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*Supplement of*

**Organic nitrate chemistry and its implications for nitrogen budgets in an isoprene- and monoterpene-rich atmosphere: constraints from aircraft (SEAC<sup>4</sup>RS) and ground-based (SOAS) observations in the Southeast US**

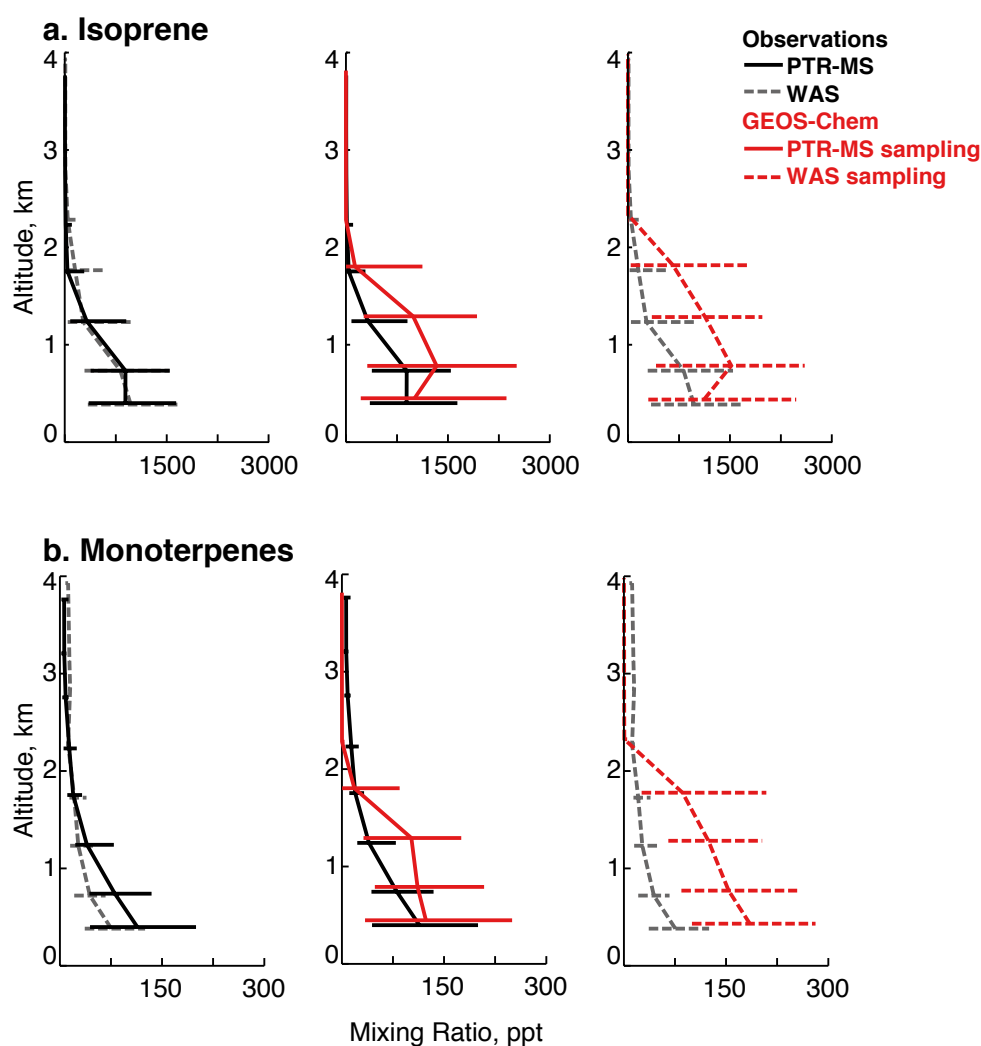
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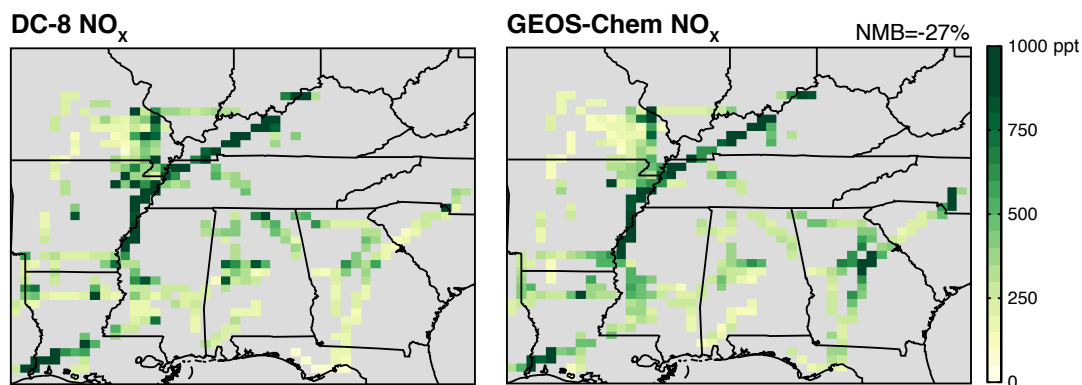
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## S1. RONO<sub>2</sub> sensitivity to NO<sub>x</sub> emissions reductions

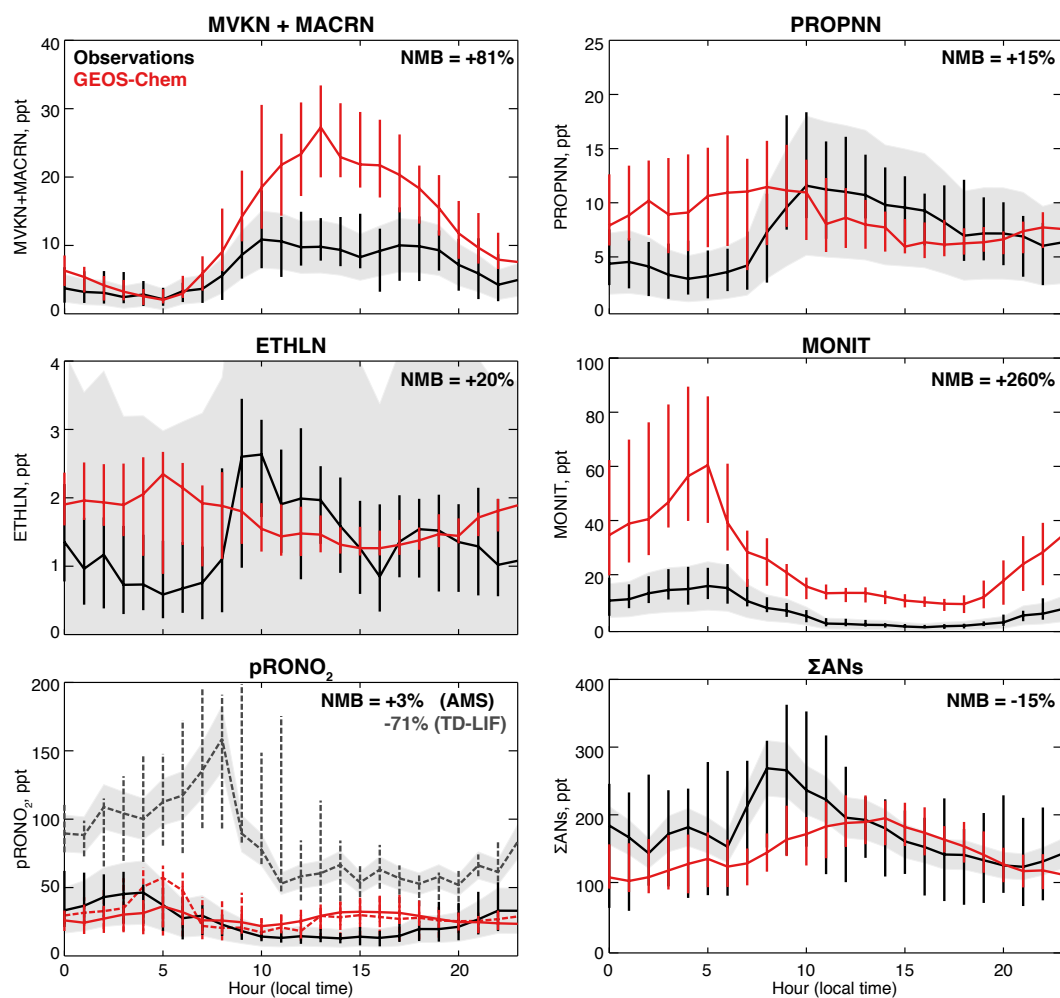
We use the same simulation as Travis et al. (2016), who reduced NO<sub>x</sub> emissions in the NEI11v1 inventory by 60% for all anthropogenic sources except power plants (equivalent to a 53% decrease in total annual NEI11v1 emissions) and also reduced soil NO<sub>x</sub> emissions in the Midwest US by 50% (Vinken et al., 2014). Figure S5 compares model results during SEAC<sup>4</sup>RS before and after applying these NO<sub>x</sub> emissions decreases. As seen in the figure, the change to NO<sub>x</sub> emissions cannot explain the model underestimate in ΣANs relative to the SEAC<sup>4</sup>RS TD-LIF measurement (-46% with original NO<sub>x</sub>, -57% with reduced NO<sub>x</sub>). The figure also shows that the change to NO<sub>x</sub> emissions does not have an appreciable effect on simulation of individual RONO<sub>2</sub> species, which fall within the experimental uncertainties of the CIT-ToF-CIMS instrument in both versions of the model.



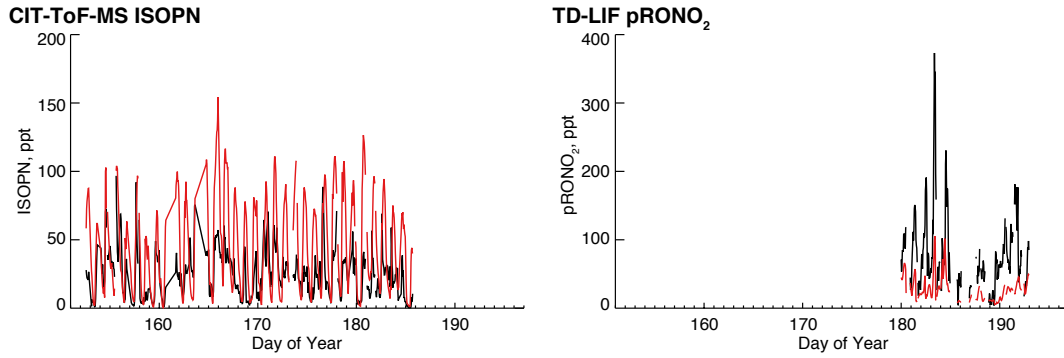
**Figure S1.** Comparison of median vertical profiles from PTR-MS (solid black) and Whole Air Sampler (WAS) measurements of isoprene and monoterpenes ( $=\alpha$ -pinene $+\beta$ -pinene for the WAS) over the Southeast US during SEAC<sup>4</sup>RS (left). The observations are also compared to the GEOS-Chem simulation sampled in the same manner as each measurement in the center (PTR-MS) and right (WAS) panels.



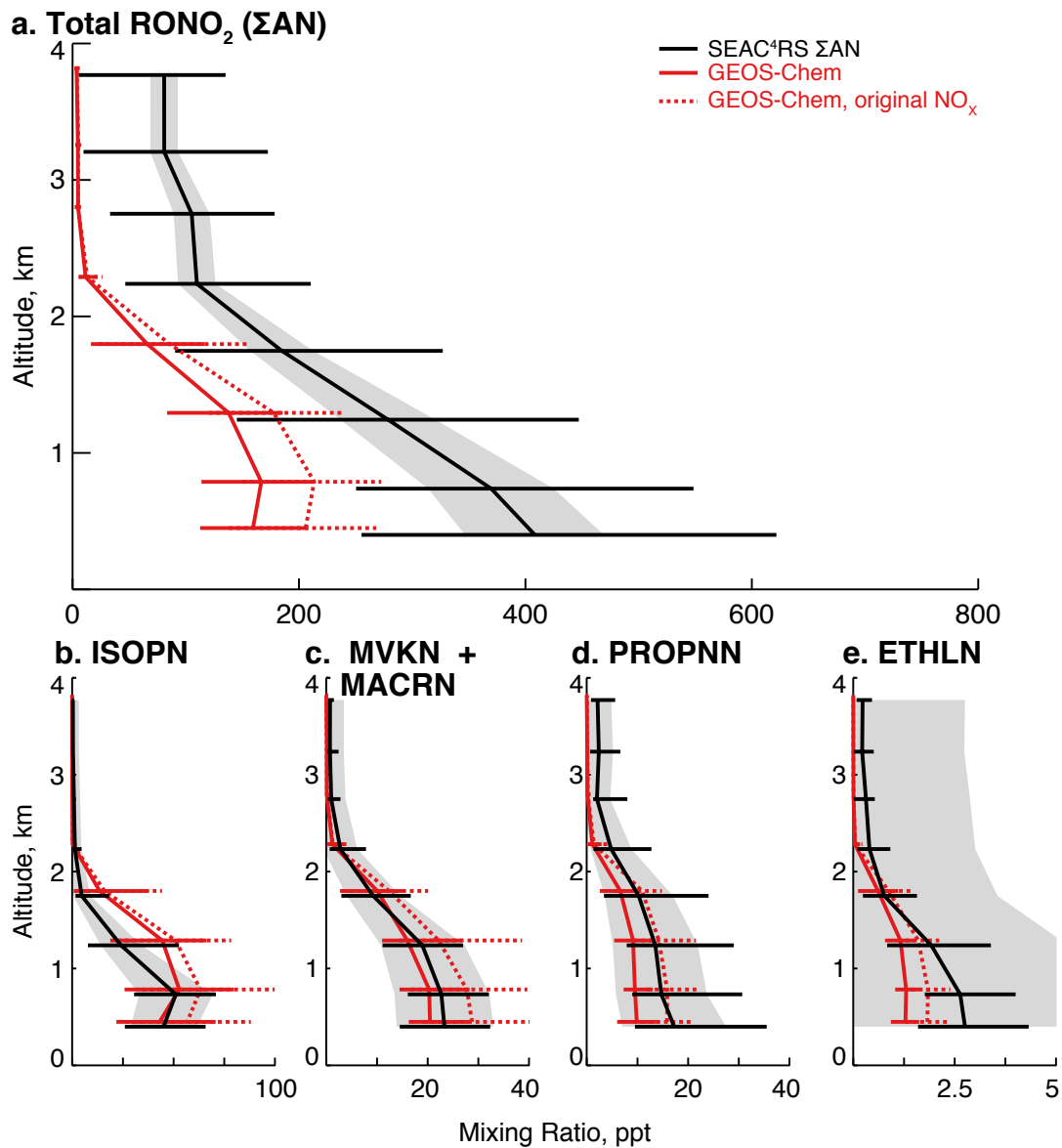
**Figure S2.** Same as Fig. 4, but for  $\text{NO}_x$ .



**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 ( $\text{pRONO}_2$ ) from the AMS (9 June – 15 July) and the TD-LIF (29 June – 15 July), and total organic nitrates ( $\Sigma\text{ANs}$ ) from the TD-LIF (1 June – 15 July).



**Figure S4.** Same as Fig. 8, but for ISOPN measured by CIT-ToF-MS and for pRONO<sub>2</sub> measured by TD-LIF.



**Figure S5.** Observed (black) and modeled (red) median 0-4 km profiles of RONO<sub>2</sub> over the Southeast US during SEAC<sup>4</sup>RS. The dotted red line shows model results before scaling non-power plant NO<sub>x</sub> emissions from the NEI11v1 inventory and soil NO<sub>x</sub> in the Midwest US.

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

Abbreviation	Name
API	alpha-pinene and other cyclic terpenes with one double bond
APIO2	RO <sub>2</sub> from API
LIM	limonene and other cyclic terpenes with two double bonds
LIMO2	RO <sub>2</sub> from LIM
PIP	peroxides from API & LIM
OLND	monoterpene-derived NO <sub>3</sub> -alkene adduct that primarily decomposes
OLNN	monoterpene-derived NO <sub>3</sub> -alkene adduct that primarily retains the NO <sub>3</sub> functional group
MONITS	saturated first generation monoterpene organic nitrate
MONITU	unsaturated first generation monoterpene organic nitrate
HONIT	second generation monoterpene organic nitrate

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

Reactants	Products	Rate Constant
API + OH	APIO2	1.21E-11*exp(440/T)
APIO2 + NO	0.82HO <sub>2</sub> + 0.82NO <sub>2</sub> + 0.23HCHO + 0.43 RCHO + 0.11 ACET + 0.44MEK + 0.07 HCOOH + 0.12MONITS + 0.06MONITU	4.00E-12
APIO2 + HO <sub>2</sub>	PIP	1.50E-11
APIO2 + MO <sub>2</sub>	HO <sub>2</sub> + 0.75HCHO + 0.25 MOH + 0.25 ROH + 0.75RCHO + 0.75MEK	3.56E-14*exp(708/T)
APIO2 + MCO <sub>3</sub>	0.5 HO <sub>2</sub> + 0.5 MO <sub>2</sub> + RCHO + MEK + RCOOH	7.40E-13*exp(765/T)
APIO2 + NO <sub>3</sub>	HO <sub>2</sub> + NO <sub>2</sub> + RCHO + MEK	1.20E-12
API + O <sub>3</sub>	0.85OH + 0.1HO <sub>2</sub> + 0.62 KO <sub>2</sub> + 0.14 CO + 0.02 H <sub>2</sub> O <sub>2</sub> + 0.65RCHO + 0.53MEK	5.0E-16*exp(-530/T)
APIO2 + NO <sub>3</sub>	0.1OLNN + 0.9 OLND	8.33E-13*exp(490/T)
LIM + OH	LIMO2	4.20E-11*exp(401/T)
LIMO2 + NO	0.686HO <sub>2</sub> + 0.78NO <sub>2</sub> + 0.22MONITU + 0.289 PRPE + 0.231HCHO + 0.491RCHO + 0.058HAC + 0.289MEK	4.00E-12
LIMO2 + HO <sub>2</sub>	PIP	1.50E-11
LIMO2 + MO <sub>2</sub>	HO <sub>2</sub> + 0.192 PRPE + 1.04 HCHO + 0.308 MACR + 0.25 MOH + 0.25 ROH	3.56E-14*exp(708/T)
LIMO2 + MCO <sub>3</sub>	0.5 HO <sub>2</sub> + 0.5 MO <sub>2</sub> + 0.192PRPE + 0.385 HCHO + 0.308 MACR + 0.5 RCOOH	7.40E-13*exp(765/T)
LIMO2 + NO <sub>3</sub>	HO <sub>2</sub> + NO <sub>2</sub> + 0.385PRPE + 0.385HCHO + 0.615MACR	1.20E-12
LIM + O <sub>3</sub>	0.85OH + 0.10HO <sub>2</sub> + 0.16 ETO <sub>2</sub> + 0.42 KO <sub>2</sub> + 0.02H <sub>2</sub> O <sub>2</sub> + 0.14CO + 0.46PRPE + 0.04HCHO + 0.79MACR +	2.95E-15*exp(-783/T)

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

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

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

**Table S4.** Reactive uptake coefficients ( $\gamma$ ) used in GEOS-Chem aerosol uptake parameterization for organic nitrates. <sup>a</sup>

Species	$\gamma$
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

<sup>a</sup> 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. <sup>a</sup>

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

<sup>a</sup> 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:  $S(\lambda) = r_{nk}(\lambda)[S_n(\lambda)+S_k(\lambda)]$ .

<sup>b</sup> Atkinson et al. (2006)

<sup>c</sup> Martinez et al. (1992)

<sup>d</sup> Roberts and Fajer (1989)

## References

- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Subcommittee, I.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II ndash; gas phase reactions of organic species, *Atmospheric Chemistry and Physics*, 6, 3625–4055, doi:10.5194/acp-6-3625-2006, 2006.
- Barnes, I., Becker, K. H., and Zhu, T.: Near UV absorption spectra and photolysis products of difunctional organic nitrates: Possible importance as NO<sub>x</sub> reservoirs, *Journal of Atmospheric Chemistry*, 17, 353–373, doi:10.1007/BF00696854, 1993.
- Martinez, R. D., Buitrago, A. A., Howell, N. W., Hearn, C. H., and Joens, J. A.: The near U.V. absorption spectra of several aliphatic aldehydes and ketones at 300 K, *Atmospheric Environment. Part A. General Topics*, 26, 785 – 792, doi: 10.1016/0960-1686(92)90238-G, 1992.
- Müller, J.-F., Peeters, J., and Stavrakou, T.: Fast photolysis of carbonyl nitrates from isoprene, *Atmospheric Chemistry and Physics*, 14, 2497–2508, doi:10.5194/acp-14-2497-2014, 2014.

- Roberts, J. M. and Fajer, R. W.: UV absorption cross sections of organic nitrates of potential atmospheric importance and estimation of atmospheric lifetimes, *Environmental Science & Technology*, 23, 945–951, doi:10.1021/es00066a003, 1989.
- Travis, K. R., Jacob, D. J., Fisher, J. A., Kim, P. S., Marais, E. A., Zhu, L., Yu, K., Miller, C. C., Yantosca, R. M., Sulprizio, M. P., Thompson, A. M., Wennberg, P. O., Crouse, J. D., St. Clair, J. M., Cohen, R. C., Laughner, J. L., Dibb, J. E., Hall, S. R., Ullmann, K., Wolfe, G. M., Neuman, J. A., and Zhou, X.: NO<sub>x</sub> emissions, isoprene oxidation pathways, vertical mixing, and implications for surface ozone in the Southeast United States, in review for *Atmospheric Chemistry and Physics*, 2016.