates (RONO₂). We used the observations, along with findings from recent laboratory, field, and modeling studies, to update and evaluate biogenic
5 volatile organic compound (BVOC) oxidation schemes in the GEOS-Chem chemical transport model (CTM). From there, we used the updated CTM with $0.25^\circ \times 0.3125^\circ$ ($\sim 25 \times 25$ km²) horizontal resolution to examine RONO₂ speciation, chemical production/loss processes, and importance as a sink for NO_x.

Our improved mechanism provides a state-of-the-science description of isoprene oxidation in the presence of NO_x, with updates including a 9% isoprene nitrate (IN) yield (Xiong et al., 2015), an increase in the population of β - vs δ -hydroxyl
10 isomers (Peeters et al., 2014), revised IN reaction rate constants and products (Jacobs et al., 2014; Lee et al., 2014), fast photolysis of carbonyl INs (Müller et al., 2014), rapid IN dry deposition (Nguyen et al., 2015), and a simplified scheme for aerosol partitioning of soluble INs (Xu et al., 2014; Marais et al., 2016) followed by particle-phase hydrolysis (Jacobs et al., 2014; Rindelaub et al., 2015). For the first time in GEOS-Chem, we have also added both OH- and NO₃-initiated monoterpene oxidation leading to the formation of monoterpene nitrates (MTNs), with similar loss processes as for INs. With these updates,
15 GEOS-Chem simulates surface-level BVOC and RONO₂ mixing ratios that are generally within the observed variability of the SEAC⁴RS and SOAS data.

Observed first generation IN (ISOPN) variability is generally reproduced without bias by GEOS-Chem, except at midday when modeled ISOPN peaks while SOAS observations indicate a gradual decline. For second generation INs, the model shows more skill for species produced primarily from β -hydroxyl isomers (MVKN+MACRN) than those from δ -hydroxyl
20 isomers and NO₃-initiated chemistry (PROPNN+ETHLN). For the latter, GEOS-Chem underestimates both magnitudes and variability relative to the SEAC⁴RS observations. While this could imply a more important role for δ -channel oxidation than included in our mechanism, theoretical considerations suggest that our assumed δ -hydroxyl contribution is already an upper limit (Peeters et al., 2014), and more measurements are needed to reconcile these theoretical and observational constraints. Better understanding of nighttime NO₃-initiated isoprene oxidation could also play an important role in improving simulation
25 of second generation INs.

The SEAC⁴RS observations imply that gas-phase INs account for 25-50% of total surface RONO₂, much less than inferred from previous modeling studies (Mao et al., 2013; Xie et al., 2013). GEOS-Chem reproduces this contribution and attributes an additional 10% of RONO₂ to MTNs. Both observations and model show 10-20% of the remaining RONO₂ at the surface is in the particle phase (pRONO₂). In the free troposphere, GEOS-Chem greatly underestimates total RONO₂ by ignoring
30 contributions from small, long-lived nitrates derived from anthropogenic VOCs and from non-hydrolyzing particulate species. This has a significant impact on simulation of reactive nitrogen export from the United States and should be remedied in future model development.

We find in the model that formation of pRONO₂ via aerosol uptake, followed by particle-phase hydrolysis, is the dominant loss process for gas-phase RONO₂. Including this large sink to aerosol results in simulated RONO₂, pRONO₂ and HNO₃

mixing ratios and nitrate deposition fluxes that are consistent with observations. RONO₂ loss via deposition is also significant, with RONO₂ (both gas-phase and particulate) responsible for ~3% of total N deposition over the Southeast US in summer.

Overall, less than a quarter of simulated gas-phase RONO₂ loss recycles atmospheric NO_x. We find in the model that RONO₂ production accounts for 21% of the net sink of NO_x emitted in the Southeast US in summer. RONO₂ production is the dominant NO_x sink only in regions where elevated BVOC emissions are paired with very low NO_x emissions. Elsewhere, the importance of the sink declines rapidly as a function of NO_x emissions. Most of the Southeast US NO_x is emitted in locations where BVOC emissions are relatively low, limiting the importance of RONO₂ as a NO_x sink.

Southeast US NO_x emissions have been declining for the past two decades (Hidy et al., 2014; Simon et al., 2015) and further reductions are projected (Lamarque et al., 2011; EPA, 2014). Previous studies have suggested these declines will trigger a more important role for RONO₂ as a NO_x sink in future (Browne and Cohen, 2012). In contrast, we find here that the NO_x sink to RONO₂ is only sensitive to NO_x emissions in regions where they are already low because of the spatial segregation between NO_x and BVOC emissions. We find that a 10% decrease in Southeast US NO_x emissions would enhance the importance of this sink by less than 0.5%. HNO₃ formation and deposition is likely to remain the dominant sink for NO_x even as NO_x emissions decrease.

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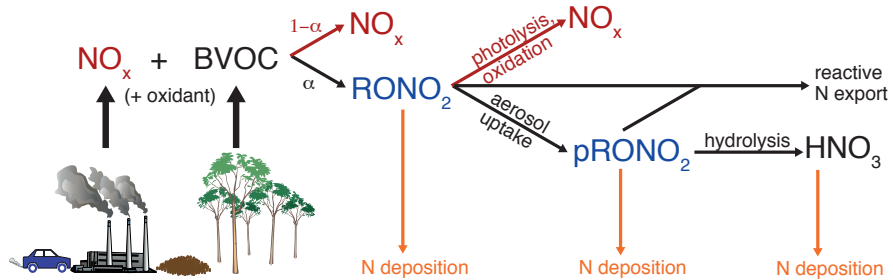


Figure 1. Schematic representation of organic nitrate chemistry and impacts. Organic nitrates are shown in blue, NO_x and processes that recycle NO_x are shown in red, and nitrogen deposition is shown in orange. Symbols courtesy of the Integration and Application Network, University of Maryland Center for Environmental Science (ian.umces.edu/symbols/).

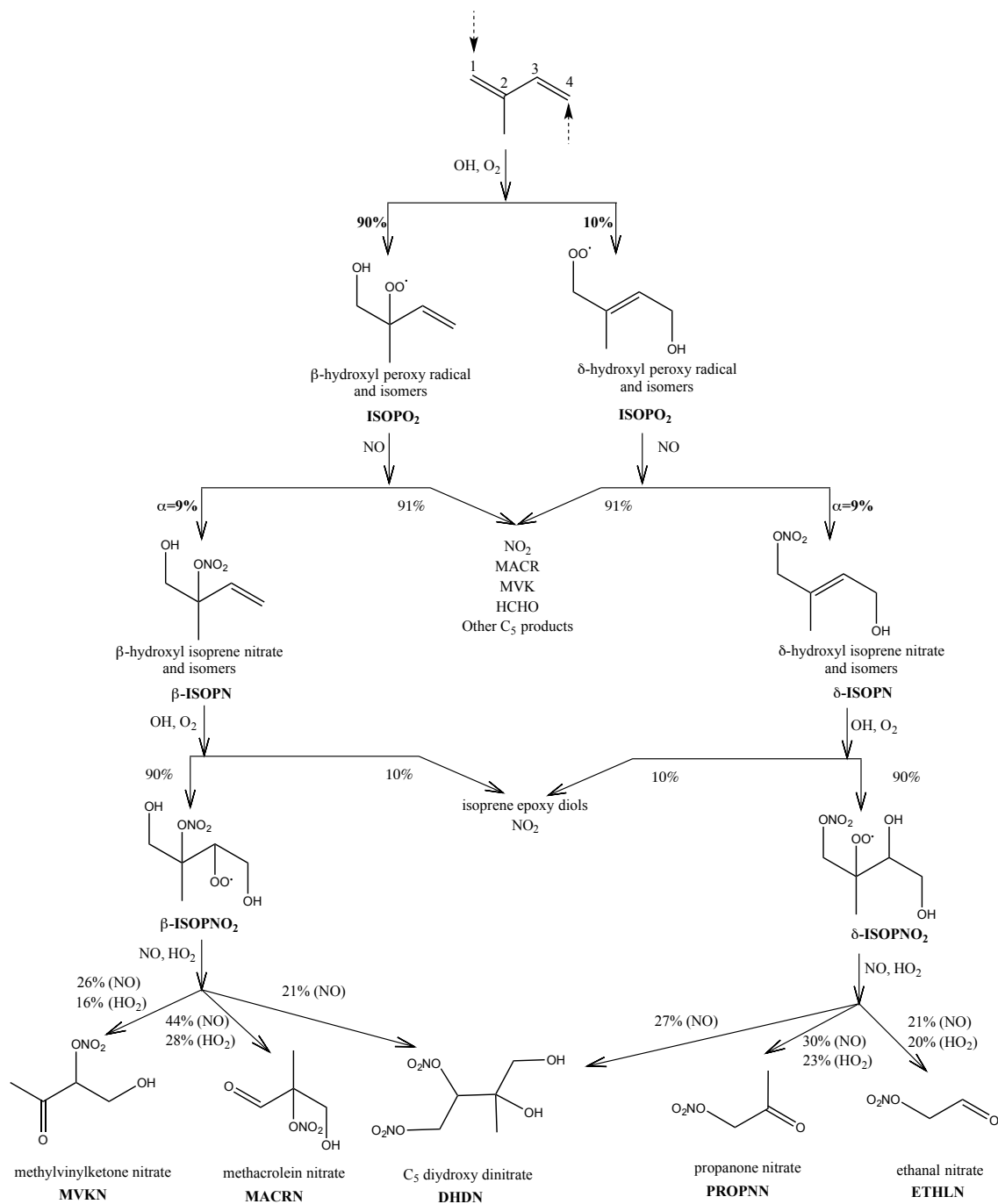


Figure 2. Schematic of the formation of isoprene nitrates (INs) from OH-initiated isoprene oxidation as implemented in GEOS-Chem. The isomers shown are indicative as the mechanism does not distinguish between isomers (except for β - vs. δ -configurations). For ISOPNO₂ oxidation, only IN products are shown, along with their yields from both NO and HO₂ pathways. Small yields (<10%) of MVKN and MACRN from δ -ISOPNO₂ are not shown.

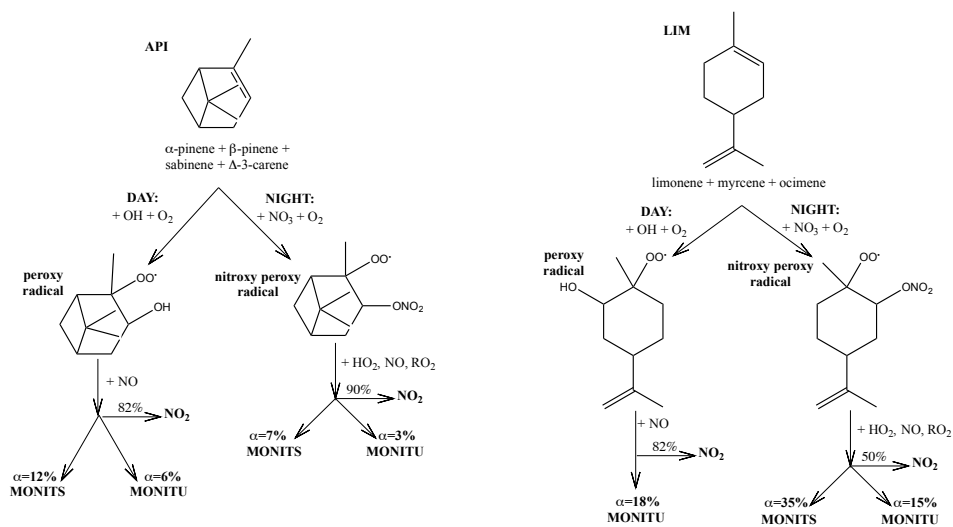


Figure 3. Simplified representation of the formation of monoterpene nitrates (MTN) from monoterpene oxidation as implemented in GEOS-Chem. For each lumped species, only one indicative form is shown.

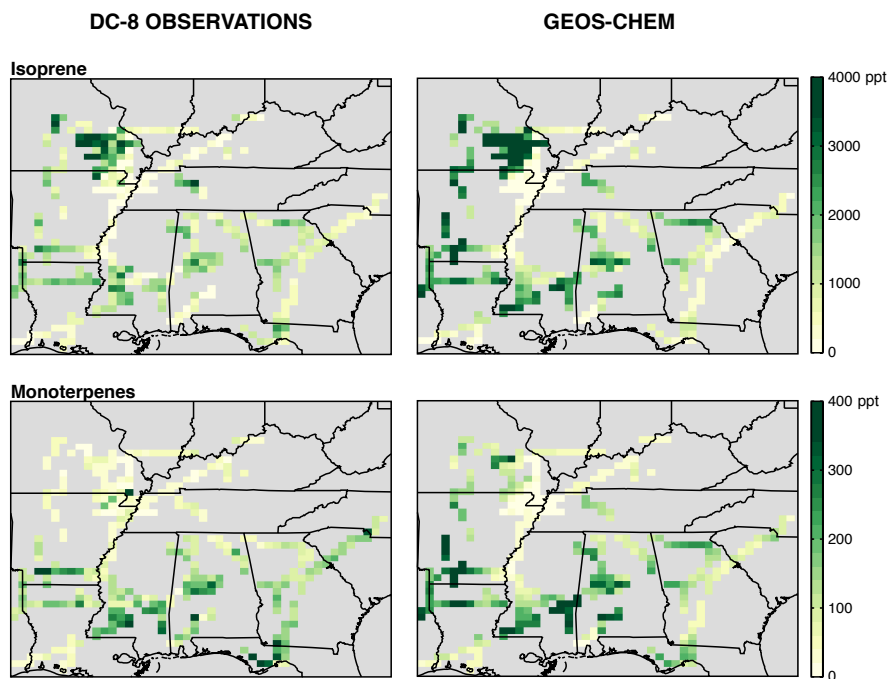


Figure 4. Observed (left) and simulated (right) mixing ratios of isoprene and monoterpenes below 1 km during the SEAC⁴RS aircraft campaign (12 Aug - 23 Sep 2013), along with the normalized mean bias (NMB) of the simulation relative to the PTR-MS measurements. The GEOS-Chem model has been sampled along the aircraft flight tracks, and the observations binned to the spatial and temporal resolution of the model. The normalized mean bias of the simulation relative to the PTR-MS measurements in the lowest 500 m is +34% for isoprene and +3% for monoterpenes.

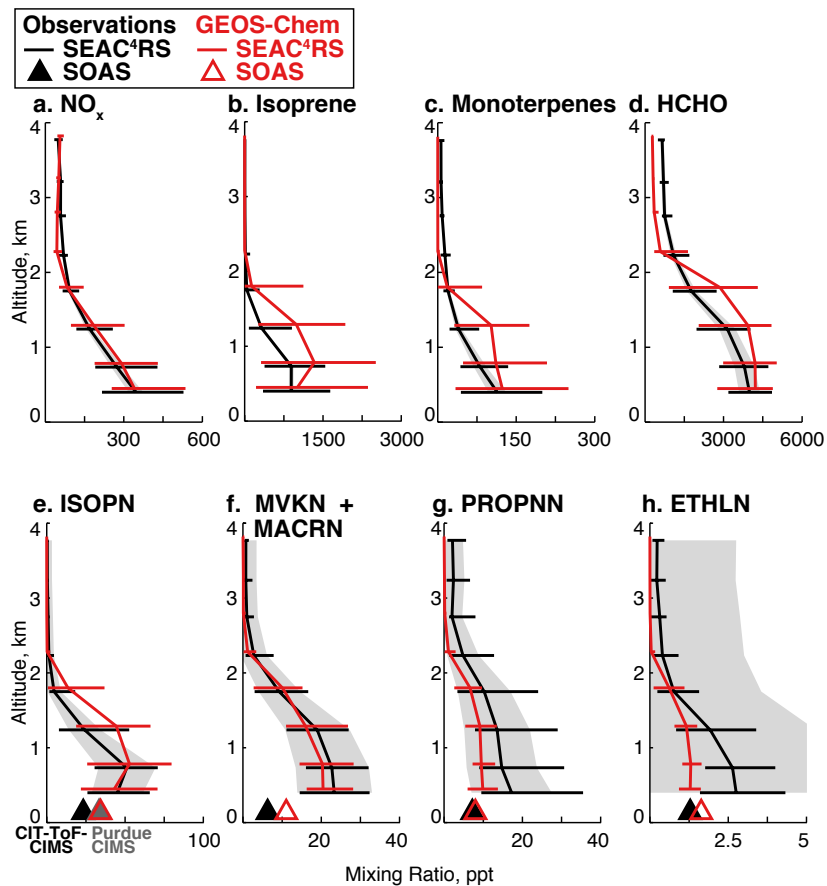


Figure 5. Observed (black) and modeled (red) median 0-4 km profiles of NO_x, biogenic VOCs, and oxidation products over the Southeast US (80-94.5°W, 29.5-40°N) during SEAC⁴RS. Data are binned in 500m increments, and horizontal lines indicate the interquartile range within each bin. Gray shading represents the measurement uncertainty. The model has been sampled in the same manner as the observations, as described in the text. For organic nitrates (e-h), SOAS campaign median surface values are shown as triangles. For ISOPN (e), the gray triangle represents the Purdue CIMS and the black triangle the CIT-ToF-CIMS.

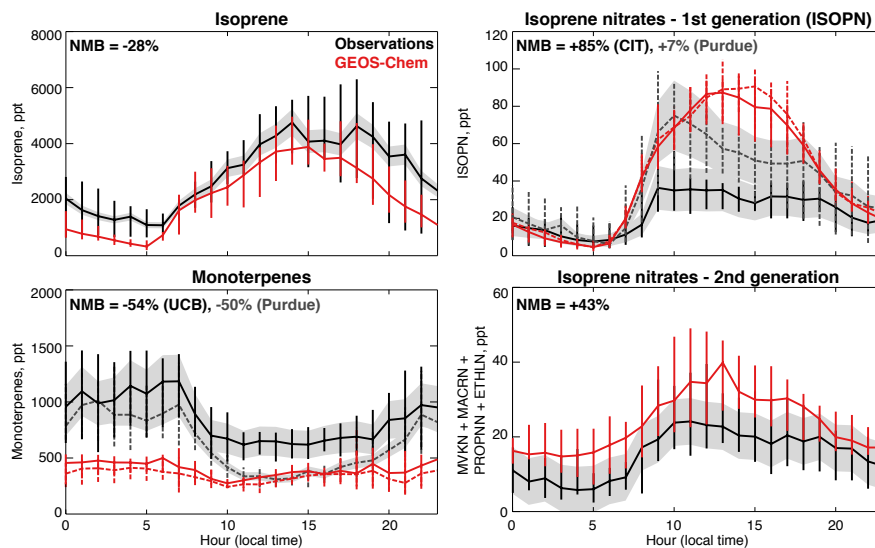


Figure 6. Observed (black, gray) and simulated (red) median diurnal cycles of isoprene, monoterpenes, first generation isoprene nitrates (ISOPN), and second generation isoprene nitrates (MVKN+MACRN+PROPNN+ETHLN) at Centreville during the 2013 SOAS campaign. Gray shading represents the measurement uncertainty, vertical bars show the interquartile range of the hourly data, and the normalized mean bias (NMB) of the simulation is given inset. The model has been sampled in the Centreville grid box only for hours with available data during 16 June - 11 July for isoprene and monoterpenes from the UC Berkeley PTR-ToF-MS (solid black), 13 June - 15 July for α -pinene + β -pinene from the Purdue 2D-GF-FID (dashed gray), 1 June - 11 July for ISOPN from the Purdue CIMS (dashed gray), and 1 June - 4 July for ISOPN and 2nd generation isoprene nitrates from the CIT-ToF-CIMS (solid black). For ISOPN and monoterpenes, differences in data availability between the two measurements result in slightly different model values (solid/dashed red lines).

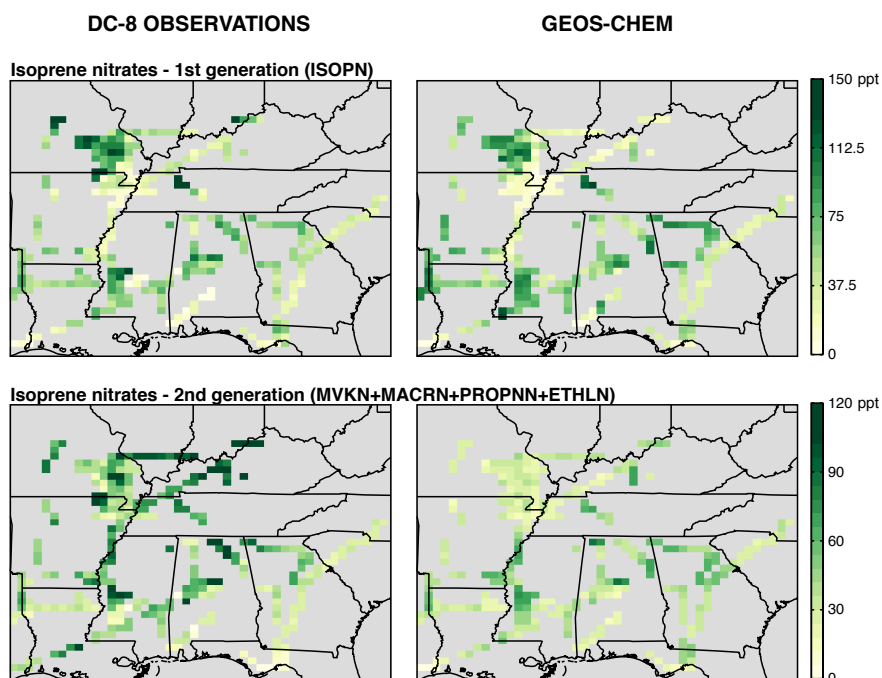


Figure 7. Observed (left) and simulated (right) mixing ratios of isoprene nitrates below 1 km during SEAC⁴RS, separated into first generation (ISOPN) and second generation (MVKN+MACRN+PROPNN+ETHLN) species, ~~along with the normalized mean bias (NMB) of the simulation.~~ The GEOS-Chem simulation has been sampled along the aircraft flight tracks, and the observations binned to the spatial and temporal resolution of the model, as described in the text. The normalized mean bias of the simulation relative to the measurements in the lowest 500 m is -0.6% for ISOPN and -35% for second generation isoprene nitrates.

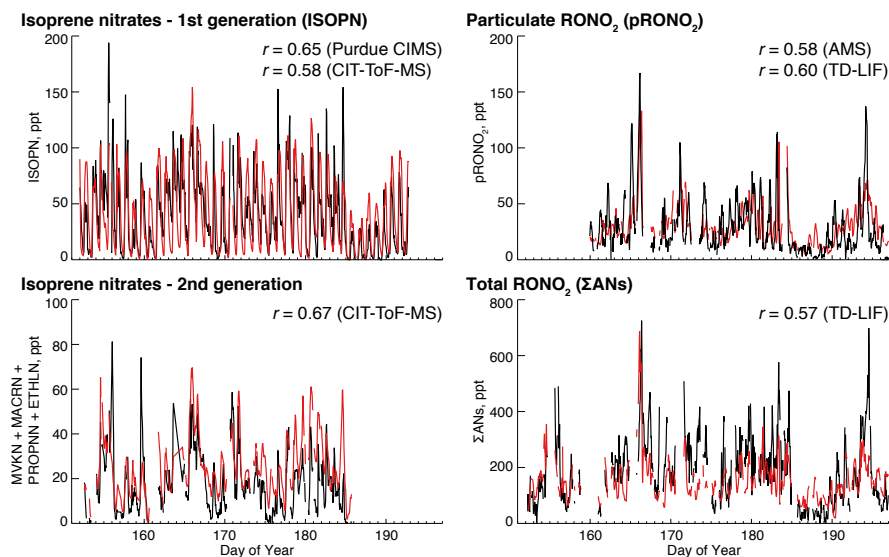


Figure 8. Timeseries of observed (black) and simulated (red) hourly mean RONO_2 at Centreville during the 2013 SOAS campaign for 1st generation isoprene nitrates (ISOPN, from the Purdue CIMS), 2nd generation isoprene nitrates (MVKN+MACRN+PROPNN+ETHLN from the CIT-ToF-CIMS), particulate RONO_2 (pRONO_2 , from the AMS) and total alkyl nitrates (ΣANs , from the TD-LIF). The model has been sampled in the Centreville grid box only for hours with available data from each instrument. The model-observation correlation coefficient (r) for each species is given inset both for the measurement shown and (where available) for additional measurement of the same species (with timeseries shown in Fig. S4).

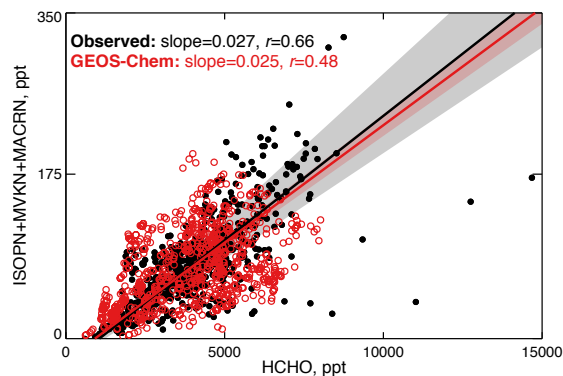


Figure 9. Observed (black) and simulated (red) correlations between HCHO and the sum of major isoprene nitrates produced via daytime isoprene oxidation (ISOPN+MVKN+MACRN) in Southeast US surface air (<1 km) during SEAC⁴RS. Thick solid lines indicate the best fit as calculated from a reduced major axis regression, and shaded areas show the 95% confidence interval on the regression slope as determined by bootstrap resampling. The regression slopes and correlation coefficients are given inset.

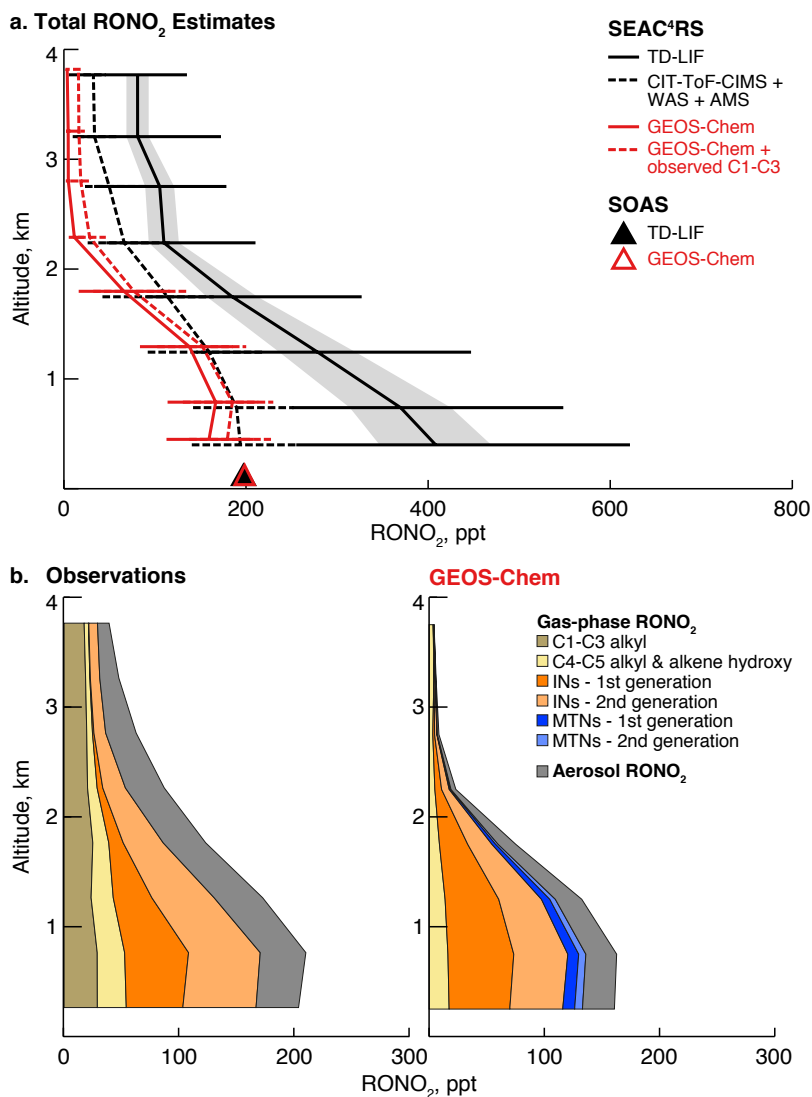
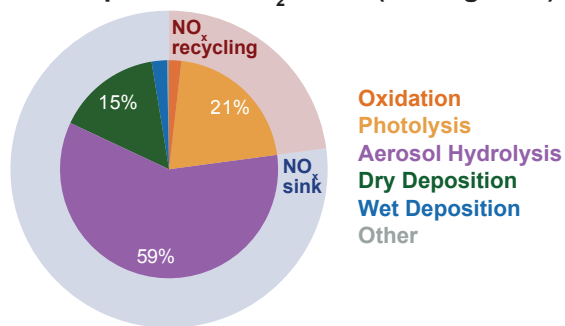


Figure 10. (a) Median vertical profiles of estimated total RONO₂ over the Southeast US during SEAC⁴RS. For the observations, the solid black line indicates the TD-LIF Σ ANs measurements (with gray shading for the measurement uncertainty) and the dashed black line the sum of CIT-ToF-CIMS, WAS, and AMS measurements of individual RONO₂ species (gas-phase and particulate). For the model, the solid red line indicates the total simulated RONO₂ and the dashed red line the sum of total simulated RONO₂ plus measured $\leq C_3$ RONO₂ that are not included in the simulation. Triangles compare the total RONO₂ during SOAS from TD-LIF Σ ANs and GEOS-Chem. (b) Mean RONO₂ composition from the observations (CIT-ToF-CIMS, WAS, and AMS) and the model. Isoprene nitrates (INs) include 1st generation (ISOPN, plus ISN1 for GEOS-Chem) and 2nd generation INs (MVKN+MACRN, PROPNN, ETHLN, NISOPOOH, plus DHDN for GEOS-Chem). Monoterpene nitrates (MTNs) are shown for the model only and include first and second generation contributions. Other gas-phase RONO₂ (yellow, brown) are mainly anthropogenic and do not represent the same species between the model and the observations.

a. Gas-phase RONO₂ Sinks (642 Mg N d⁻¹)



b. Terminal NO_x Sinks (2.18 Gg N d⁻¹)

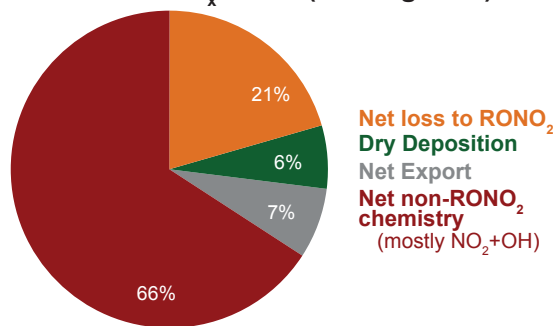


Figure 11. Simulated relative importance of gas-phase loss processes (%) in the Southeast US boundary layer (80-94.5°W, 29.5-40°N, <2 km) during August-September 2013 for (a) gas-phase RONO₂ and (b) NO_x. In (a), outer circles group losses into those that recycle NO_x (pale red) and those that serve as terminal NO_x sinks (pale blue). Loss processes that recycle RONO₂ by converting between RONO₂ species (e.g. first to second generation) are not included. In (b), net loss to RONO₂ is calculated as the difference between NO_x consumed during RONO₂ production and NO_x recycled during RONO₂ loss, with recycling efficiencies from (a). Net non-RONO₂ chemistry is the difference between NO_x chemical production and chemical loss excluding all RONO₂ chemistry, and net export is the difference between emissions and all other sinks. Absolute loss rates from all processes combined (Mg N day⁻¹) are given in the sub-plot titles.

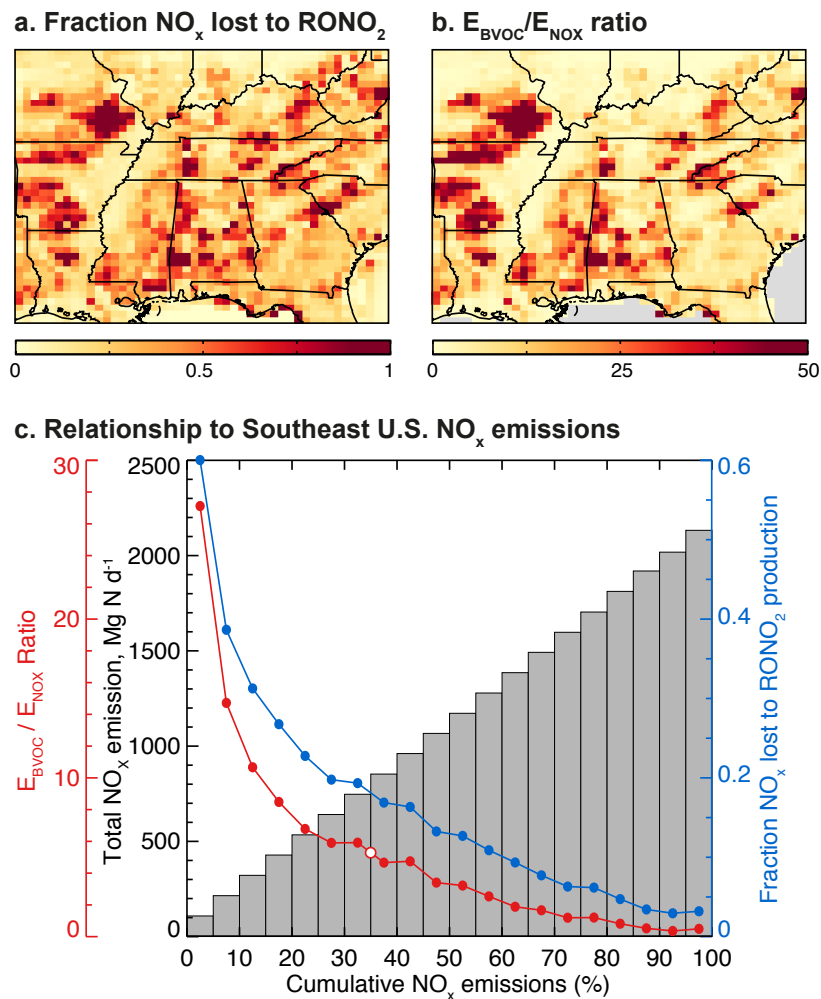


Figure 12. Importance of organic nitrates as a sink for NO_x, as a function of BVOC and NO_x emissions. (a) Simulated fraction of emitted NO_x that is lost to RONO₂ production in Southeast US surface air. (b) Ratio of BVOC (isoprene + monoterpene) emissions (E_{BVOC}) to NO_x emissions (E_{NOx}). (c) Mean values of variables from (a) and (b) as a function of cumulative NO_x emissions in the Southeast US. Model grid squares have been sorted by NO_x emissions then grouped into bins that each represent 5% of total Southeast US NO_x emissions. Values shown for the fractional NO_x sink due to RONO₂ production (blue) and the mean E_{BVOC}/E_{NOx} emissions ratio (red) represent the mean within each bin. NO_x emissions are shown as cumulative totals (gray) in Mg N day⁻¹. The Southeast US mean E_{BVOC}/E_{NOx} emissions ratio (5.3) is highlighted with a white circle.

Table 1. Gas-phase organic nitrates in GEOS-Chem along with their principal formation and loss pathways, removal processes (ordered by importance), and lifetimes in Southeast US surface air during SEAC⁴RS.^a

Species	Model name	Principal formation pathways ^a	Removal Processes ^b	Lifetime (hr) ^c	Removal Processes ^c	Lifetime ^c
β -hydroxy isoprene nitrate	ISOPNB	ISOP + OH	aerosol hydrolysis deposition oxidation photolysis	1.8		
δ -hydroxy isoprene nitrate	ISOPND	ISOP + OH	deposition oxidation aerosol hydrolysis photolysis	4.0		
C ₅ nitrooxy carbonyl	ISN1	ISOP + NO ₃	deposition photolysis oxidation aerosol hydrolysis	0.29		
C ₅ nitrooxy hydroperoxide ^{d,e}	INPN	ISOP + NO ₃	n/a	n/a		
methyl vinyl ketone nitrate	MVKN	ISOPNB + OH	deposition aerosol hydrolysis photolysis oxidation	3.1		
methacrolein nitrate	MACRN	ISOPNB + OH	photolysis deposition aerosol hydrolysis oxidation	1.5		
propanone nitrate	PROPNN	ISOPND + OH ISN1 + NO ₃	deposition photolysis oxidation	3.3		
ethanal nitrate	ETHLN	ISOPND + OH	deposition photolysis oxidation	1.5		
C ₅ dihydroxy dinitrate	DHDN	ISOPND + OH ISOPND + OH	aerosol hydrolysis deposition	4.6		
saturated first generation monoterpene nitrate	MONITS	API + OH API + NO ₃ LIM + NO ₃	deposition aerosol hydrolysis oxidation photolysis	1.8		
unsaturated first generation monoterpene nitrate	MONITU	API + OH API + NO ₃ LIM + OH LIM + NO ₃	oxidation deposition aerosol hydrolysis photolysis	0.85		
second generation monoterpene nitrate	HONIT	MONITU + OH MONITS + OH	aerosol hydrolysis deposition photolysis oxidation	1.7		

^a Model results are averaged over Southeast US surface air sampled along the SEAC⁴RS flight tracks.

^b Primary precursor(s) and associated oxidant(s). The related peroxy radicals and their oxidants can be seen in Figs. 1 and 2.

^c Removal processes for each species are ordered by their contribution to total loss during SEAC⁴RS. Losses due to oxidation, photolysis, and aerosol uptake are calculated along the SEAC⁴RS flight tracks. Deposition includes both dry and wet scavenging and is calculated from regional means over all Southeast US grid boxes. Wet deposition in the model is calculated for lumped species ISOPNB+ISOPND, MVKN+MACRN, and MONITU+MONITS and individually for all others. For this table, we assume partitioning of 90% ISOPNB (10% ISOPND) based on the initial formation yields and a 50:50 ratio between the other lumped species. Wet scavenging is only a small contribution to total RONO₂ deposition, and this assumption has minimal impact on these values.

^d Lifetimes are the combined lifetimes against deposition as calculated over all grid boxes and against oxidation, photolysis, and aerosol hydrolysis as calculated along the flight tracks, with further note c. These are representative of daytime conditions only, as determined by the timing of the SEAC⁴RS flights.

^e INPN is not treated as a transported species, so diagnostics needed to calculate removal rates and lifetime are not available.

S1. RONO₂ sensitivity to NO_x emissions reductions

We use the same simulation as Travis et al. (2016), who reduced NO_x emissions in the NEI11v1 inventory by 60% for all anthropogenic sources except power plants (equivalent to a 53% decrease in total annual NEI11v1 emissions) and also reduced soil NO_x emissions in the Midwest US by 50% (Vinken et al., 2014). Figure S5 compares model results during SEAC⁴RS before and after applying these NO_x emissions decreases. As seen in the figure, the change to NO_x emissions cannot explain the model underestimate in ΣANs relative to the SEAC⁴RS TD-LIF measurement (-46% with original NO_x, -57% with reduced NO_x). The figure also shows that the change to NO_x emissions does not have an appreciable effect on simulation of individual RONO₂ species, which fall within the experimental uncertainties of the CIT-ToF-CIMS instrument in both versions of the model.

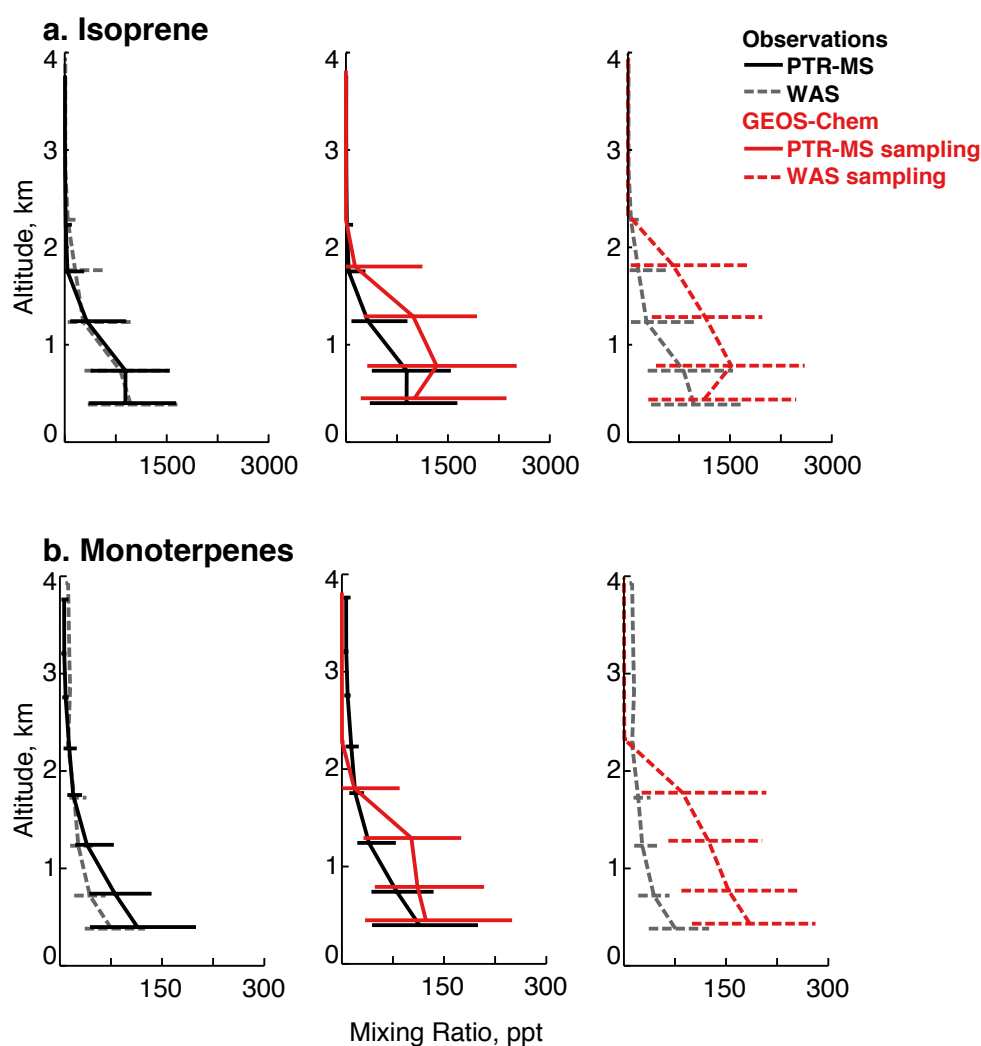


Figure S1. Comparison of median vertical profiles from PTR-MS (solid black) and Whole Air Sampler (WAS) measurements of isoprene and monoterpenes ($=\alpha$ -pinene $+\beta$ -pinene for the WAS) over the Southeast US during SEAC⁴RS (left). The observations are also compared to the GEOS-Chem simulation sampled in the same manner as each measurement in the center (PTR-MS) and right (WAS) panels.

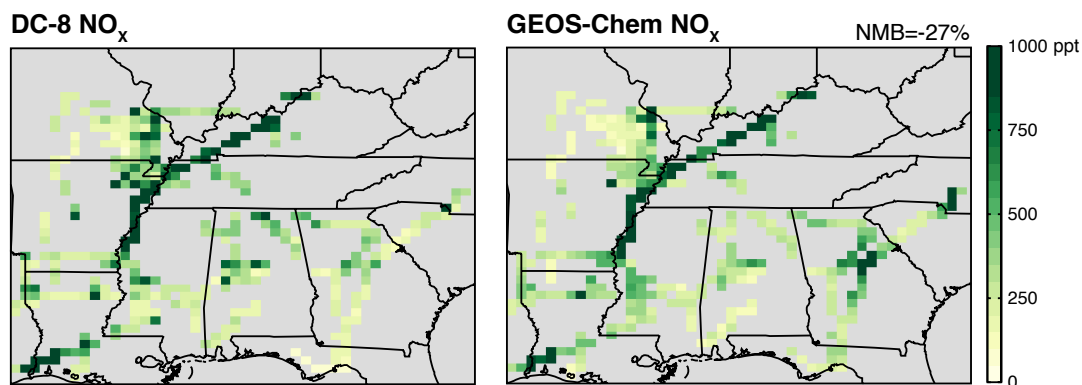


Figure S2. Same as Fig. 4, but for NO_x .

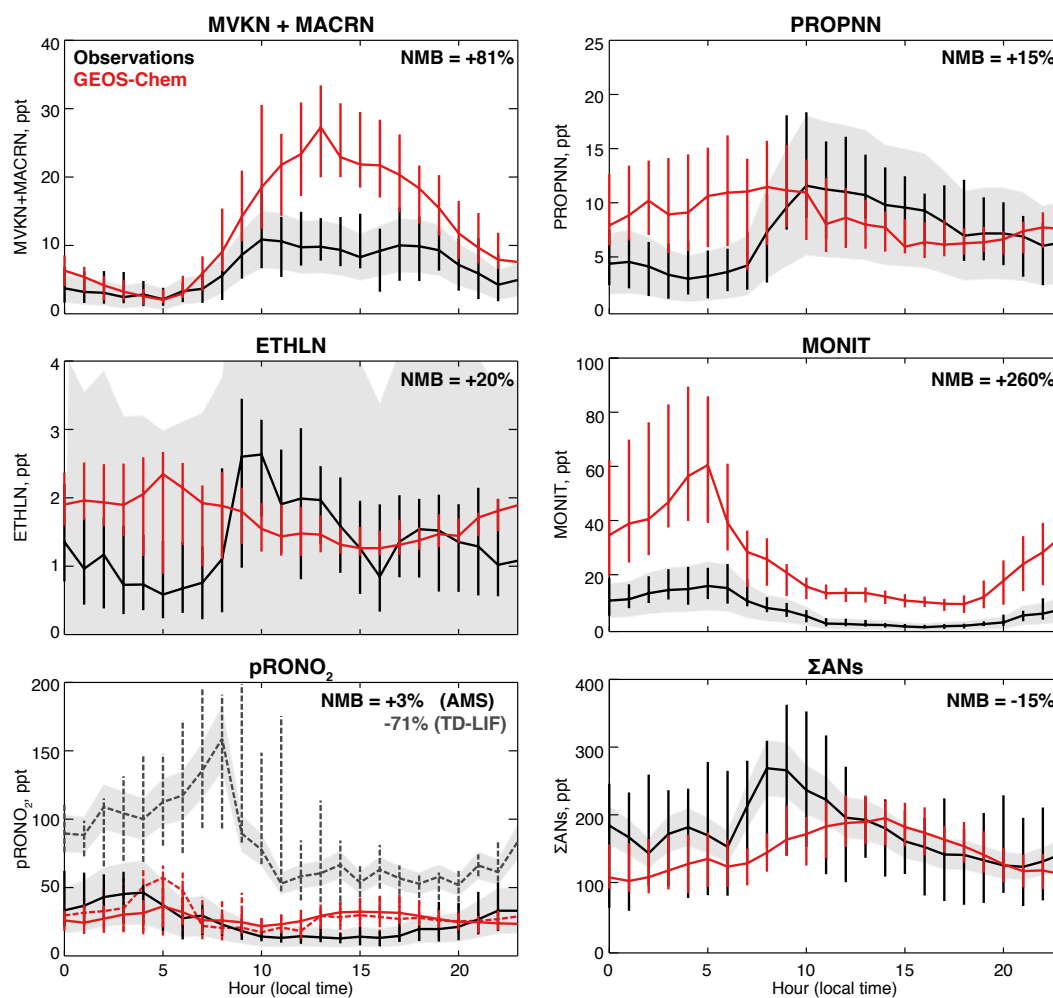


Figure S3. Same as Fig. 6, but for individual second generation isoprene nitrates (MVKN+MACRN, PROPNN, ETHLN) and summed first generation monoterpene nitrates (MONIT) from the CIT-ToF-MS (1 June – 4 July), particulate organic nitrates (pRONO_2) from the AMS (9 June – 15 July) and the TD-LIF (29 June – 15 July), and total organic nitrates (ΣANs) from the TD-LIF (1 June – 15 July).

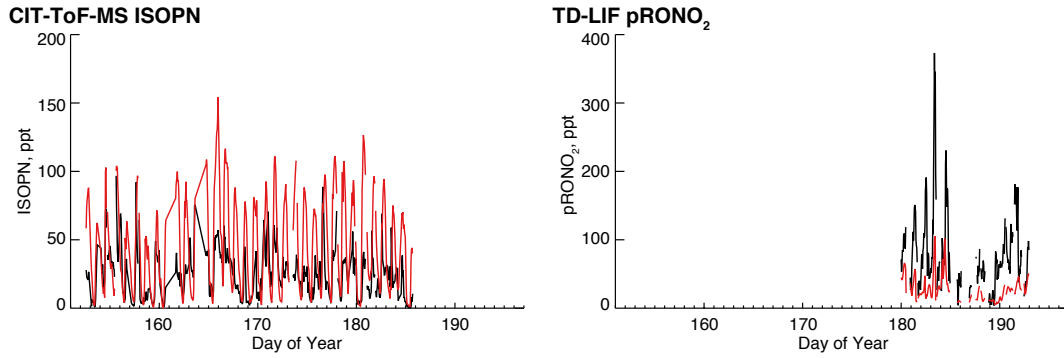


Figure S4. Same as Fig. 8, but for ISOPN measured by CIT-ToF-MS and for pRONO₂ measured by TD-LIF.

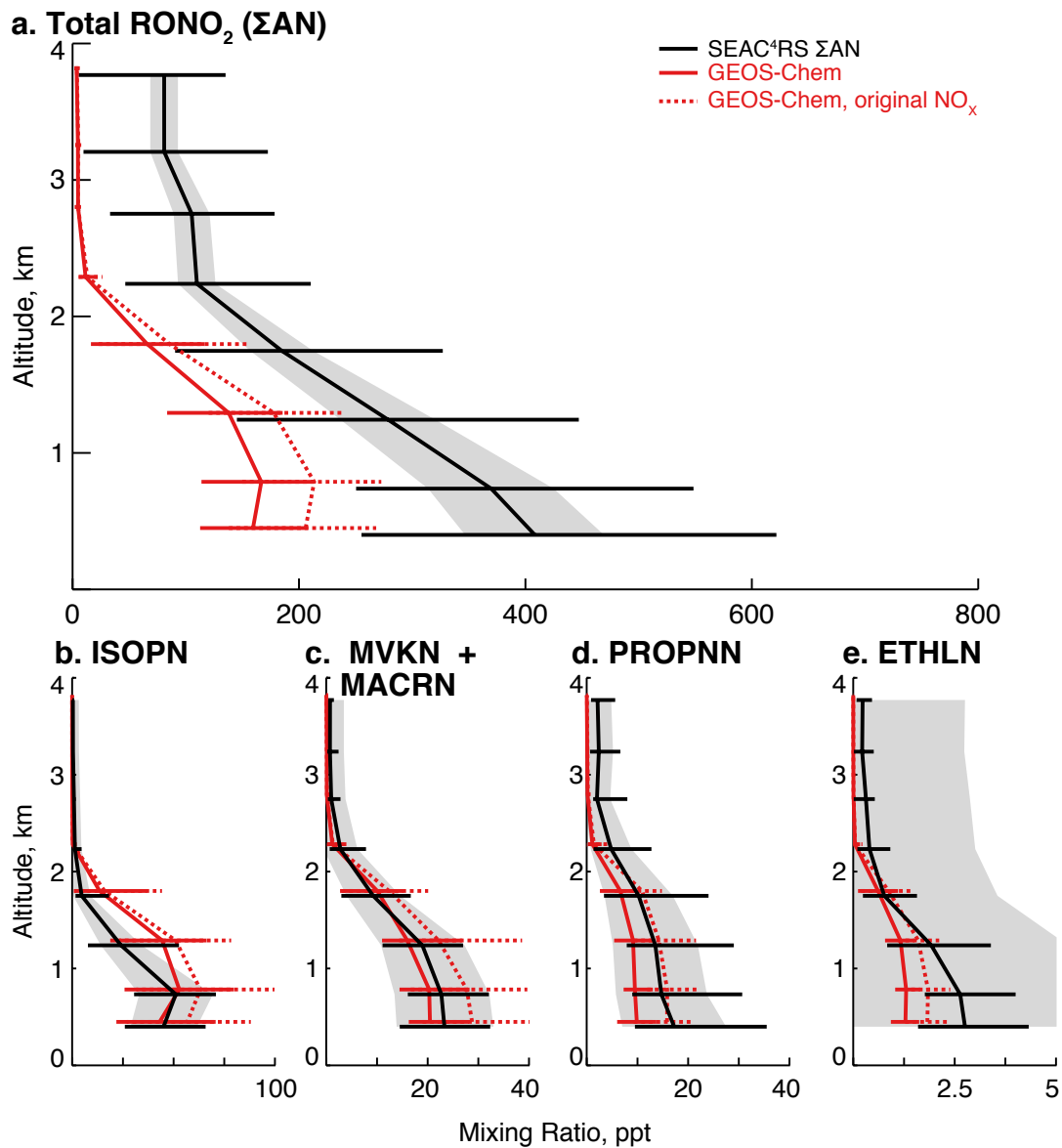


Figure S5. Observed (black) and modeled (red) median 0-4 km profiles of RONO₂ over the Southeast US during SEAC⁴RS. The dotted red line shows model results before scaling non-power plant NO_x emissions from the NEI11v1 inventory and soil NO_x in the Midwest US.

Table S1. New species added to GEOS-Chem for monoterpene nitrate chemistry.

<u>Abbreviation</u>	<u>Name</u>
<u>API</u>	<u>alpha-pinene and other cyclic terpenes with one double bond</u>
<u>APIO2</u>	<u>RO₂ from API</u>
<u>LIM</u>	<u>limonene and other cyclic terpenes with two double bonds</u>
<u>LIMO2</u>	<u>RO₂ from LIM</u>
<u>PIP</u>	<u>peroxides from API & LIM</u>
<u>OLND</u>	<u>monoterpene-derived NO₃-alkene adduct that primarily decomposes</u>
<u>OLNN</u>	<u>monoterpene-derived NO₃-alkene adduct that primarily retains the NO₃ functional group</u>
<u>MONITS</u>	<u>saturated first generation monoterpene organic nitrate</u>
<u>MONITU</u>	<u>unsaturated first generation monoterpene organic nitrate</u>
<u>HONIT</u>	<u>second generation monoterpene organic nitrate</u>

Table S2. New kinetic reactions added to GEOS-Chem for monoterpene nitrate chemistry.

<u>Reactants</u>	<u>Products</u>	<u>Rate Constant</u>
<u>API + OH</u>	<u>APIO2</u>	<u>1.21E-11*exp(440/T)</u>
<u>APIO2 + NO</u>	<u>0.82HO2 + 0.82NO2 + 0.23HCHO + 0.43 RCHO + 0.11 ACET + 0.44MEK + 0.07 HCOOH + 0.12MONITS + 0.06MONITU</u>	<u>4.00E-12</u>
<u>APIO2 + HO2</u>	<u>PIP</u>	<u>1.50E-11</u>
<u>APIO2 + MO2</u>	<u>HO2 + 0.75HCHO + 0.25 MOH + 0.25 ROH + 0.75RCHO + 0.75MEK</u>	<u>3.56E-14*exp(708/T)</u>
<u>APIO2 + MCO3</u>	<u>0.5 HO2 + 0.5 MO2 + RCHO + MEK + RCOOH</u>	<u>7.40E-13*exp(765/T)</u>
<u>APIO2 + NO3</u>	<u>HO2 + NO2 + RCHO + MEK</u>	<u>1.20E-12</u>
<u>API + O3</u>	<u>0.85OH + 0.1HO2 + 0.62 KO2 + 0.14 CO + 0.02 H2O2 + 0.65RCHO + 0.53MEK</u>	<u>5.0E-16*exp(-530/T)</u>
<u>APIO2 + NO3</u>	<u>0.1OLNN + 0.9 OLND</u>	<u>8.33E-13*exp(490/T)</u>
<u>LIM + OH</u>	<u>LIMO2</u>	<u>4.20E-11*exp(401/T)</u>
<u>LIMO2 + NO</u>	<u>0.686HO2 + 0.78NO2 + 0.22MONITU + 0.289 PRPE + 0.231HCHO + 0.491RCHO + 0.058HAC + 0.289MEK</u>	<u>4.00E-12</u>
<u>LIMO2 + HO2</u>	<u>PIP</u>	<u>1.50E-11</u>
<u>LIMO2 + MO2</u>	<u>HO2 + 0.192 PRPE + 1.04 HCHO + 0.308 MACR + 0.25 MOH + 0.25 ROH</u>	<u>3.56E-14*exp(708/T)</u>
<u>LIMO2 + MCO3</u>	<u>0.5 HO2 + 0.5 MO2 + 0.192PRPE + 0.385 HCHO + 0.308 MACR + 0.5 RCOOH</u>	<u>7.40E-13*exp(765/T)</u>
<u>LIMO2 + NO3</u>	<u>HO2 + NO2 + 0.385PRPE + 0.385HCHO + 0.615MACR</u>	<u>1.20E-12</u>
<u>LIM + O3</u>	<u>0.85OH + 0.10HO2 + 0.16 ETO2 + 0.42 KO2 + 0.02H2O2 + 0.14CO + 0.46PRPE + 0.04HCHO + 0.79MACR +</u>	<u>2.95E-15*exp(-783/T)</u>

	<u>0.01HCOOH + 0.07 RCOOH</u>	
<u>LIM + NO3</u>	<u>0.5OLNN + 0.5OLND</u>	<u>1.22E-11</u>
<u>PIP + OH</u>	<u>0.49OH + 0.44R4O2 + 0.08RCHO + 0.41MEK</u>	<u>3.4E-12*exp(190/T)</u>
<u>OLNN + NO</u>	<u>HO2 + NO2 + MONITS</u>	<u>4.00E-12</u>
<u>OLND + NO</u>	<u>2.0 NO2 + 0.287 HCHO + 1.24 RCHO + 0.464 MEK</u>	<u>4.00E-12</u>
<u>OLNN + HO2</u>	<u>0.7MONITS + 0.3MONITU</u>	<u>1.66E-13*exp(1300/T)</u>
<u>OLND + HO2</u>	<u>0.7MONITS + 0.3MONITU</u>	<u>1.66E-13*exp(1300/T)</u>
<u>OLNN + MO2</u>	<u>2.0 HO2 + HCHO + 0.7MONITS + 0.3MONITU</u>	<u>1.60E-13*exp(708/T)</u>
<u>OLND + MO2</u>	<u>0.5 HO2 + 0.5 NO2 + 0.965 HCHO + 0.93 RCHO + 0.348 MEK + 0.25 MOH + 0.25 ROH + 0.35 MONITS + 0.15 MONITU</u>	<u>9.68E-14*exp(708/T)</u>
<u>OLNN + MCO3</u>	<u>HO2 + MO2 + 0.7 MONITS + 0.3 MONITU</u>	<u>8.85E-13*exp(765/T)</u>
<u>OLND + MCO3</u>	<u>0.5MO2 + NO2 + 0.287 HCHO + 1.24 RCHO + 0.464 MEK + 0.5 RCOOH</u>	<u>5.37E-13*exp(765/T)</u>
<u>OLNN + NO3</u>	<u>HO2 + NO2 + 0.7 MONITS + 0.3 MONITU</u>	<u>1.20E-12</u>
<u>OLND + NO3</u>	<u>2.0NO2 + 0.287 HCHO + 1.24 RCHO + 0.464 MEK</u>	<u>1.20E-12</u>
<u>OLNN + OLNN</u>	<u>HO2 + 1.4 MONITS + 0.6 MONITU</u>	<u>7.0E-14*exp(1000/T)</u>
<u>OLNN + OLND</u>	<u>0.5 HO2 + 0.5 NO2 + 0.202HCHO + 0.64 RCHO + 0.149 MEK +1.05 MONITS + 0.45 MONITU</u>	<u>4.25E-14*exp(1000/T)</u>
<u>OLND + OLND</u>	<u>NO2 + 0.504 HCHO + 1.21 RCHO + 0.285MEK + 0.7 MONITS + 0.3 MONITU</u>	<u>2.96E-14*exp(1000/T)</u>
<u>MONITS + OH</u>	<u>HONIT</u>	<u>4.80E-12</u>
<u>MONITU + OH</u>	<u>HONIT</u>	<u>7.29E-11</u>
<u>MONITU + O3</u>	<u>HONIT</u>	<u>1.67E-16</u>
<u>MONITU + NO3</u>	<u>HONIT</u>	<u>3.15E-13*exp(-448/T)</u>
<u>MONITS + NO3</u>	<u>HONIT</u>	<u>3.15E-13*exp(-448/T)</u>
<u>HONIT + OH</u>	<u>NO3 + HKET</u>	<u>same as HNO3 + OH</u>

Table S3. New photolysis reactions added to GEOS-Chem for monoterpene nitrate chemistry

<u>Species</u>	<u>Photolysis Products</u>	<u>j-value used</u>
<u>PIP</u>	<u>OH + HO2 + RCHO</u>	<u>j(H2O2)</u>
<u>MONITS</u>	<u>MEK + NO2</u>	<u>j(ONIT1)</u>
<u>MONITU</u>	<u>RCHO + NO2</u>	<u>j(ONIT1)</u>
<u>HONIT</u>	<u>HKET + NO2</u>	<u>j(ONIT1)</u>

Table S4. Reactive uptake coefficients (γ) used in GEOS-Chem aerosol uptake parameterization for organic nitrates.^a

Species	γ
ISOPNB	0.005
ISOPND	0.005
ISN1	0.005
INPN	n/a
MVKN	0.005
MACRN	0.005
PROPNN	n/a
ETHLN	n/a
R4N2	0.005
DHDN	0.005
MONITS	0.01
MONITU	0.01
HONIT	0.01

^a For full species names, see Table 1. Species that do not partition to the aerosol are indicated with “n/a”.

Table S5. Monofunctional analogues used in calculation of updated absorption cross sections for carbonyl nitrates.^a

Species	Ketone analogue	Nitrate analogue
ETHLN	ethanal ^b	ethyl nitrate ^b
MACRN	i-butyraldehyde ^c	tert-butyl nitrate ^d
MVKN	2-butanone ^b	2-butyl nitrate ^b

^a Wavelength-dependent cross sections for carbonyl nitrates are calculated following Müller et al. (2014) by first calculating the PROPNN cross section enhancement ratio $r_{nk}(\lambda) = S_{nk}(\lambda)/(S_n(\lambda)+S_k(\lambda))$, where $S_{nk}(\lambda)$ is the PROPNN cross section measured by Barnes et al. (1993) and $S_n(\lambda)$ and $S_k(\lambda)$ are the cross sections of the associated monofunctional nitrate and ketone, respectively. Cross sections for other carbonyl nitrates are calculated by applying the PROPNN enhancement ratio to the cross sections of the appropriate monofunctional ketones and nitrates as given in the table: $S(\lambda) = r_{nk}(\lambda)[S_n(\lambda)+S_k(\lambda)]$.

^b Atkinson et al. (2006)

^c Martinez et al. (1992)

^d Roberts and Fajer (1989)

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