

University of New Hampshire

## University of New Hampshire Scholars' Repository

---

Earth Systems Research Center

Institute for the Study of Earth, Oceans, and  
Space (EOS)

---

11-1-2016

### Why do models overestimate surface ozone in the Southeast United States

Katherine R. Travis  
*Harvard University*

Daniel J. Jacob  
*Harvard University*

Jenny A. Fisher  
*University of Wollongong*

Patrick S. Kim  
*Harvard University*

Eloise A. Marais  
*Harvard University*

*See next page for additional authors*

Follow this and additional works at: <https://scholars.unh.edu/ersc>

---

#### Recommended Citation

Travis, K. R., D. J. Jacob, J. A. Fisher, P. S. Kim, E. A. Marais, L. Zhu, K. Yu, C. C. Miller, R. M. Yantosca, M. P. Sulprizio, A. M. Thompson, P. O. Wennberg, J. D. Crounse, J. M. St. Clair, R. C. Cohen, J. L. Lauher, J. E. Dibb, S. R. Hall, K. Ullman, G. M Wolfe, I. B. Pollack, J. Peischl, J. A. Neuman, and X. Zhou (2016), Why do models overestimate surface ozone in the Southeast United States, *Atmospheric Chemistry and Physics*, 16, 13,561-13,577, <https://dx.doi.org/10.5194/acp-16-13561-2016>

This Article is brought to you for free and open access by the Institute for the Study of Earth, Oceans, and Space (EOS) at University of New Hampshire Scholars' Repository. It has been accepted for inclusion in Earth Systems Research Center by an authorized administrator of University of New Hampshire Scholars' Repository. For more information, please contact [Scholarly.Communication@unh.edu](mailto:Scholarly.Communication@unh.edu).

---

## Authors

Katherine R. Travis, Daniel J. Jacob, Jenny A. Fisher, Patrick S. Kim, Eloise A. Marais, Lei Zhu, Karen Yu, Christopher C. Miller, Robert M. Yantosca, Melissa P. Sulprizio, Anne M. Thompson, Paul O. Wennberg, John D. Crounse, Jason M. St. Clair, Ronald C. Cohen, Joshua L. Laughner, Jack E. Dibb, Samuel R. Hall, Kirk Ullmann, and Glenn M. Wolfe



## Why do models overestimate surface ozone in the Southeast United States?

Katherine R. Travis<sup>1</sup>, Daniel J. Jacob<sup>1,2</sup>, Jenny A. Fisher<sup>3,4</sup>, Patrick S. Kim<sup>2</sup>, Eloise A. Marais<sup>1</sup>, Lei Zhu<sup>1</sup>, Karen Yu<sup>1</sup>, Christopher C. Miller<sup>1</sup>, Robert M. Yantosca<sup>1</sup>, Melissa P. Sulprizio<sup>1</sup>, Anne M. Thompson<sup>5</sup>, Paul O. Wennberg<sup>6,7</sup>, John D. Crounse<sup>6</sup>, Jason M. St. Clair<sup>6</sup>, Ronald C. Cohen<sup>8</sup>, Joshua L. Laughner<sup>8</sup>, Jack E. Dibb<sup>9</sup>, Samuel R. Hall<sup>10</sup>, Kirk Ullmann<sup>10</sup>, Glenn M. Wolfe<sup>11,12</sup>, Illana B. Pollack<sup>13</sup>, Jeff Peischl<sup>14,15</sup>, Jonathan A. Neuman<sup>14,15</sup>, and Xianliang Zhou<sup>16,17</sup>

<sup>1</sup>Harvard John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA

<sup>2</sup>Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA

<sup>3</sup>Centre for Atmospheric Chemistry, School of Chemistry, University of Wollongong, Wollongong, NSW, Australia

<sup>4</sup>School of Earth and Environmental Sciences, University of Wollongong, Wollongong, NSW, Australia

<sup>5</sup>NASA Goddard Space Flight Center, Greenbelt, Maryland, USA

<sup>6</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA

<sup>7</sup>Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA, USA

<sup>8</sup>Department of Chemistry, University of California, Berkeley, CA, USA

<sup>9</sup>Earth System Research Center, University of New Hampshire, Durham, NH, USA

<sup>10</sup>Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO, USA

<sup>11</sup>Atmospheric Chemistry and Dynamics Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD, USA

<sup>12</sup>Joint Center for Earth Systems Technology, University of Maryland Baltimore County, Baltimore, MD, USA

<sup>13</sup>Department of Atmospheric Science, Colorado State University, Colorado, USA

<sup>14</sup>University of Colorado, Cooperative Institute for Research in Environmental Sciences, Boulder, CO, USA

<sup>15</sup>NOAA Earth System Research Lab, Boulder, CO, USA

<sup>16</sup>Department of Environmental Health Sciences, State University of New York, Albany, New York 12201, USA

<sup>17</sup>Wadsworth Center, New York State Department of Health, Albany, New York, USA

Correspondence to: Katherine R. Travis (ktravis@fas.harvard.edu)

Received: 3 February 2016 – Published in Atmos. Chem. Phys. Discuss.: 16 March 2016

Revised: 5 October 2016 – Accepted: 6 October 2016 – Published: 1 November 2016

**Abstract.** Ozone pollution in the Southeast US involves complex chemistry driven by emissions of anthropogenic nitrogen oxide radicals ( $\text{NO}_x \equiv \text{NO} + \text{NO}_2$ ) and biogenic isoprene. Model estimates of surface ozone concentrations tend to be biased high in the region and this is of concern for designing effective emission control strategies to meet air quality standards. We use detailed chemical observations from the SEAC<sup>4</sup>RS aircraft campaign in August and September 2013, interpreted with the GEOS-Chem chemical transport model at  $0.25^\circ \times 0.3125^\circ$  horizontal resolution, to better understand the factors controlling surface ozone in the Southeast US. We find that the National Emission Inventory (NEI) for  $\text{NO}_x$  from the US Environmental Protection

Agency (EPA) is too high. This finding is based on SEAC<sup>4</sup>RS observations of  $\text{NO}_x$  and its oxidation products, surface network observations of nitrate wet deposition fluxes, and OMI satellite observations of tropospheric  $\text{NO}_2$  columns. Our results indicate that NEI  $\text{NO}_x$  emissions from mobile and industrial sources must be reduced by 30–60 %, dependent on the assumption of the contribution by soil  $\text{NO}_x$  emissions. Upper-tropospheric  $\text{NO}_2$  from lightning makes a large contribution to satellite observations of tropospheric  $\text{NO}_2$  that must be accounted for when using these data to estimate surface  $\text{NO}_x$  emissions. We find that only half of isoprene oxidation proceeds by the high- $\text{NO}_x$  pathway to produce ozone; this fraction is only moderately sensitive to changes in  $\text{NO}_x$

emissions because isoprene and  $\text{NO}_x$  emissions are spatially segregated. GEOS-Chem with reduced  $\text{NO}_x$  emissions provides an unbiased simulation of ozone observations from the aircraft and reproduces the observed ozone production efficiency in the boundary layer as derived from a regression of ozone and  $\text{NO}_x$  oxidation products. However, the model is still biased high by  $6 \pm 14$  ppb relative to observed surface ozone in the Southeast US. Ozonesondes launched during midday hours show a 7 ppb ozone decrease from 1.5 km to the surface that GEOS-Chem does not capture. This bias may reflect a combination of excessive vertical mixing and net ozone production in the model boundary layer.

## 1 Introduction

Ozone in surface air is harmful to human health and vegetation. Ozone is produced when volatile organic compounds (VOCs) and carbon monoxide (CO) are photochemically oxidized in the presence of nitrogen oxide radicals ( $\text{NO}_x \equiv \text{NO} + \text{NO}_2$ ). The mechanism for producing ozone is complicated, involving hundreds of chemical species interacting with transport on all scales. In October 2015, the US Environmental Protection Agency (EPA) set a new National Ambient Air Quality Standard (NAAQS) for surface ozone as a maximum daily 8 h average (MDA8) of 0.070 ppm not to be exceeded more than three times per year. This is the latest in a succession of gradual tightening of the NAAQS from 0.12 ppm (1 h average) to 0.08 ppm in 1997 and to 0.075 ppm in 2008, responding to accumulating evidence that ozone is detrimental to public health even at low concentrations (EPA, 2013). Chemical transport models (CTMs) tend to significantly overestimate surface ozone in the Southeast US (Lin et al., 2008; Fiore et al., 2009; Reidmiller et al., 2009; Brown-Steiner et al., 2015; Canty et al., 2015), and this is an issue for the design of pollution control strategies (McDonald-Buller et al., 2011). Here we examine the causes of this overestimate by using the GEOS-Chem CTM to simulate NASA SEAC<sup>4</sup>RS aircraft observations of ozone and its precursors over the region in August–September 2013 (Toon et al., 2016), together with additional observations from surface networks and satellite.

A number of explanations have been proposed for the ozone model overestimates in the Southeast US. Fiore et al. (2003) suggested excessive modeled ozone inflow from the Gulf of Mexico. Lin et al. (2008) proposed that the ozone dry deposition velocity could be underestimated. McDonald-Buller et al. (2011) pointed out the potential role of halogen chemistry as a sink of ozone. Isoprene emitted from vegetation is the principal VOC precursor of ozone in the Southeast US in summer, and Fiore et al. (2005) found that uncertainties in isoprene emissions and in the loss of  $\text{NO}_x$  from formation of isoprene nitrates could also affect the ozone simulation. Horowitz et al. (2007) found a large sensitivity of ozone

to the fate of isoprene nitrates and the extent to which they release  $\text{NO}_x$  when oxidized. Squire et al. (2015) found that the choice of isoprene oxidation mechanism can alter both the sign and magnitude of the response of ozone to isoprene and  $\text{NO}_x$  emissions.

The SEAC<sup>4</sup>RS aircraft campaign in August–September 2013 provides an outstanding opportunity to improve our understanding of ozone chemistry over the Southeast US. The SEAC<sup>4</sup>RS DC-8 aircraft hosted an unprecedented chemical payload including isoprene and its oxidation products,  $\text{NO}_x$  and its oxidation products, and ozone. The flights featured extensive boundary layer mapping of the southeast as well as vertical profiling to the free troposphere (Toon et al., 2016). We use the GEOS-Chem global CTM with high horizontal resolution over North America ( $0.25^\circ \times 0.3125^\circ$ ) to simulate and interpret the SEAC<sup>4</sup>RS observations. We integrate into our analysis additional Southeast US observations during the summer of 2013, including from the NOMADSS aircraft campaign, the SOAS surface site in Alabama, the SEACIONS ozonesonde network, the EPA Clean Air Status and Trends Network (CASTNET) ozone network, the National Acid Deposition Program (NADP) nitrate wet deposition network, and  $\text{NO}_2$  satellite data from the OMI instrument. Several companion papers apply GEOS-Chem to simulate other aspects of SEAC<sup>4</sup>RS and concurrent data for the Southeast US, including aerosol sources and optical depth (Kim et al., 2015), isoprene organic aerosol (Marais et al., 2016), organic nitrates (Fisher et al., 2016), formaldehyde and its relation to satellite observations (Zhu et al., 2016), and sensitivity to model resolution (Yu et al., 2016).

## 2 GEOS-Chem model description

We use the GEOS-Chem global 3-D CTM (Bey et al., 2001) in version 9.02 (<http://www.geos-chem.org>) with modifications described below. GEOS-Chem is driven with assimilated meteorological data from the Goddard Earth Observing System (GEOS-5.11.0) of the NASA Global Modeling and Assimilation Office (GMAO). The GEOS-5.11.0 data have a native horizontal resolution of  $0.25^\circ$  latitude by  $0.3125^\circ$  longitude and a temporal resolution of 3 h (1 h for surface variables and mixing depths). We use a nested version of GEOS-Chem (Chen et al., 2009) with native  $0.25^\circ \times 0.3125^\circ$  horizontal resolution over North America and adjacent oceans ( $130^\circ\text{--}60^\circ\text{W}$ ,  $9.75^\circ\text{--}60^\circ\text{N}$ ) and dynamic boundary conditions from a global simulation with  $4^\circ \times 5^\circ$  horizontal resolution. Turbulent boundary layer mixing follows a non-local parameterization based on K-theory (Holtslag and Boville, 1993) implemented in GEOS-Chem by Lin and McElroy (2010). Daytime mixing depths are reduced by 40 % from the GEOS-5.11.0 data as described by Kim et al. (2015) and Zhu et al. (2016) to match aircraft lidar observations. The GEOS-Chem nested model simulation is conducted for August–

September 2013, following 6 months of initialization at  $4^\circ \times 5^\circ$  resolution.

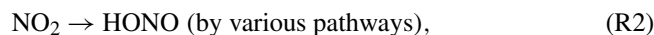
## 2.1 Chemistry

The chemical mechanism in GEOS-Chem version 9.02 is described by Mao et al. (2010, 2013). We modified aerosol reactive uptake of  $\text{HO}_2$  to produce  $\text{H}_2\text{O}_2$  instead of  $\text{H}_2\text{O}$  in order to better match  $\text{H}_2\text{O}_2$  observations in SEAC<sup>4</sup>RS. We also include a number of updates to isoprene chemistry, listed comprehensively in the Supplement (Tables S1 and S2) and described here more specifically for the low- $\text{NO}_x$  pathways. Companion papers describe the isoprene chemistry updates relevant to isoprene nitrates (Fisher et al., 2016) and organic aerosol formation (Marais et al., 2016). Oxidation of biogenic monoterpenes is also added to the GEOS-Chem mechanism (Fisher et al., 2016) but does not significantly affect ozone.

A critical issue in isoprene chemistry is the fate of the isoprene peroxy radicals ( $\text{ISOPO}_2$ ) produced from the oxidation of isoprene by OH (the dominant isoprene sink). When  $\text{NO}_x$  is sufficiently high,  $\text{ISOPO}_2$  reacts mainly with NO to produce ozone (high- $\text{NO}_x$  pathway). At lower  $\text{NO}_x$  levels,  $\text{ISOPO}_2$  may instead react with  $\text{HO}_2$  or other organic peroxy radicals, or isomerize, in which case ozone is not produced (low- $\text{NO}_x$  pathways). Here we increase the molar yield of isoprene hydroperoxide ( $\text{ISOPOOH}$ ) from the  $\text{ISOPO}_2 + \text{HO}_2$  reaction to 94 % based on observations of the minor channels of this reaction (Liu et al., 2013). Oxidation of  $\text{ISOPOOH}$  by OH produces isoprene epoxides (IEPOX) that subsequently react with OH or are taken up by aerosol (Paulot et al., 2009b; Marais et al., 2016). We use updated rates and products from Bates et al. (2014) for the reaction of IEPOX with OH.

$\text{ISOPO}_2$  isomerization produces hydroperoxy-aldehydes (HPALDs) (Peeters et al., 2009; Crounse et al., 2011; Wolfe et al., 2012), and we explicitly include this in the GEOS-Chem mechanism. HPALDs go on to react with OH or photolyze at roughly equal rates over the Southeast US. We use the HPALD + OH reaction rate constant from Wolfe et al. (2012) and the products of the reaction from Squire et al. (2015). The HPALD photolysis rate is calculated using the absorption cross section of MACR, with a quantum yield of 1, as recommended by Peeters and Müller (2010). The photolysis products are taken from Stavrou et al. (2010). Self-reaction of  $\text{ISOPO}_2$  is updated following Xie et al. (2013).

A number of studies have suggested that conversion of  $\text{NO}_2$  to nitrous acid (HONO) by gas-phase or aerosol-phase pathways could provide a source of  $\text{HO}_x$  radicals following HONO photolysis (Li et al., 2014; Zhou et al., 2014). This mechanism would also provide a catalytic sink for ozone when  $\text{NO}_2$  is produced by the  $\text{NO} + \text{ozone}$  reaction, viz.,

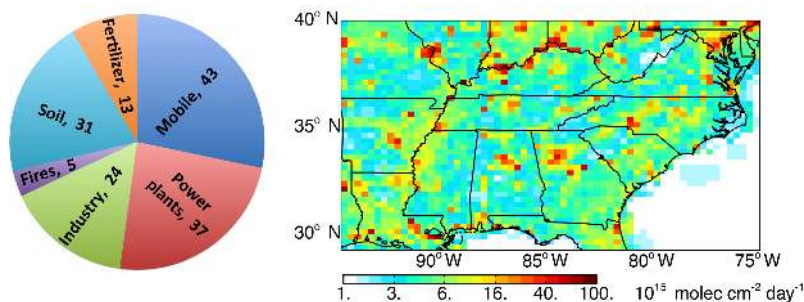


Observations of HONO from the NOMADSS campaign (<https://www2.acom.ucar.edu/campaigns/nomadss>) indicate a mean daytime HONO concentration of 10 ppt in the Southeast US boundary layer (Zhou et al., 2014), whereas the standard gas-phase mechanism in GEOS-Chem version 9.02 yields less than 1 ppt. We add the pathway proposed by Li et al. (2014), in which HONO is produced by the reaction of the  $\text{HO}_2 \cdot \text{H}_2\text{O}$  complex with  $\text{NO}_2$ , but with a slower rate constant ( $k_{\text{HO}_2 \cdot \text{H}_2\text{O} + \text{NO}_2} = 2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) to match the observed  $\sim 10$  ppt daytime HONO in the Southeast US boundary layer. The resulting impact on boundary layer ozone concentrations is negligible.

## 2.2 Dry deposition

The GEOS-Chem dry deposition scheme uses a resistance-in-series model based on Wesely (1989) as implemented by Wang et al. (1998). Underestimation of dry deposition has been invoked as a cause for model overestimates of ozone in the eastern US (Lin et al., 2008; Walker, 2014). Daytime ozone deposition is determined principally by stomatal uptake. Here, we decrease the stomatal resistance from  $200 \text{ s m}^{-1}$  for both coniferous and deciduous forests (Wesely, 1989) by 20 % to match summertime measurements of the ozone dry deposition velocity for a pine forest in North Carolina (Finkelstein et al., 2000) and for the Ozarks oak forest in southeastern Missouri (Wolfe et al., 2015), both averaging  $0.8 \text{ cm s}^{-1}$  in the daytime. The mean ozone deposition velocity in GEOS-Chem along the SEAC<sup>4</sup>RS boundary layer flight tracks in the Southeast US averages  $0.7 \pm 0.3 \text{ cm s}^{-1}$  for the daytime (09:00–16:00 local) surface layer. Deposition is suppressed in the model at night due to both stomatal closure and near-surface stratification, consistent with the Finkelstein et al. (2000) observations.

Deposition flux measurements for isoprene oxidation products at the Alabama SOAS site (<http://soas2013.rutgers.edu>) indicate higher deposition velocities than simulated by the standard GEOS-Chem model (Nguyen et al., 2015). The diurnal cycle of dry deposition in GEOS-Chem compares well with the observations from SOAS (Nguyen et al., 2015). As an expedient, Nguyen et al. (2015) scaled the Henry's law coefficients for these species in GEOS-Chem to match their observed deposition velocities and we follow their approach here. Other important depositing species include  $\text{HNO}_3$  and peroxyacetyl nitrate (PAN), with mean deposition velocities along the SEAC<sup>4</sup>RS Southeast US flight tracks in daytime of  $3.9$  and  $0.6 \text{ cm s}^{-1}$ , respectively.



**Figure 1.** Surface NO<sub>x</sub> emissions in the Southeast US in GEOS-Chem for August and September 2013 including fuel combustion, soils, fertilizer use, and open fires (total emissions = 153 Gg N). Anthropogenic emissions from mobile sources and industry in the National Emission Inventory (NEI11v1) for 2013 have been decreased by 60 % to match atmospheric observations (see text). Lightning contributes an additional 25 Gg N to the free troposphere (not included in the figure). The emissions are mapped on the 0.25° × 0.3125° GEOS-Chem grid. The pie chart gives the sum of August–September 2013 emissions (Gg N) over the Southeast US domain as shown on the map (94.5–75° W, 29.5–40° N).

### 2.3 Emissions

We use hourly US anthropogenic emissions from the 2011 EPA National Emissions Inventory (NEI11v1) at a horizontal resolution of 0.1° × 0.1° and adjusted to 2013 using national annual scaling factors (EPA NEI, 2015). The scaling factor for NO<sub>x</sub> emissions is 0.89, for a 2013 US NEI total of 3.5 Tg N a<sup>-1</sup>. Further information on the use of the NEI11v1 in GEOS-Chem can be found at [http://wiki.seas.harvard.edu/geos-chem/index.php/EPA/NEI11\\_North\\_American\\_emissions](http://wiki.seas.harvard.edu/geos-chem/index.php/EPA/NEI11_North_American_emissions). Soil NO<sub>x</sub> emissions, including emissions from fertilizer application, are computed according to Hudman et al. (2012), with a 50 % reduction in the Midwestern US based on a previous comparison with OMI NO<sub>2</sub> observations (Vinken et al., 2014). Open fire emissions are from the daily Quick Fire Emissions Database (QFED) (Darmanov and da Silva, 2014) with diurnal variability from the Western Regional Air Partnership (Air Sciences, 2005). We emit 40 % of open fire NO<sub>x</sub> emissions as PAN and 20 % as HNO<sub>3</sub> to account for fast oxidation taking place in the fresh plume (Alvarado et al., 2010). Following Fischer et al. (2014), we inject 35 % of fire emissions above the boundary layer, evenly between 3.5 and 5.5 km altitude. Lightning is an additional source of NO<sub>x</sub> but is mainly released in the upper troposphere, as described below.

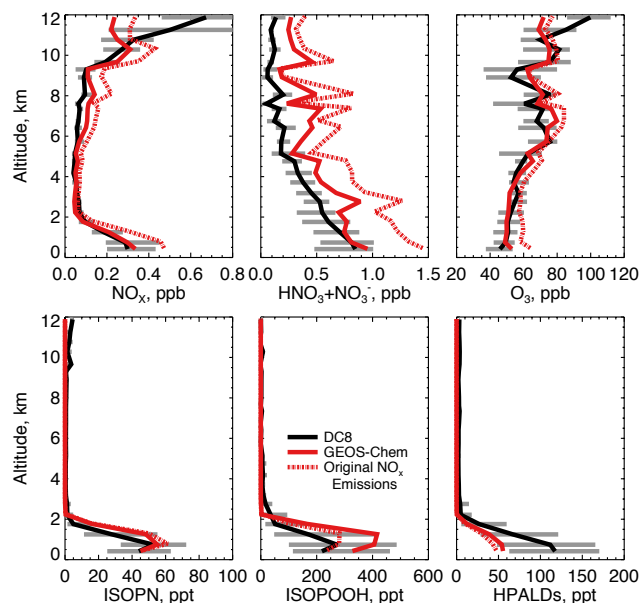
Initial implementation of the above inventory in GEOS-Chem resulted in an 60–70 % overestimation of NO<sub>x</sub> and HNO<sub>3</sub> measured from the SEAC<sup>4</sup>RS DC-8 aircraft and a 70 % overestimation of nitrate (NO<sub>3</sub><sup>-</sup>) wet deposition fluxes measured by the NADP across the Southeast US. Correcting this bias required a ~40 % decrease in surface NO<sub>x</sub> emissions. Assuming strongly reduced soil and fertilizer NO<sub>x</sub> emissions (18 % of total NO<sub>x</sub> emissions in the southeast) and open fires (2 %), also considering the large uncertainty in these emissions, would be insufficient to correct this bias. Emissions from power plant stacks are directly measured but account for only 12 % of NEI NO<sub>x</sub> emissions on an annual

basis (EPA NEI, 2015). Several local studies in recent years have found that NEI NO<sub>x</sub> emissions for mobile sources may be too high by a factor of 2 or more (Castellanos et al., 2011; Fujita et al., 2012; Brioude et al., 2013; Anderson et al., 2014). We can achieve the required 40 % decrease in total NO<sub>x</sub> emissions by reducing NEI emissions from mobile and industrial sources (all sources except power plants) by 60 % or alternatively by reducing these sources by 30 % and zeroing out soil and fertilizer NO<sub>x</sub> emissions. Since it is apparent that there is some minimum contribution by soil NO<sub>x</sub> emissions, we assessed the impact of the approach of reducing the non-power-plant NEI emissions by 60 %. The spatial overlap between anthropogenic and soil NO<sub>x</sub> emissions is such that we cannot readily arbitrate between these two scenarios. Comparisons with observations will be presented in the next section.

We constrain the lightning NO<sub>x</sub> source with satellite data as described by Murray et al. (2012). Lightning NO<sub>x</sub> is mainly released at the top of convective updrafts following Ott et al. (2010). The standard GEOS-Chem model uses higher NO<sub>x</sub> yields for midlatitudes lightning (500 mol flash<sup>-1</sup>) than for tropical (260 mol flash<sup>-1</sup>) (Huntrieser et al., 2007, 2008; Hudman et al., 2007; Ott et al., 2010) with a fairly arbitrary boundary between the two at 23° N in North America and 35° N in Eurasia. Zhang et al. (2014) previously found that this leads GEOS-Chem to overestimate background ozone in the southwestern US and we find the same here for the eastern US and the Gulf of Mexico. We treat here all lightning in the 35° S–35° N band as tropical and thus remove the distinction between North America and Eurasia.

Figure 1 gives the resulting surface NO<sub>x</sub> emissions for the Southeast US for August and September 2013. With the original NEI inventory, fuel combustion accounted for 81 % of total surface NO<sub>x</sub> emissions in the Southeast US (not including lightning). If the required reduction of non-power-plant





**Figure 2.** Median vertical concentration profiles of  $\text{NO}_x$ , total inorganic nitrate (gas  $\text{HNO}_3$  + aerosol  $\text{NO}_3^-$ ), ozone, isoprene nitrate (ISOPN), isoprene hydroperoxide (ISOPOOH), and hydroperoxy-aldehydes (HPALD) for the SEAC<sup>4</sup>RS flights over the Southeast US (domain of Fig. 1). Observations from the DC-8 aircraft are compared to GEOS-Chem model results. The dashed red line shows model results before adjustment of  $\text{NO}_x$  emissions from fuel combustion and lightning (see text). The 25th and 75th percentiles of the DC-8 observations are shown as grey bars. The SEAC<sup>4</sup>RS observations have been filtered to remove open fire plumes, stratospheric air, and urban plumes as described in the text. Model results are sampled along the flight tracks at the time of flights and gridded to the model resolution. Profiles are binned to the nearest 0.5 km. The NOAA  $\text{NO}_y\text{O}_3$  four-channel chemiluminescence (CL) instrument made measurements of ozone and  $\text{NO}_y$  (Ryerson et al., 1998),  $\text{NO}$  (Ryerson et al., 2000), and  $\text{NO}_2$  (Pollack et al., 2010). Total inorganic nitrate was measured by the University of New Hampshire Soluble Acidic Gases and Aerosol (UNH SAGA) instrument (Dibb et al., 2003) and was mainly gas-phase  $\text{HNO}_3$  for the SEAC<sup>4</sup>RS conditions. ISOPOOH, ISOPN, and HPALDs were measured by the Caltech single mass analyzer CIMS (Crounse et al., 2006; Paulot et al., 2009a; Crounse et al., 2011).

NEI emissions is 60 %, the contribution from fuel combustion would be 68 %.

Biogenic VOC emissions are from MEGAN v2.1, including isoprene, acetone, acetaldehyde, monoterpenes, and  $> \text{C}_2$  alkenes. We reduce MEGAN v2.1 isoprene emissions by 15 % to better match SEAC<sup>4</sup>RS observations of isoprene fluxes from the Ozarks (Wolfe et al., 2015) and observed formaldehyde (Zhu et al., 2016). Yu et al. (2016) show the resulting isoprene emissions for the SEAC<sup>4</sup>RS period.

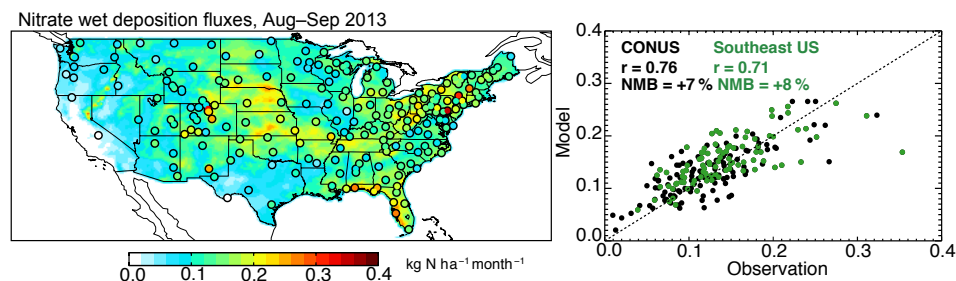
### 3 Overestimate of $\text{NO}_x$ emissions in the EPA NEI inventory

Figure 2 shows simulated and observed median vertical distributions of  $\text{NO}_x$ , total inorganic nitrate (gas-phase  $\text{HNO}_3$  + aerosol  $\text{NO}_3^-$ ), and ozone concentrations along the SEAC<sup>4</sup>RS flight tracks over the Southeast US. Here and elsewhere the data exclude urban plumes as diagnosed by  $[\text{NO}_2] > 4$  ppb, open fire plumes as diagnosed by  $[\text{CH}_3\text{CN}] > 200$  ppt, and stratospheric air as diagnosed by  $[\text{O}_3]/[\text{CO}] > 1.25 \text{ mol mol}^{-1}$ . These filters exclude < 1, 7, and 6 % of the data, respectively. We would not expect the model to be able to capture these features even at native resolution (Yu et al., 2016).

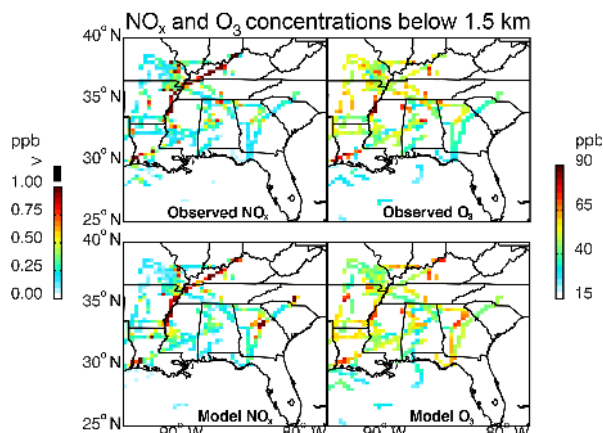
Model results in Fig. 2 are shown both with the original  $\text{NO}_x$  emissions (dashed line) and with non-power-plant NEI fuel emissions decreased by 60 % (solid line). Decreasing emissions corrects the model bias for  $\text{NO}_x$  and also largely corrects the bias for inorganic nitrate. Boundary layer ozone is overestimated by 12 ppb with the original  $\text{NO}_x$  emissions but this bias disappears after decreasing the  $\text{NO}_x$  emissions. Results are very similar if we decrease the non-power-plant NEI fuel emissions by only 30 % and zero out soil and fertilizer emissions. Thus the required decrease of  $\text{NO}_x$  emissions may involve an overestimation of both anthropogenic and soil emissions.

Further support for decreasing  $\text{NO}_x$  emissions is offered by observed nitrate wet deposition fluxes from the NADP network (NADP, 2007). Figure 3 compares simulated and observed fluxes for the model with decreased  $\text{NO}_x$  emissions. Model values have been corrected for precipitation bias following the method of Paulot et al. (2014), in which the monthly deposition flux is assumed to scale to the 0.6th power of the precipitation bias. We diagnose precipitation bias in the GEOS-5.11.0 data relative to high-resolution PRISM observations (<http://prism.oregonstate.edu>). For the Southeast US, the precipitation bias is −34 % in August and −21 % in September 2013. We see from Fig. 3 that the model with decreased  $\text{NO}_x$  emissions reproduces the spatial variability in the observations with only +8 % bias over the Southeast US and +7 % over the contiguous US. In comparison, the model with original emissions had a 63 % overestimation of the nitrate wet deposition flux nationally and a 71 % overestimation in the southeast. The high deposition fluxes along the Gulf of Mexico in Fig. 3, both in the model and in the observations, reflect particularly large precipitation.

The model with decreased  $\text{NO}_x$  emissions also reproduces the spatial distribution of  $\text{NO}_x$  in the Southeast US boundary layer as observed in SEAC<sup>4</sup>RS. This is shown in Fig. 4 with simulated and observed concentrations of  $\text{NO}_x$  along the flight tracks below 1.5 km altitude. The spatial correlation coefficient is 0.71. There are no obvious spatial patterns of model bias that would point to specific source sectors as responsible for the  $\text{NO}_x$  emission overestimate, beyond the



**Figure 3.** Nitrate wet deposition fluxes across the US in August–September 2013. Mean observations from the NADP network (circles in the left panel) are compared to model values with decreased  $\text{NO}_x$  emissions (background). Also shown is a scatterplot of simulated vs. observed values at individual sites for the whole contiguous US (black) and for the Southeast US (green). The correlation coefficient ( $r$ ) and normalized mean bias (NMB) are shown inset, along with the 1 : 1 line.



**Figure 4.** Ozone and  $\text{NO}_x$  concentrations in the boundary layer (0–1.5 km) during SEAC<sup>4</sup>RS (6 August to 23 September 2013). Observations from the aircraft and simulated values are averaged over the  $0.25^\circ \times 0.3125^\circ$  GEOS-Chem grid.  $\text{NO}_x$  above 1 ppb is shown in black. The spatial correlation coefficient is 0.71 for both  $\text{NO}_x$  and  $\text{O}_3$ . The normalized mean bias is  $-11.5\%$  for  $\text{NO}_x$  and  $4.5\%$  for  $\text{O}_3$ .

blanket 30–60 % decrease of non-power-plant NEI emissions needed to correct the regional emission total.

#### 4 Using satellite $\text{NO}_2$ data to verify $\text{NO}_x$ emissions: sensitivity to upper troposphere

Observations of tropospheric  $\text{NO}_2$  columns by solar backscatter from the OMI satellite instrument offer an additional constraint on  $\text{NO}_x$  emissions (Duncan et al., 2014; Lu et al., 2015). We compare the tropospheric columns simulated by GEOS-Chem with the NASA operational retrieval (Level 2, v2.1) (NASA, 2012; Bucsela et al., 2013) and the Berkeley High-Resolution (BEHR) retrieval (Russell et al., 2011). The NASA retrieval has been validated to agree with surface measurements to within  $\pm 20\%$  (Lamsal et al., 2014). Both retrievals fit the observed backscattered solar spectra to

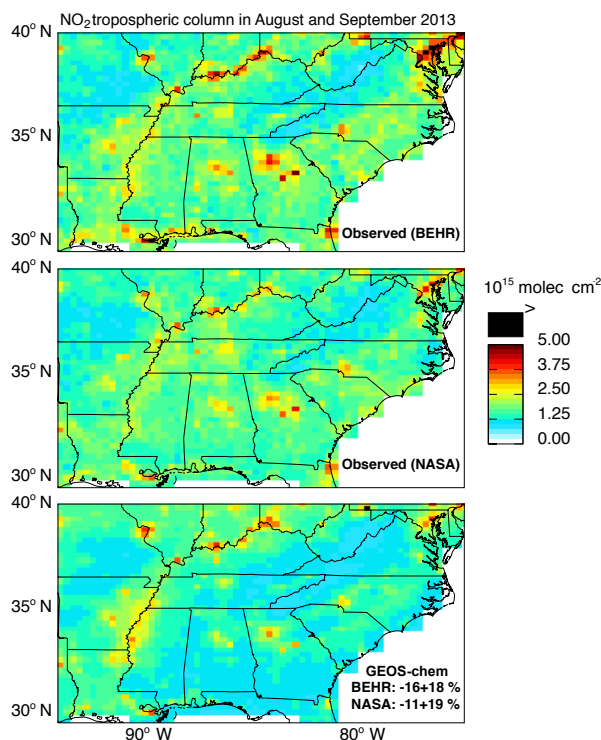
obtain a slant tropospheric  $\text{NO}_2$  column,  $\Omega_s$ , along the optical path of the backscattered radiation detected by the satellite. The slant column is converted to the vertical column,  $\Omega_v$ , by using an air mass factor (AMF) that depends on the vertical profile of  $\text{NO}_2$  and on the scattering properties of the surface and the atmosphere (Palmer et al., 2001):

$$\Omega_v = \frac{\Omega_s}{\text{AMF}} = \frac{\Omega_s}{\text{AMF}_G \int_0^{z_T} w(z) S(z) dz} \quad (1)$$

In Eq. (4),  $\text{AMF}_G$  is the geometric air mass factor that depends on the viewing geometry of the satellite,  $w(z)$  is a scattering weight calculated by a radiative transfer model that describes the sensitivity of the backscattered radiation to  $\text{NO}_2$  as a function of altitude,  $S(z)$  is a shape factor describing the normalized vertical profile of  $\text{NO}_2$  number density, and  $z_T$  is the tropopause. Scattering weights for  $\text{NO}_2$  retrievals typically increase by a factor of 3 from the surface to the upper troposphere (Martin et al., 2002). Here we use our GEOS-Chem shape factors to recalculate the AMFs in the NASA and BEHR retrievals as recommended by Lamsal et al. (2014) for comparing model and observations. We filter out cloudy scenes (cloud radiance fraction  $> 0.5$ ) and bright surfaces (surface reflectivity  $> 0.3$ ).

Figure 5 shows the mean  $\text{NO}_2$  tropospheric columns from BEHR, NASA, and GEOS-Chem (with  $\text{NO}_x$  emission reductions applied) over the Southeast US for August–September 2013. The BEHR retrieval is on average 6 % higher than the NASA retrieval. GEOS-Chem is on average  $11 \pm 19\%$  lower than the NASA retrieval and  $16 \pm 18\%$  lower than the BEHR retrieval. With the original NEI  $\text{NO}_x$  emissions, GEOS-Chem would be biased high against both retrievals by 26–31 %. The low bias in the model with reduced  $\text{NO}_x$  emissions does not appear to be caused by an overcorrection of surface emissions but rather by the upper troposphere. Figure 6 (top left panel) shows the mean vertical profile of  $\text{NO}_2$  number density as measured from the aircraft by two independent instruments (NOAA and UC Berkeley) and simulated by GEOS-Chem. At the surface, the median difference is  $1.8 \times 10^9 \text{ molecules cm}^{-3}$ , which is

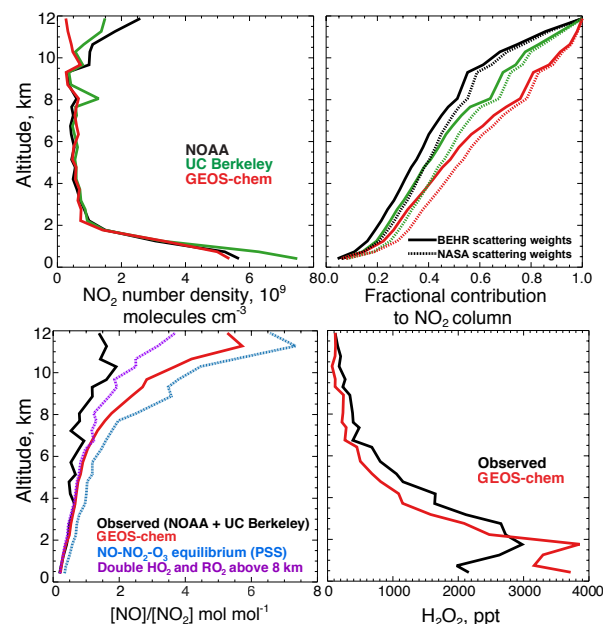




**Figure 5.**  $\text{NO}_2$  tropospheric columns over the Southeast US in August–September 2013. GEOS-Chem (sampled at the 13:30 local time overpass of OMI) is compared to OMI satellite observations using the BEHR and NASA retrievals. Values are plotted on the  $0.25^\circ \times 0.3125^\circ$  GEOS-Chem grid. The GEOS-Chem mean bias over the figure domain and associated spatial standard deviation are inset in the bottom panel.

within the NOAA and UC Berkeley measurement uncertainties of  $\pm 0.030$  ppbv  $\pm 7\%$  and  $\pm 5\%$ , respectively. The observations show a secondary maximum in the upper troposphere above 10 km, absent in GEOS-Chem. It has been suggested that aircraft measurements of  $\text{NO}_2$  in the upper troposphere could be biased high due to decomposition in the instrument inlet of thermally unstable  $\text{NO}_x$  reservoirs such as  $\text{HNO}_4$  and methyl peroxy nitrate (Browne et al., 2011; Reed et al., 2016). This would not affect the UC Berkeley measurement (Nault et al., 2015) and could possibly account for the difference with the NOAA measurement in Fig. 6.

The top right panel of Fig. 6 shows the cumulative contributions from different altitudes to the slant  $\text{NO}_2$  column measured by the satellite, using the median vertical profiles from the left panel and applying mean altitude-dependent scattering weights from the NASA and BEHR retrievals. The boundary layer below 1.5 km contributes only 19–28 % of the column. The upper troposphere above 8 km contributes 32–49 % in the aircraft observations and 23 % in GEOS-Chem. Much of the observed upper-tropospheric  $\text{NO}_2$  likely originates from lightning and is broadly distributed across the southeast because of the long lifetime of  $\text{NO}_x$  at that alti-



**Figure 6.** Vertical distribution of  $\text{NO}_2$  over the Southeast US during SEAC<sup>4</sup>RS (August–September 2013) and contributions to tropospheric  $\text{NO}_2$  columns measured from space by OMI. The top left panel shows median vertical profiles of  $\text{NO}_2$  number density measured from the SEAC<sup>4</sup>RS aircraft by the NOAA and UC Berkeley instruments and simulated by GEOS-Chem. The top right panel shows the fractional contribution of  $\text{NO}_2$  below a given altitude to the total tropospheric  $\text{NO}_2$  slant column measured by OMI, accounting for increasing sensitivity with altitude as determined from the retrieval scattering weights. The bottom left panel shows the median vertical profiles of the daytime  $[\text{NO}]/[\text{NO}_2]$  molar concentration ratio in the aircraft observations (NOAA for NO and UC Berkeley for  $\text{NO}_2$ ) and in GEOS-Chem. Also shown is the ratio computed from  $\text{NO}-\text{NO}_2-\text{O}_3$  photochemical steady state (PSS) as given by Reactions (4) and (6) (blue) and including Reaction (5) with doubled  $\text{HO}_2$  and  $\text{RO}_2$  concentrations above 8 km (purple). The bottom right panel shows the median  $\text{H}_2\text{O}_2$  profile from the model and from the SEAC<sup>4</sup>RS flights over the Southeast US.  $\text{H}_2\text{O}_2$  was measured by the Caltech CIMS (see Fig. 2).

tude (Li et al., 2005; Bertram et al., 2007; Hudman et al., 2007). The  $\text{NO}_2$  vertical profile (shape factor) assumed in the BEHR retrieval does not include any lightning influence, and the Global Modeling Initiative (GMI) model vertical profile assumed in the NASA retrieval has little contribution from the upper troposphere (Lamsal et al., 2014). These underestimates of upper-tropospheric  $\text{NO}_2$  in the retrieval shape factors will cause a negative bias in the AMF and therefore a positive bias in the retrieved vertical columns.

The GEOS-Chem underestimate of observed upper-tropospheric  $\text{NO}_2$  in Fig. 6 is partly driven by  $\text{NO}/\text{NO}_2$  partitioning. The bottom left panel of Fig. 6 shows the  $[\text{NO}]/[\text{NO}_2]$  concentration ratio in GEOS-Chem and in the observations (NOAA for NO, UC Berkeley for  $\text{NO}_2$ ). One would expect the  $[\text{NO}]/[\text{NO}_2]$  concentration ratio in the

daytime upper troposphere to be controlled by photochemical steady state:



If Reaction (R5) plays only a minor role then  $[\text{NO}]/[\text{NO}_2] \approx k_6/(k_4[\text{O}_3])$ , defining the NO–NO<sub>2</sub>–O<sub>3</sub> photochemical steady state (PSS). The PSS plotted in Fig. 6 agrees closely with GEOS-Chem. Such agreement has previously been found when comparing photochemical models with observed  $[\text{NO}]/[\text{NO}_2]$  ratios from aircraft in the marine upper troposphere (Schultz et al., 1999) and lower stratosphere (Del Negro et al., 1999). The SEAC<sup>4</sup>RS observations show large departure. The NO<sub>2</sub> photolysis frequencies  $k_6$  computed locally by GEOS-Chem are on average within 10 % of the values determined in SEAC<sup>4</sup>RS from measured actinic fluxes (Shetter and Muller, 1999), so this is not the problem.

A possible explanation is that the model underestimates peroxy radical concentrations and hence the contribution of Reaction (5) in the upper troposphere. Zhu et al. (2016) found that GEOS-Chem underestimates the observed HCHO concentrations in the upper troposphere during SEAC<sup>4</sup>RS by a factor of 3, implying that the model underestimates the HO<sub>x</sub> source from convective injection of HCHO and peroxides (Jaeglé et al., 1997; Prather and Jacob, 1997; Müller and Brasseur, 1999). HO<sub>2</sub> observations over the central US in summer during the SUCCESS aircraft campaign suggest that this convective injection increases HO<sub>x</sub> concentrations in the upper troposphere by a factor of 2 (Jaeglé et al., 1998). The bottom right panel of Fig. 6 shows median modeled and observed vertical profiles of the HO<sub>x</sub> reservoir hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) during SEAC<sup>4</sup>RS over the Southeast US. GEOS-Chem underestimates observed H<sub>2</sub>O<sub>2</sub> by a mean factor of 1.7 above 8 km. The bottom left panel of Fig. 6 shows the  $[\text{NO}]/[\text{NO}_2]$  ratio in GEOS-Chem with HO<sub>2</sub> and RO<sub>2</sub> doubled above 8 km. Such a change corrects significantly the bias relative to observations.

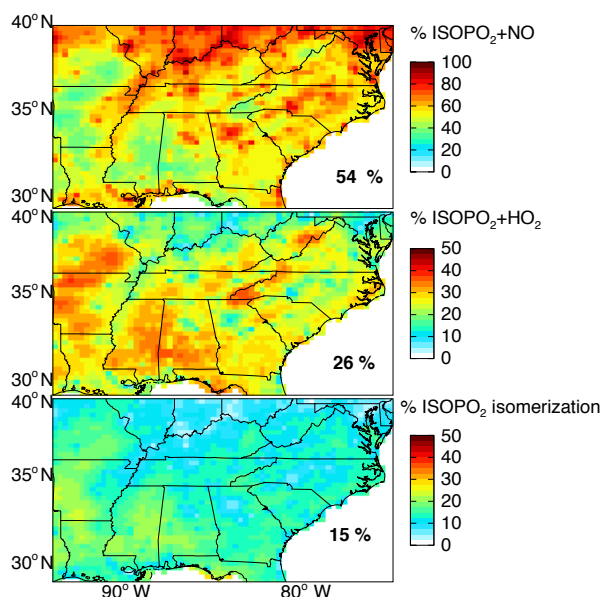
The PSS and GEOS-Chem simulation of the NO/NO<sub>2</sub> concentration ratio in Fig. 6 use  $k_4 = 3.0 \times 10^{-12} \exp[-1500/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and spectroscopic information for  $k_6$  from Sander et al. (2011). It is possible that the strong thermal dependence of  $k_4$  has some error, considering that only one direct measurement has been published for the cold temperatures of the upper troposphere (Borders and Birks, 1982). Cohen et al. (2000) found that reducing the activation energy of  $k_4$  by 15 % improved model agreement in the lower stratosphere. Correcting the discrepancy between simulated and observed  $[\text{NO}]/[\text{NO}_2]$  ratios in the upper troposphere in Fig. 6 would require a similar reduction to the activation energy of  $k_4$ , but this reduction would negatively impact the surface comparison. This inconsistency of the observed  $[\text{NO}]/[\text{NO}_2]$  ratio with

basic theory needs to be resolved, as it affects the inference of NO<sub>x</sub> emissions from satellite NO<sub>2</sub> column measurements. Notwithstanding this inconsistency, we find that NO<sub>2</sub> in the upper troposphere makes a significant contribution to the tropospheric NO<sub>2</sub> column observed from space.

## 5 Isoprene oxidation pathways

Measurements aboard the SEAC<sup>4</sup>RS aircraft included first-generation isoprene nitrates (ISOPN), isoprene hydroperoxide (ISOPOOH), and hydroperoxy-aldehydes (HPALDs) (Crounse et al., 2006; Paulot et al., 2009a; St. Clair et al., 2010; Crounse et al., 2011; Beaver et al., 2012; Nguyen et al., 2015). Although measurement uncertainties are large (30, 40, and 50 %, respectively; Nguyen et al., 2015), these are unique products of the ISOPO<sub>2</sub> + NO, ISOPO<sub>2</sub> + HO<sub>2</sub>, and ISOPO<sub>2</sub> isomerization pathways and thus track whether oxidation of isoprene proceeds by the high-NO<sub>x</sub> pathway (producing ozone) or the low-NO<sub>x</sub> pathways. Figure 2 (bottom row) compares simulated and observed concentrations. All three gases are restricted to the boundary layer because of their short lifetimes. Mean model concentrations in the lowest altitude bin (Fig. 2, approximately 400 m above ground) differ from observations by +19 % for ISOPN, +70 % for ISOPOOH, and –50 % for HPALDs. The GEOS-Chem simulation of organic nitrates including ISOPN is further discussed in Fisher et al. (2016). Our HPALD source is based on the ISOPO<sub>2</sub> isomerization rate constant from Crounse et al. (2011). A theoretical calculation by Peeters et al. (2014) suggests a rate constant that is  $1.8 \times$  higher, which would reduce the model bias for HPALDs and ISOPOOH and increase boundary layer OH by 8 %. 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. For both ISOPOOH and HPALDs, GEOS-Chem captures much of the spatial variability ( $r = 0.80$  and  $0.79$ , respectively).

Figure 7 shows the model branching ratios for the fate of the ISOPO<sub>2</sub> radical by tracking the mass of ISOPO<sub>2</sub> reacting via the high-NO<sub>x</sub> pathway (ISOPO<sub>2</sub> + NO) and the low-NO<sub>x</sub> pathways over the Southeast US domain. The mean branching ratios for the Southeast US are ISOPO<sub>2</sub> + NO 54 %, ISOPO<sub>2</sub> + HO<sub>2</sub> 26 %, ISOPO<sub>2</sub> isomerization 15 %, and ISOPO<sub>2</sub> + RO<sub>2</sub> 5 %. The lack of dominance of the high-NO<sub>x</sub> pathway is due in part to the spatial segregation of isoprene and NO<sub>x</sub> emissions (Yu et al., 2016). This segregation also buffers the effect of changing NO<sub>x</sub> emissions on the fate of isoprene. Our original simulation with higher total NO<sub>x</sub> emissions (unadjusted NEI11v1) had a branching ratio for the ISOPO<sub>2</sub> + NO reaction of only 62 %.

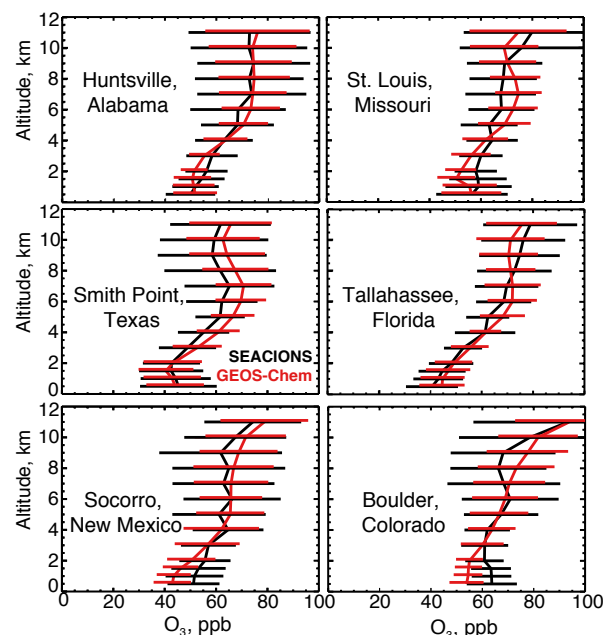


**Figure 7.** Branching ratios for the fate of the isoprene peroxy radical ( $\text{ISOPO}_2$ ) as simulated by GEOS-Chem over the Southeast US for August–September 2013. Values are percentages of  $\text{ISOPO}_2$  that react with NO,  $\text{HO}_2$ , or isomerize from the total mass of isoprene reacting over the domain. Note the difference in scale between the top panel and the lower two panels. Regional mean percentages for the Southeast US are shown inset. They add up to less than 100 % because of the small  $\text{ISOPO}_2$  sink from reaction with other organic peroxy radicals ( $\text{RO}_2$ ).

## 6 Implications for ozone: aircraft and ozonesonde observations

Figure 2 compares simulated and observed median vertical profiles of ozone concentrations over the Southeast US during SEAC<sup>4</sup>RS. There is no significant bias through the depth of the tropospheric column. The median ozone concentration below 1.5 km is 49 ppb in the observations and 51 ppb in the model. We also find excellent model agreement across the US with the SEACIONS ozonesonde network (Fig. 8). The successful simulation of ozone is contingent on the decrease in  $\text{NO}_x$  emissions. As shown in Fig. 2, a simulation with the original NEI emissions overestimates boundary layer ozone by 12 ppb.

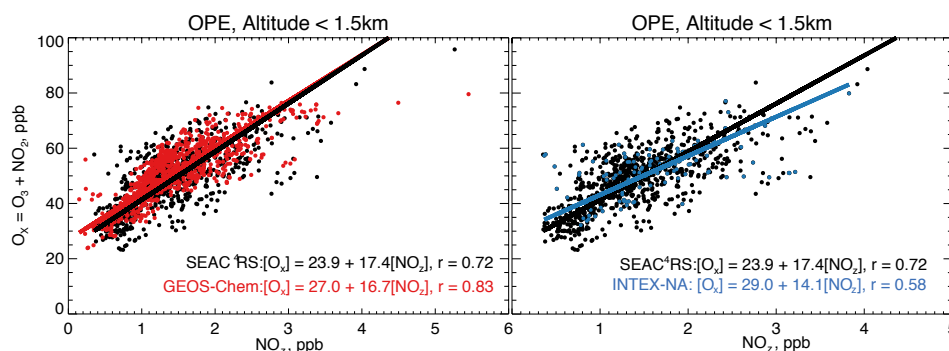
The model also has success in reproducing the spatial variability of boundary layer ozone seen from the aircraft, as shown in Fig. 4. The correlation coefficient is  $r = 0.71$  on the  $0.25^\circ \times 0.3125^\circ$  model grid, and patterns of high and low ozone concentration are consistent. The highest observed ozone ( $> 75$  ppb) was found in air influenced by agricultural burning along the Mississippi River and by outflow from Houston over Louisiana. GEOS-Chem does not capture the extreme values and this probably reflects a dilution effect (Yu et al., 2016).



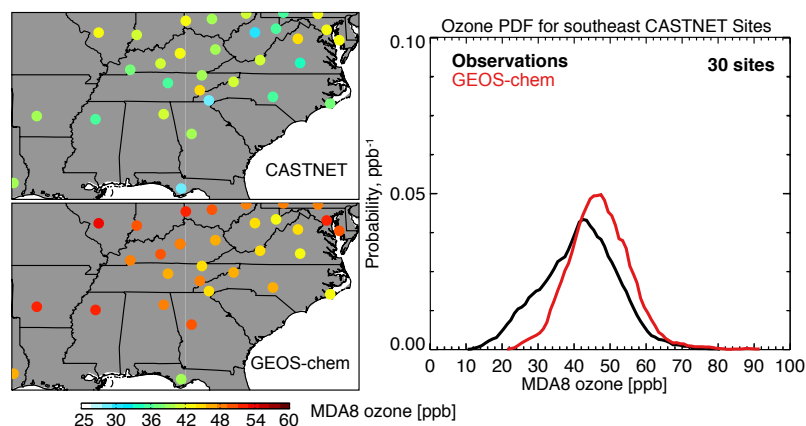
**Figure 8.** Mean ozonesonde vertical profiles at the US SEACIONS sites (<http://croc.gsfc.nasa.gov/seacions/>) during the SEAC<sup>4</sup>RS campaign in August–September 2013. An average of 20 sondes were launched per site between 09:00 and 16:00 local time. Ozonesondes at Smith Point, Texas, were only launched in September. Model values are coincident with the launches. Data are averaged vertically over 0.5 km bins below 2 km altitude and 1.0 km bins above. Also shown are standard deviations.

A critical parameter for understanding ozone production is the ozone production efficiency (OPE) (Liu et al., 1987), defined as the number of ozone molecules produced per molecule of  $\text{NO}_x$  emitted. This can be estimated from atmospheric observations by the relationship between odd oxygen ( $\text{O}_x \equiv \text{O}_3 + \text{NO}_2$ ) and the sum of products of  $\text{NO}_x$  oxidation, collectively called  $\text{NO}_z$  and including inorganic and organic nitrates (Trainer et al., 1993; Zaveri, 2003). The  $\text{O}_x$  vs.  $\text{NO}_z$  linear relationship (as derived from a linear regression) provides an upper estimate of the OPE because of rapid deposition of  $\text{NO}_y$ , mainly  $\text{HNO}_3$  (Trainer et al., 2000; Rickard et al., 2002).

Figure 9 shows the observed and simulated daytime (09:00–16:00 local)  $\text{O}_x$  vs.  $\text{NO}_z$  relationship in the SEAC<sup>4</sup>RS data below 1.5 km, where  $\text{NO}_z$  is derived from the observations as  $\text{NO}_y - \text{NO}_x \equiv \text{HNO}_3 + \text{aerosol nitrate} + \text{PAN} + \text{alkyl nitrates}$ . The resulting OPE from the observations ( $17.4 \pm 0.4 \text{ mol mol}^{-1}$ ) agrees well with GEOS-Chem ( $16.7 \pm 0.3 \text{ mol mol}^{-1}$ ). Previous work during the INTEX-NA aircraft campaign in summer 2004 found an OPE of 8 below 4 km (Mena-Carrasco et al., 2007). By selecting INTEX-NA data only for the southeast and below 1.5 km we find an OPE of  $14.1 \pm 1.1$  (Fig. 9, right panel). The median  $\text{NO}_z$  was 1.1 ppb during SEAC<sup>4</sup>RS and 1.5 ppb during INTEX-NA, a decrease of approximately 40 %. With



**Figure 9.** Ozone production efficiency (OPE) over the Southeast US in summer estimated from the relationship between odd oxygen ( $O_x$ ) and the sum of  $NO_x$  oxidation products ( $NO_z$ ) below 1.5 km altitude. The left panel compares SEAC<sup>4</sup>RS observations to GEOS-Chem values for August–September 2013 (data from Fig. 2). The right panel compares SEAC<sup>4</sup>RS observations to INTEX-NA aircraft observations collected over the same Southeast US domain in summer 2004 (Singh et al., 2006).  $NO_z$  is defined here as  $HNO_3$  + aerosol nitrate + PAN + alkyl nitrates, all of which were measured from the SEAC<sup>4</sup>RS and INTEX-NA aircraft. The slope and intercept of the reduced-major-axis (RMA) regression are provided inset with the correlation coefficient ( $r$ ). Observations for INTEX-NA were obtained from <ftp://ftp-air.larc.nasa.gov/pub/INTEXA/>.



**Figure 10.** Maximum daily 8 h average (MDA8) ozone concentrations at the 30 CASTNET sites in the Southeast US in June–August 2013. The left panels show seasonal mean values in the observations and GEOS-Chem. The right panel shows the probability density functions (pdfs) of daily values at the 30 sites.

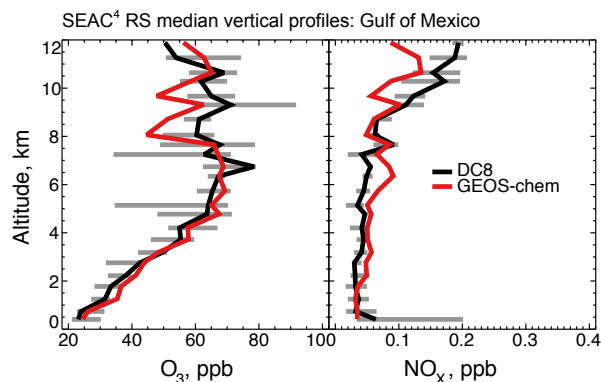
the original NEI11v1  $NO_x$  emissions (53 % higher), the OPE from GEOS-Chem would be  $14.7 \pm 0.3$ . Both the INTEX-NA data and the model are consistent with the expectation that OPE increases with decreasing  $NO_x$  emissions (Liu et al., 1987).

## 7 Implications for ozone: surface air

Figure 10 compares maximum daily 8 h average (MDA8) ozone values at the US CASTNET (EPA, 2016) sites in June–August 2013 to the corresponding GEOS-Chem values. The model has a mean positive bias of  $6 \pm 14$  ppb with no significant spatial pattern. The model is unable to match the low tail in the observations, including a significant population with MDA8 ozone less than 20 ppb. The improvements to dry deposition described in Sect. 2.2 minimally reduce (approx-

mately 1 ppb) GEOS-Chem ozone compared to SEAC<sup>4</sup>RS boundary layer and CASTNET surface MDA8 ozone observations. The reduction of daytime mixing depths described in Sect. 2 results in a small increase in mean MDA8 ozone (approximately 2 ppb).

The positive bias in the model for surface ozone is remarkable considering that the model has little bias relative to aircraft observations below 1.5 km altitude (Figs. 2 and 4). A standard explanation for model overestimates of surface ozone over the Southeast US, first proposed by Fiore et al. (2003) and echoed in the review by McDonald-Buller et al. (2011), is excessive ozone over the Gulf of Mexico, which is the prevailing low-altitude inflow. We find that this is not the case. SEAC<sup>4</sup>RS included four flights over the Gulf of Mexico, and Fig. 11 compares simulated and observed vertical profiles of ozone and  $NO_x$  concentrations that show no



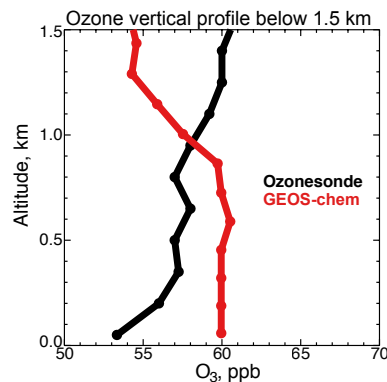
**Figure 11.** Median vertical profiles of ozone and  $\text{NO}_x$  concentrations over the Gulf of Mexico during SEAC<sup>4</sup>RS. Observations are from four SEAC<sup>4</sup>RS flights over the Gulf of Mexico (12 August and 4, 13, 16 September). GEOS-Chem model values are sampled along the flight tracks. The 25th and 75th percentiles of the aircraft observations are shown as horizontal bars.

systematic bias. The median ozone concentration in the marine boundary layer is 26 ppb in the observations and 29 ppb in the model. This successful simulation is due to our adjustment of lightning  $\text{NO}_x$  emission (Sect. 2.3); a sensitivity test with the original (twice higher) GEOS-Chem lightning emissions in the southern US increases surface ozone over the Gulf of Mexico by up to 6 ppb. The aircraft observations in Fig. 4 further show no indication of a coastal depletion that might be associated with halogen chemistry. Remarkably, the median ozone over the Gulf of Mexico is higher than approximately 8 % of MDA8 values at sites in the southeast.

It appears instead that there is a model bias in boundary layer vertical mixing and chemistry. Figure 12 shows the median ozonesonde profile at a higher vertical resolution over the Southeast US (Huntsville, Alabama, and St. Louis, Missouri, sites) during SEAC<sup>4</sup>RS as compared to GEOS-Chem below 1.5 km. The ozonesondes indicate a decrease of 7 ppb from 1.5 km to the surface, whereas GEOS-Chem features a reverse gradient of increasing ozone from 1.5 to 1 km with flat concentrations below. This implies a combination of two model errors in the boundary layer: (1) excessive vertical mixing and (2) net ozone production whereas observations indicate net ozone loss.

## 8 Conclusions

We used aircraft (SEAC<sup>4</sup>RS), surface, satellite, and ozonesonde observations from August and September 2013, interpreted with the GEOS-Chem chemical transport model, to better understand the factors controlling surface ozone in the Southeast US. Models tend to overestimate ozone in that region. Determining the reasons behind this overestimate is critical to the design of efficient emission control strategies to meet the ozone NAAQS.



**Figure 12.** Median vertical profile of ozone concentrations over St. Louis, Missouri, and Huntsville, Alabama, during August and September 2013. Observations from SEACIONS ozonesondes launched between 10:00 and 13:00 local time (57 launches) are compared to GEOS-Chem results sampled at the times of the ozonesonde launches and at the vertical resolution of the model (11 layers below 1.5 km, red circles). The ozonesonde data are shown at 150 m resolution. Altitude is above local ground level.

A major finding from this work is that NEI11v1 for  $\text{NO}_x$  (the limiting precursor for ozone formation) is biased high across the US by as much as a factor of 2. Evidence for this comes from (1) SEAC<sup>4</sup>RS observations of  $\text{NO}_x$  and its oxidation products, (2) NADP network observations of nitrate wet deposition fluxes, and (3) OMI satellite observations of  $\text{NO}_2$ . Presuming no error in emissions from large power plants with continuous emission monitors (14 % of unadjusted NEI inventory), we find that emissions from other industrial sources and mobile sources must be 30–60 % lower than NEI values, depending on the assumption of the contribution from soil  $\text{NO}_x$  emissions. We thus estimate that anthropogenic fuel  $\text{NO}_x$  emissions in the US in 2013 were 1.7–2.6  $\text{Tg N a}^{-1}$ , as compared to 3.5  $\text{Tg N a}^{-1}$  given in the NEI.

OMI  $\text{NO}_2$  satellite data over the Southeast US are consistent with this downward correction of  $\text{NO}_x$  emissions but interpretation is complicated by the large contribution of the free troposphere to the  $\text{NO}_2$  tropospheric column retrieved from the satellite. Observed (aircraft) and simulated vertical profiles indicate that  $\text{NO}_2$  below 2 km contributes only 20–35 % of the tropospheric column detected from space while  $\text{NO}_2$  above 8 km (mainly from lightning) contributes 25–50 %. Current retrievals of satellite  $\text{NO}_2$  data do not properly account for this elevated pool of upper-tropospheric  $\text{NO}_2$ , so that the reported tropospheric  $\text{NO}_2$  columns are biased high. More work is needed on the chemistry maintaining high levels of  $\text{NO}_2$  in the upper troposphere.

Isoprene emitted by vegetation is the main VOC precursor of ozone in the southeast in summer, but we find that only 50 % reacts by the high- $\text{NO}_x$  pathway to produce ozone. This is consistent with detailed aircraft observations of isoprene oxidation products from the aircraft. The high- $\text{NO}_x$



fraction is only weakly sensitive to the magnitude of  $\text{NO}_x$  emissions because isoprene and  $\text{NO}_x$  emissions are spatially segregated. The ability to properly describe high- and low- $\text{NO}_x$  pathways for isoprene oxidation is critical for simulating ozone and it appears that the GEOS-Chem mechanism is successful for this purpose.

Our updated GEOS-Chem simulation with decreased  $\text{NO}_x$  emissions provides an unbiased simulation of boundary layer and free-tropospheric ozone measured from aircraft and ozonesondes during SEAC<sup>4</sup>RS. Decreasing  $\text{NO}_x$  emissions is critical to this success as the original model with NEI emissions overestimated boundary layer ozone by 12 ppb. The ozone production efficiency (OPE) inferred from  $\text{O}_3$  vs.  $\text{NO}_2$  aircraft correlations in the mixed layer is also well reproduced. Comparison to the INTEx-NA aircraft observations over the southeast in summer 2004 indicates a 14 % increase in OPE associated with a 40 % reduction in  $\text{NO}_x$  emissions.

Despite the successful simulation of boundary layer ozone (Figs. 2 and 9), GEOS-Chem overestimates MDA8 surface ozone observations in the Southeast US in summer by  $6 \pm 14$  ppb. Daytime ozonesonde data indicate a 7 ppb decrease from 1.5 km to the surface that GEOS-Chem does not capture. This may be due to excessive boundary layer mixing and net ozone production in the model. Excessive mixing in GEOS-Chem may be indicative of an overestimate of sensible heat flux (Holtslag and Boville, 1993), and thus an investigation of boundary layer meteorological variables is warranted. Such a bias may not be detected in the comparison of GEOS-Chem with aircraft data, generally collected under fair-weather conditions and with minimal sampling in the lower part of the boundary layer. An investigation of relevant meteorological variables and boundary layer source and sink terms in the ozone budget to determine the source of bias and its prevalence across models will be the topic of a follow-up paper.

## 9 Data availability

The SEAC<sup>4</sup>RS airborne trace gas and particle measurements and SEACIONS ozonesonde measurements are available from the NASA LaRC Airborne Science Data for Atmospheric Composition (<http://www-air.larc.nasa.gov/cgi-bin/ArcView/seac4rs>) with doi:10.5067/Aircraft/SEAC4RS/Aerosol-TraceGas-Cloud.

Observations for INTEx-NA were also obtained from NASA LaRC (<http://www-air.larc.nasa.gov/cgi-bin/ArcView/intexna>) with doi:10.5067/Aircraft/INTExA/Aerosol-TraceGas.

**The Supplement related to this article is available online at doi:10.5194/acp-16-13561-2016-supplement.**

**Acknowledgements.** We are grateful to the entire NASA SEAC<sup>4</sup>RS team for their help in the field. We thank Tom Ryerson for his measurements of NO and  $\text{NO}_2$  from the NOAA  $\text{NO}_y\text{O}_3$  instrument. We thank L. Gregory Huey for the use of his CIMS PAN measurements. We thank Fabien Paulot and Jingqiu Mao for their helpful discussions of isoprene chemistry. We thank Christoph Keller for his help in implementing the NEI11v1 emissions into GEOS-Chem. We acknowledge the EPA for providing the 2011 North American emission inventory and in particular George Pouliot for his help and advice. These emission inventories are intended for research purposes. A technical report describing the 2011 modeling platform can be found at [https://www.epa.gov/sites/production/files/2015-10/documents/nei2011v2\\_tsd\\_14aug2015.pdf](https://www.epa.gov/sites/production/files/2015-10/documents/nei2011v2_tsd_14aug2015.pdf). A description of the 2011 NEI can be found at <https://www.epa.gov/air-emissions-inventories/national-emissions-inventory>. This work was supported by the NASA Earth Science Division and by STAR Fellowship Assistance Agreement no. 91761601-0 awarded by the US Environmental Protection Agency (EPA). It has not been formally reviewed by EPA. The views expressed in this publication are solely those of the authors. JAF acknowledges support from a University of Wollongong Vice Chancellor's Postdoctoral Fellowship. This research was undertaken with the assistance of resources provided at the NCI National Facility systems at the Australian National University through the National Computational Merit Allocation Scheme supported by the Australian Government.

Edited by: L. Ganzeveld

Reviewed by: three anonymous referees

## References

- Air Sciences, Inc.: 2002 Fire Emission Inventory for the WRAP Region – Phase II, Western Governors Association/Western Regional Air Partnership, Denver and Portland, 2005.
- Alvarado, M. J., Logan, J. A., Mao, J., Apel, E., Riemer, D., Blake, D., Cohen, R. C., Min, K.-E., Perring, A. E., Browne, E. C., Wooldridge, P. J., Diskin, G. S., Sachse, G. W., Fuelberg, H., Sessions, W. R., Harrigan, D. L., Huey, G., Liao, J., Case-Hanks, A., Jimenez, J. L., Cubison, M. J., Vay, S. A., Weinheimer, A. J., Knapp, D. J., Montzka, D. D., Flocke, F. M., Pollack, I. B., Wennberg, P. O., Kurten, A., Crounse, J., Clair, J. M. St., Wisthaler, A., Mikoviny, T., Yantosca, R. M., Carouge, C. C., and Le Sager, P.: Nitrogen oxides and PAN in plumes from boreal fires during ARCTAS-B and their impact on ozone: an integrated analysis of aircraft and satellite observations, *Atmos. Chem. Phys.*, 10, 9739–9760, doi:10.5194/acp-10-9739-2010, 2010.
- Anderson, D. C., Loughner, C. P., Diskin, G., Weinheimer, A., Canty, T., P., Salawitch, R. J., Worden, H. M., Fried, A., Mikoviny, T., Wisthaler, A., and Dickerson, R. R.: Measured and modeled CO and  $\text{NO}_y$  in DISCOVER-AQ: An evaluation of emissions and chemistry over the eastern US, *Atmos. Environ.*, 96, 78–87, doi:10.1016/j.atmosenv.2014.07.004, 2014.
- Bates, K. H., Crounse, J. D., St Clair, J. M., Bennett, N. B., Nguyen, T. B., Seinfeld, J. H., Stoltz, B. M., and Wennberg, P. O.: Gas Phase Production and Loss of Isoprene Epoxidiols, *J. Phys. Chem. A*, 118, 1237–1246, doi:10.1021/Jp4107958, 2014.



- Beaver, M. R., Clair, J. M. St., Paulot, F., Spencer, K. M., Crounse, J. D., LaFranchi, B. W., Min, K. E., Pusede, S. E., Wooldridge, P. J., Schade, G. W., Park, C., Cohen, R. C., and Wennberg, P. O.: Importance of biogenic precursors to the budget of organic nitrates: observations of multifunctional organic nitrates by CIMS and TD-LIF during BEARPEX 2009, *Atmos. Chem. Phys.*, 12, 5773–5785, doi:10.5194/acp-12-5773-2012, 2012.
- Bertram, T. H., Perring, A. E., Wooldridge, P. J., Crounse, J. D., Kwan, A. J., Wennberg, P. O., Scheuer, E., Dibb, J., Avery, M., Sachse, G., Vay, S. A., Crawford, J. H., McNaughton, C. S., Clarke, A., Pickering, K. E., Fuelberg, H., Huey, G., Blake, D. R., Singh, H. B., Hall, S. R., Shetter, R. E., Fried, A., Heikes, B. G., and Cohen, R. C.: Direct Measurements of the Convective Recycling of the Upper Troposphere, *Science*, 315, 816–820, doi:10.1126/science.1134548, 2007.
- Bey, I., Jacob, D. J., Yantosca, R. M., Logan, J. A., Field, B. D., Fiore, A. M., Li, Q. B., Liu, H. G. Y., Mickley, L. J., and Schultz, M. G.: Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, *J. Geophys. Res.-Atmos.*, 106, 23073–23095, doi:10.1029/2001jd000807, 2001.
- Borders, R. A., and Birks, J. W.: High-Precision Measurements of Activation Energies over Small Temperature Intervals: Curvature in the Arrhenius Plot for the Reaction  $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ , *J. Phys. Chem. A*, 86, 3295–3302, 1982.
- Brioude, J., Angevine, W. M., Ahmadov, R., Kim, S.-W., Evan, S., McKeen, S. A., Hsie, E.-Y., Frost, G. J., Neuman, J. A., Pollock, I. B., Peischl, J., Ryerson, T. B., Holloway, J., Brown, S. S., Nowak, J. B., Roberts, J. M., Wofsy, S. C., Santoni, G. W., Oda, T., and Trainer, M.: Top-down estimate of surface flux in the Los Angeles Basin using a mesoscale inverse modeling technique: assessing anthropogenic emissions of  $\text{CO}$ ,  $\text{NO}_x$  and  $\text{CO}_2$  and their impacts, *Atmos. Chem. Phys.*, 13, 3661–3677, doi:10.5194/acp-13-3661-2013, 2013.
- Browne, E. C., Perring, A. E., Wooldridge, P. J., Apel, E., Hall, S. R., Huey, L. G., Mao, J., Spencer, K. M., Clair, J. M. St., Weinheimer, A. J., Wisthaler, A., and Cohen, R. C.: Global and regional effects of the photochemistry of  $\text{CH}_3\text{O}_2\text{NO}_2$ : evidence from ARCTAS, *Atmos. Chem. Phys.*, 11, 4209–4219, doi:10.5194/acp-11-4209-2011, 2011.
- Brown-Steiner, B., Hess, P. G., and Lin, M. Y.: On the capabilities and limitations of GCM simulations of summertime regional air quality: A diagnostic analysis of ozone and temperature simulations in the US using CESM CAM-Chem, *Atmos. Environ.*, 101, 134–148, doi:10.1016/j.atmosenv.2014.11.001, 2015.
- Bucsela, E. J., Krotkov, N. A., Celarier, E. A., Lamsal, L. N., Swartz, W. H., Bhartia, P. K., Boersma, K. F., Veefkind, J. P., Gleason, J. F., and Pickering, K. E.: A new stratospheric and tropospheric  $\text{NO}_2$  retrieval algorithm for nadir-viewing satellite instruments: applications to OMI, *Atmos. Meas. Tech.*, 6, 2607–2626, doi:10.5194/amt-6-2607-2013, 2013.
- Canty, T. P., Hembeck, L., Vinciguerra, T. P., Anderson, D. C., Goldberg, D. L., Carpenter, S. F., Allen, D. J., Loughner, C. P., Salawitch, R. J., and Dickerson, R. R.: Ozone and  $\text{NO}_x$  chemistry in the eastern US: evaluation of CMAQ/CB05 with satellite (OMI) data, *Atmos. Chem. Phys.*, 15, 10965–10982, doi:10.5194/acp-15-10965-2015, 2015.
- Castellanos, P., Marufu, L. T., Doddridge, B. G., Taubman, B. F., Schwab, J. J., Hains, J. C., Ehrman, S. H., and Dickerson, R. R.: Ozone, oxides of nitrogen, and carbon monoxide during pollution events over the eastern United States: An evaluation of emissions and vertical mixing, *J. Geophys. Res.*, 116, D16307, doi:10.1029/2010JD014540, 2011.
- Chen, D., Wang, Y., McElroy, M. B., He, K., Yantosca, R. M., and Le Sager, P.: Regional CO pollution and export in China simulated by the high-resolution nested-grid GEOS-Chem model, *Atmos. Chem. Phys.*, 9, 3825–3839, doi:10.5194/acp-9-3825-2009, 2009.
- Cohen, R. C., Perkins, K. K., Koch, L. C., Stimpfle, R. M., Wennberg, P. O., Hanisco, T. F., Lanzendorf, E. J., Bonne, G. P., Voss, P. B., Salawitch, R. J., Del Negro, L. A., Wilson, J. C., McElroy, C. T., and Bui, T. P.: Quantitative constraints on the atmospheric chemistry of nitrogen oxides: An analysis along chemical coordinates, *J. Geophys. Res.*, 105, 24283–24304, 2000.
- Crounse, J. D., McKinney, K. A., Kwan, A. J., and Wennberg, P. O.: Measurement of gas-phase hydroperoxides by chemical ionization mass spectrometry (CIMS), *Anal. Chem.*, 78, 6726–6732, 2006.
- Crounse, J. D., Paulot, F., Kjaergaard, H. G., and Wennberg, P. O.: Peroxy radical isomerization in the oxidation of isoprene, *Phys. Chem. Chem. Phys.*, 13, 13607–13613, doi:10.1039/c1cp21330j, 2011.
- Darmenov, A. and da Silva, A.: The Quick Fire Emissions Dataset (QFED) – Documentation of versions 2.1, 2.2 and 2.4, NASA Technical Report Series on Global Modeling and Data Assimilation, NASA TM-2013-104606, 32, 183 pp., Draft Document (12 939 kB), 2013.
- Dibb, J. E., Talbot, R. W., Scheuer, E. M., Seid, G., Avery, M. A., and Singh, H. B.: Aerosol chemical composition in Asian continental outflow during the TRACE-P campaign: Comparison with PEM-West B, *J. Geophys. Res.*, 108, 8815, doi:10.1029/2002jd003111, 2003.
- Del Negro, L. A., Fahey, D. W., Gao, R. S., Donnelly, S. G., Keim, E. R., Neuman, J. A., Cohen, R. C., Perkins, K. K., Koch, L. C., Salawitch, R. J., Lloyd, S. A., Proffitt, M. H., Margitan, J. J., Stimpfle, R. M., Bonne, G. P., Voss, P. B., Wennberg, P. O., McElroy, C. T., Swartz, W. H., Kusterer, T. L., Anderson, D. E., Lait, L. R., and Bui, T. P.: Comparison of modeled and observed values of  $\text{NO}_2$  and  $\text{JNO}_2$  during the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission, *J. Geophys. Res.*, 104, 26687, doi:10.1029/1999jd900246, 1999.
- Duncan, B. N., Prados, A. I., Lamsal, L. N., Liu, Y., Streets, D. G., Gupta, P., Hilsenrath, E., Kahn, R. A., Nielsen, J. E., Beyersdorf, A. J., Burton, S. P., Fiore, A. M., Fishman, J., Henze, D. K., Hostetler, C. A., Krotkov, N. A., Lee, P., Lin, M., Pawson, S., Pfister, G., Pickering, K. E., Pierce, R. B., Yoshida, Y., and Ziemba, L. D.: Satellite data of atmospheric pollution for U.S. air quality applications: Examples of applications, summary of data end-user resources, answers to FAQs, and common mistakes to avoid, *Atmos. Environ.*, 94, 647–662, doi:10.1016/j.atmosenv.2014.05.061, 2014.
- EPA: Integrated Science Assessment for Ozone and Related Photochemical Oxidants, US Environmental Protection Agency, Research Triangle Park, NC, 2013.
- EPA: US Environmental Protection Agency Clean Air Markets Division Clean Air Status and Trends Network (CASTNET)

- [Hourly Ozone], available at: [www.epa.gov/castnet?Date](http://www.epa.gov/castnet?Date), last access: 18 March 2016.
- EPA NEI (National Emissions Inventory v1): Air Pollutant Emission Trends Data, available at: <http://www.epa.gov/ttn/chief/trends/index.html> last access: 23 June 2015.
- Finkelstein, P. L., Ellestad, T. G., Clarke, J. F., Meyers, T. P., Schwede, D. B., Hebert, E. O., and Neal, J. A.: Ozone and sulfur dioxide dry deposition to forests: Observations and model evaluation, *J. Geophys. Res.-Atmos.*, 105, 15365–15377, doi:10.1029/2000jd900185, 2000.
- Fiore, A. M., Jacob, D. J., Liu, H., Yantosca, R. M., Fairlie, T. D., and Li, Q.: Variability in surface ozone background over the United States: Implications for air quality policy, *J. Geophys. Res.-Atmos.*, 108, 4787, doi:10.1029/2003jd003855, 2003.
- Fiore, A. M., Horowitz, L. W., Purves, D. W., Levy, H., Evans, M. J., Wang, Y., Li, Q., and Yantosca, R.: Evaluating the contribution of changes in isoprene emissions to surface ozone trends over the eastern United States, *J. Geophys. Res.*, 110, D12303, doi:10.1029/2004jd005485, 2005.
- Fiore, A. M., Dentener, F. J., Wild, O., Cuvelier, C., Schultz, M. G., Hess, P., Textor, C., Schulz, M., Doherty, R. M., Horowitz, L. W., MacKenzie, I. A., Sanderson, M. G., Shindell, D. T., Stevenson, D. S., Szopa, S., Van Dingenen, R., Zeng, G., Atherton, C., Bergmann, D., Bey, I., Carmichael, G., Collins, W. J., Duncan, B. N., Faluvegi, G., Folberth, G., Gauss, M., Gong, S., Hauglustaine, D., Holloway, T., Isaksen, I. S. A., Jacob, D. J., Jonson, J. E., Kaminski, J. W., Keating, T. J., Lupu, A., Marmer, E., Montanaro, V., Park, R. J., Pitari, G., Pringle, K. J., Pyle, J. A., Schroeder, S., Vivanco, M. G., Wind, P., Wojcik, G., Wu, S., and Zuber, A.: Multimodel estimates of intercontinental source-receptor relationships for ozone pollution, *J. Geophys. Res.*, 114, D04301, doi:10.1029/2008jd010816, 2009.
- Fischer, E. V., Jacob, D. J., Yantosca, R. M., Sulprizio, M. P., Millet, D. B., Mao, J., Paulot, F., Singh, H. B., Roiger, A., Ries, L., Talbot, R. W., Dzepina, K., and Pandey Deolal, S.: Atmospheric peroxyacetyl nitrate (PAN): a global budget and source attribution, *Atmos. Chem. Phys.*, 14, 2679–2698, doi:10.5194/acp-14-2679-2014, 2014.
- Fisher, J. A., Jacob, D. J., Travis, K. R., Kim, P. S., Marais, E. A., Chan Miller, C., Yu, K., Zhu, L., Yantosca, R. M., Sulprizio, M. P., Mao, J., Wennberg, P. O., Crounse, J. D., Teng, A. P., Nguyen, T. B., St. Clair, J. M., Cohen, R. C., Romer, P., Nault, B. A., Wooldridge, P. J., Jimenez, J. L., Campuzano-Jost, P., Day, D. A., Hu, W., Shepson, P. B., Xiong, F., Blake, D. R., Goldstein, A. H., Misztal, P. K., Hanisco, T. F., Wolfe, G. M., Ryerson, T. B., Wisthaler, A., and Mikoviny, T.: 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, *Atmos. Chem. Phys.*, 16, 5969–5991, doi:10.5194/acp-16-5969-2016, 2016.
- Fujita, E. M., Campbell, D. E., Zielinska, B., Chow, J. C., Lindhjem, C. E., DenBleyker, A., Bishop, G. A., Schuchmann, B. G., Stedman, D. H., and Lawson, D. R.: Comparison of the MOVES2010a, MOBILE6.2, and EMFAC2007 mobile source emission models with on-road traffic tunnel and remote sensing measurements, *J. Air Waste Manage.*, 62, 1134–1149, doi:10.1080/10962247.2012.699016, 2012.
- Holtzlag, A. and Boville, B.: Local versus nonlocal boundary-layer diffusion in a global climate model, *J. Climate*, 6, 1825–1842, 1993.
- Horowitz, L. W., Fiore, A. M., Milly, G. P., Cohen, R. C., Perring, A., Wooldridge, P. J., Hess, P. G., Emmons, L. K., and Lamarque, J. F.: Observational constraints on the chemistry of isoprene nitrates over the eastern United States, *J. Geophys. Res.-Atmos.*, 112, D12S08, doi:10.1029/2006jd007747, 2007.
- Hudman, R. C., Jacob, D. J., Turquety, S., Leibensperger, E. M., Murray, L. T., Wu, S., Gilliland, A. B., Avery, M., Bertram, T. H., Brune, W., Cohen, R. C., Dibb, J. E., Flocke, F. M., Fried, A., Holloway, J., Neuman, J. A., Orville, R., Perring, A., Ren, X., Sachse, G. W., Singh, H. B., Swanson, A., and Wooldridge, P. J.: Surface and lightning sources of nitrogen oxides over the United States: Magnitudes, chemical evolution, and outflow, *J. Geophys. Res.*, 112, D12S05, doi:10.1029/2006jd007912, 2007.
- Hudman, R. C., Moore, N. E., Mebust, A. K., Martin, R. V., Russell, A. R., Valin, L. C., and Cohen, R. C.: Steps towards a mechanistic model of global soil nitric oxide emissions: implementation and space based-constraints, *Atmos. Chem. Phys.*, 12, 7779–7795, doi:10.5194/acp-12-7779-2012, 2012.
- Huntrieser, H., Schlager, H., Roiger, A., Lichtenstern, M., Schumann, U., Kurz, C., Brunner, D., Schwierz, C., Richter, A., and Stohl, A.: Lightning-produced NO<sub>x</sub> over Brazil during TROC-CINOX: airborne measurements in tropical and subtropical thunderstorms and the importance of mesoscale convective systems, *Atmos. Chem. Phys.*, 7, 2987–3013, doi:10.5194/acp-7-2987-2007, 2007.
- Huntrieser, H., Schumann, U., Schlager, H., Höller, H., Giez, A., Betz, H.-D., Brunner, D., Forster, C., Pinto Jr., O., and Calheiros, R.: Lightning activity in Brazilian thunderstorms during TROC-CINOX: implications for NO<sub>x</sub> production, *Atmos. Chem. Phys.*, 8, 921–953, doi:10.5194/acp-8-921-2008, 2008.
- Jaeglé, L., Jacob, D. J., Wennberg, P. O., Spivakovsky, C. M., Hanisco, T. F., Lanzendorf, E. L., Hints, E. J., Fahey, D. W., Keim, E. R., Proffitt, M. H., Atlas, E., Flocke, F., Schauffler, S., McElroy, C. T., Midwinter, C., Pfister, L., and Wilson, J. C.: Observed OH and HO<sub>2</sub> in the upper troposphere suggest a major source from convective injection of peroxides, *Geophys. Res. Lett.*, 24, 3181–3184, 1997.
- Jaeglé, L., Jacob, D. J., Wang, Y., Weinheimer, A. J., Ridley, B. A., Campos, T. L., Sachse, G. W., and Hagen, D. E.: Sources and chemistry of NO<sub>x</sub> in the upper troposphere over the United States, *Geophys. Res. Lett.*, 25, 1705–1708, 1998.
- Kim, P. S., Jacob, D. J., Fisher, J. A., Travis, K., Yu, K., Zhu, L., Yantosca, R. M., Sulprizio, M. P., Jimenez, J. L., Campuzano-Jost, P., Froyd, K. D., Liao, J., Hair, J. W., Fenn, M. A., Butler, C. F., Wagner, N. L., Gordon, T. D., Welti, A., Wennberg, P. O., Crounse, J. D., St. Clair, J. M., Teng, A. P., Millet, D. B., Schwarz, J. P., Markovic, M. Z., and Perring, A. E.: Sources, seasonality, and trends of southeast US aerosol: an integrated analysis of surface, aircraft, and satellite observations with the GEOS-Chem chemical transport model, *Atmos. Chem. Phys.*, 15, 10411–10433, doi:10.5194/acp-15-10411-2015, 2015.
- Lamsal, L. N., Krotkov, N. A., Celarier, E. A., Swartz, W. H., Pickering, K. E., Bucsela, E. J., Gleason, J. F., Martin, R. V., Philip, S., Irie, H., Cede, A., Herman, J., Weinheimer, A., Szykman, J. J., and Knepp, T. N.: Evaluation of OMI operational standard NO<sub>2</sub> column retrievals using in situ and surface-based NO<sub>2</sub> observa-

- tions, *Atmos. Chem. Phys.*, 14, 11587–11609, doi:10.5194/acp-14-11587-2014, 2014.
- Li, Q., Jacob, D. J., Park, R., Wang, Y., Heald, C. L., Hudman, R., and Yantosca, R. M.: North American pollution outflow and the trapping of convectively lifted pollution by upper-level anticyclone, *J. Geophys. Res.*, 110, D10301, doi:10.1029/2004JD005039, 2005.
- Li, X., Rohrer, F., Hofzumahaus, A., Brauers, T., Haseler, R., Bohn, B., Broch, S., Fuchs, H., Gomm, S., Holland, F., Jäger, J., Kaiser, J., Keutsch, F. N., Lohse, I., Lu, K., Tillmann, R., Wegener, R., Wolfe, G. M., Mentel, T. F., Kiendler-Scharr, A., and Wahner, A.: Missing gas-phase source of HONO inferred from Zeppelin measurements in the troposphere, *Science*, 344, 292–296, doi:10.1126/science.1248999, 2014.
- Lin, J., Youn, D., Liang, X., and Wuebbles, D.: Global model simulation of summertime U.S. ozone diurnal cycle and its sensitivity to PBL mixing, spatial resolution, and emissions, *Atmos. Environ.*, 42, 8470–8483, doi:10.1016/j.atmosenv.2008.08.012, 2008.
- Lin, J.-T. and McElroy, M. B.: Impacts of boundary layer mixing on pollutant vertical profiles in the lower troposphere: Implications to satellite remote sensing, *Atmos. Environ.*, 44, 1726–1739, doi:10.1016/j.atmosenv.2010.02.009, 2010.
- Liu, S. C., Trainer, M., Fehsenfeld, F. C., Parrish, D. D., Williams, E. J., Fahey, D. W., Hubler, G., and Murphy, P. C.: Ozone Production in the Rural Troposphere and the Implications for Regional and Global Ozone Distributions, *J. Geophys. Res.*, 92, 4191–4207, 1987.
- Liu, Y. J., Herdinger-Blatt, I., McKinney, K. A., and Martin, S. T.: Production of methyl vinyl ketone and methacrolein via the hydroperoxyl pathway of isoprene oxidation, *Atmos. Chem. Phys.*, 13, 5715–5730, doi:10.5194/acp-13-5715-2013, 2013.
- Lu, Z., Streets, D. G., de Foy, B., Lamsal, L. N., Duncan, B. N., and Xing, J.: Emissions of nitrogen oxides from US urban areas: estimation from Ozone Monitoring Instrument retrievals for 2005–2014, *Atmos. Chem. Phys.*, 15, 10367–10383, doi:10.5194/acp-15-10367-2015, 2015.
- Mao, J., Jacob, D. J., Evans, M. J., Olson, J. R., Ren, X., Brune, W. H., Clair, J. M. St., Crounse, J. D., Spencer, K. M., Beaver, M. R., Wennberg, P. O., Cubison, M. J., Jimenez, J. L., Fried, A., Weibring, P., Walega, J. G., Hall, S. R., Weinheimer, A. J., Cohen, R. C., Chen, G., Crawford, J. H., McNaughton, C., Clarke, A. D., Jaeglé, L., Fisher, J. A., Yantosca, R. M., Le Sager, P., and Carouge, C.: Chemistry of hydrogen oxide radicals ( $\text{HO}_x$ ) in the Arctic troposphere in spring, *Atmos. Chem. Phys.*, 10, 5823–5838, doi:10.5194/acp-10-5823-2010, 2010.
- Mao, J., Paulot, F., Jacob, D. J., Cohen, R. C., Crounse, J. D., Wennberg, P. O., Keller, C. A., Hudman, R. C., Barkley, M. P., and Horowitz, L. W.: Ozone and organic nitrates over the eastern United States: Sensitivity to isoprene chemistry, *J. Geophys. Res.-Atmos.*, 118, 11256–11268, doi:10.1002/jgrd.50817, 2013.
- Marais, E. A., Jacob, D. J., Jimenez, J. L., Campuzano-Jost, P., Day, D. A., Hu, W., Krechmer, J., Zhu, L., Kim, P. S., Miller, C. C., Fisher, J. A., Travis, K., Yu, K., Hanisco, T. F., Wolfe, G. M., Arkinson, H. L., Pye, H. O. T., Froyd, K. D., Liao, J., and McNeill, V. F.: Aqueous-phase mechanism for secondary organic aerosol formation from isoprene: application to the south-east United States and co-benefit of  $\text{SO}_2$  emission controls, *Atmos. Chem. Phys.*, 16, 1603–1618, doi:10.5194/acp-16-1603-2016, 2016.
- Martin, R. V., Chance, K., Jacob, D. J., Kurosu, T. P., Spurr, R. J. D., Bucsela, E., Gleason, J. F., Palmer, P. I., Bey, I., Fiore, A. M., Li, Q., Yantosca, R. M., and Koelmeijer, R. B. A.: An improved retrieval of tropospheric nitrogen dioxide from GOME, *J. Geophys. Res.*, 107, 4437, doi:10.1029/2001jd001027, 2002.
- McDonald-Buller, E. C., Allen, D. T., Brown, N., Jacob, D. J., Jaffe, D., Kolb, C. E., Lefohn, A. S., Oltmans, S., Parrish, D. D., Yarwood, G., and Zhang, L.: Establishing policy relevant background (PRB) ozone concentrations in the United States, *Environ. Sci. Technol.*, 45, 9484–9497, doi:10.1021/es2022818, 2011.
- Mena-Carrasco, M., Tang, Y., Carmichael, G. R., Chai, T., Thongbongchoo, N., Campbell, J. E., Kulkarni, S., Horowitz, L., Vukovich, J., Avery, M., Brune, W., Dibb, J. E., Emmons, L., Flocke, F., Sachse, G. W., Tan, D., Shetter, R., Talbot, R. W., Streets, D. G., Frost, G., and Blake, D.: Improving regional ozone modeling through systematic evaluation of errors using the aircraft observations during the International Consortium for Atmospheric Research on Transport and Transformation, *J. Geophys. Res.*, 112, D12S19, doi:10.1029/2006jd007762, 2007.
- Müller, J. F. and Brasseur, G.: Sources of upper tropospheric  $\text{HO}_x$ : A three-dimensional study, *J. Geophys. Res.*, 104, 1705–1715, 1999.
- Murray, L. T., Jacob, D. J., Logan, J. A., Hudman, R. C., and Koshak, W. J.: Optimized regional and interannual variability of lightning in a global chemical transport model constrained by LIS/OTD satellite data, *J. Geophys. Res.*, 117, D20307, doi:10.1029/2012jd017934, 2012.
- NADP: National Atmospheric Deposition Program (NRSP-3) in: Illinois State Water Survey, Office, N. P., 2204 Griffith Dr., Champaign, IL 61820, 2007.
- NASA, U. G.: OMI/Aura Level 2 Nitrogen Dioxide ( $\text{NO}_2$ ) Trace Gas Column Data 1-Orbit subset Swath along CloudSat track 1-Orbit Swath  $13 \times 24$  km, version 003, Center, N. G. S. F., 2012.
- Nault, B. A., Garland, C., Pusede, S. E., Wooldridge, P. J., Ullmann, K., Hall, S. R., and Cohen, R. C.: Measurements of  $\text{CH}_3\text{O}_2\text{NO}_2$  in the upper troposphere, *Atmos. Meas. Tech.*, 8, 987–997, doi:10.5194/amt-8-987-2015, 2015.
- Nguyen, T. B., Crounse, J. D., Teng, A. P., St Clair, J. M., Paulot, F., Wolfe, G. M., and Wennberg, P. O.: Rapid deposition of oxidized biogenic compounds to a temperate forest, *P. Natl. Acad. Sci USA*, 112, 392–401, doi:10.1073/pnas.1418702112, 2015.
- Ott, L. E., Pickering, K. E., Stenchikov, G. L., Allen, D. J., DeCaria, A. J., Ridley, B., Lin, R.-F., Lang, S., and Tao, W.-K.: Production of lightning  $\text{NO}_x$  and its vertical distribution calculated from three-dimensional cloud-scale chemical transport model simulations, *J. Geophys. Res.*, 115, D04301, doi:10.1029/2009jd011880, 2010.
- Palmer, P. I., Jacob, D. J., Chance, K., Martin, R. V., Spurr, R. J. D., Kurosu, T. P., Bey, I., Yantosca, R., Fiore, A., and Li, Q.: Air mass factor formulation for spectroscopic measurements from satellites: Application to formaldehyde retrievals from the Global Ozone Monitoring Experiment, *J. Geophys. Res.*, 106, 14539, doi:10.1029/2000jd900772, 2001.
- Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kroll, J. H., Seinfeld, J. H., and Wennberg, P. O.: Isoprene photooxidation: new insights into the production of acids and organic nitrates, *Atmos. Chem. Phys.*, 9, 1479–1501, doi:10.5194/acp-9-1479-2009, 2009a.

- Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kurten, A., St Clair, J. M., Seinfeld, J. H., and Wennberg, P. O.: Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene, *Science*, 325, 730–733, doi:10.1126/Science.1172910, 2009b.
- Paulot, F., Jacob, D. J., Pinder, R. W., Bash, J. O., Travis, K., and Henze, D. K.: Ammonia emissions in the United States, European Union, and China derived by high-resolution inversion of ammonium wet deposition data: Interpretation with a new agricultural emissions inventory (MASAGE\_NH<sub>3</sub>), *J. Geophys. Res.-Atmos.*, 119, 4343–4364, doi:10.1002/2013jd021130, 2014.
- Peeters, J. and Müller, J. F.: HO(x) radical regeneration in isoprene oxidation via peroxy radical isomerisations. II: experimental evidence and global impact, *Phys. Chem. Chem. Phys.*, 12, 14227–14235, doi:10.1039/c0cp00811g, 2010.
- Peeters, J., Nguyen, T. L., and Vereecken, L.: HO<sub>x</sub> radical regeneration in the oxidation of isoprene, *Phys. Chem. Chem. Phys.*, 11, 5935–5939, doi:10.1039/b908511d, 2009.
- Peeters, J., Müller, J. F., Stavrou, T., and Nguyen, V. S.: Hydroxyl radical recycling in isoprene oxidation driven by hydrogen bonding and hydrogen tunneling: the upgraded LIM1 mechanism, *J. Phys. Chem. A*, 118, 8625–8643, doi:10.1021/jp5033146, 2014.
- Pollack, I. B., Lerner, B. M., and Ryerson, T. B.: Evaluation of ultraviolet light-emitting diodes for detection of atmospheric NO<sub>2</sub> by photolysis – chemiluminescence, *J. Atmos. Chem.*, 65, 111–125, doi:10.1007/s10874-011-9184-3, 2010.
- Prather, M. J. and Jacob, D. J.: A persistent imbalance in HO<sub>x</sub> and NO<sub>x</sub> photochemistry of the upper troposphere driven by deep tropical convection, *Geophys. Res. Lett.*, 24, 3189–3192, 1997.
- Reed, C., Evans, M. J., Di Carlo, P., Lee, J. D., and Carpenter, L. J.: Interferences in photolytic NO<sub>2</sub> measurements: explanation for an apparent missing oxidant?, *Atmos. Chem. Phys.*, 16, 4707–4724, doi:10.5194/acp-16-4707-2016, 2016.
- Reidmiller, D. R., Fiore, A. M., Jaffe, D. A., Bergmann, D., Cuvelier, C., Dentener, F. J., Duncan, B. N., Folberth, G., Gauss, M., Gong, S., Hess, P., Jonson, J. E., Keating, T., Lupu, A., Marmer, E., Park, R., Schultz, M. G., Shindell, D. T., Szopa, S., Vivanco, M. G., Wild, O., and Zuber, A.: The influence of foreign vs. North American emissions on surface ozone in the US, *Atmos. Chem. Phys.*, 9, 5027–5042, doi:10.5194/acp-9-5027-2009, 2009.
- Rickard, A. R., Salisbury, G., Monks, P. S., Lewis, A. C., Baugitte, S., Bandy, B. J., Clemmshaw, K. C., and Penkett, S. A.: Comparison of Measured Ozone Production Efficiencies in the Marine Boundary Layer at Two European Coastal Sites under Different Pollution Regimes, *J. Atmos. Chem.*, 43, 107–134, 2002.
- Russell, A. R., Perring, A. E., Valin, L. C., Bucala, E. J., Browne, E. C., Wooldridge, P. J., and Cohen, R. C.: A high spatial resolution retrieval of NO<sub>2</sub> column densities from OMI: method and evaluation, *Atmos. Chem. Phys.*, 11, 8543–8554, doi:10.5194/acp-11-8543-2011, 2011.
- Ryerson, T. B., Buhr, M. P., Frost, G. J., Goldan, P. D., Holloway, J. S., Hübler, G., Jobson, B. T., Kuster, W. C., McKeen, S. A., Parrish, D. D., Roberts, J. M., Sueper, D. T., Trainer, M., Williams, J., and Fehsenfeld, F. C.: Emissions lifetimes and ozone formation in power plant plumes, *J. Geophys. Res.*, 103, 22569–22583, 1998.
- Ryerson, T. B., Williams, E. J., and Fehsenfeld, F. C.: An efficient photolysis system for fast-response NO<sub>2</sub> measurements, *J. Geophys. Res.*, 105, 26447, doi:10.1029/2000jd900389, 2000.
- Sander, S. P., Abbatt, J., Barker, J. R., Burkholder, J. B., Friedl, R. R., Golden, D. M., Huie, R. E., Kolb, C. E., Kurylo, M. J., Moortgat, G. K., Orkin, V. L., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17, JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, 2011.
- Schultz, M. G., Jacob, D. J., Wang, Y., Logan, J. A., Atlas, E. L., Blake, D. R., Blake, N. J., Bradshaw, J. D., Browell, E. V., Fenn, M. A., Flocke, F., Gregory, G. L., Heikes, B. G., Sachse, G. W., Sandholm, S. T., Shetter, R. E., Singh, H. B., and Talbot, R. W.: On the origin of tropospheric ozone and NO<sub>x</sub> over the tropical South Pacific, *J. Geophys. Res.*, 104, 5829, doi:10.1029/98jd02309, 1999.
- Shetter, R. E. and Muller, M.: Photolysis frequency measurements using actinic flux spectroradiometry during the PEM-Tropics mission: Instrumentation description and some results, *J. Geophys. Res.*, 104, 5647–5661, doi:10.1029/98JD01381, 1999.
- Singh, H. B., Brune, W. H., Crawford, J. H., Jacob, D. J., and Russell, P. B.: Overview of the summer 2004 Intercontinental Chemical Transport Experiment–North America (INTEX-A), *J. Geophys. Res.*, 111, doi:10.1029/2006jd007905, 2006.
- Squire, O. J., Archibald, A. T., Griffiths, P. T., Jenkin, M. E., Smith, D., and Pyle, J. A.: Influence of isoprene chemical mechanism on modelled changes in tropospheric ozone due to climate and land use over the 21st century, *Atmos. Chem. Phys.*, 15, 5123–5143, doi:10.5194/acp-15-5123-2015, 2015.
- St. Clair, J. M., McCabe, D. C., Crounse, J. D., Steiner, U., and Wennberg, P. O.: Chemical ionization tandem mass spectrometer for the in situ measurement of methyl hydrogen peroxide, *Rev. Sci. Instrum.*, 81, 094102, doi:10.1063/1.3480552, 2010.
- St. Clair, J. M., Rivera-Rios, J. C., Crounse, J. D., Knap, H. C., Bates, K. H., Teng, A. P., Jorgensen, S., Kjaergaard, H. G., Keutsch, F. N., and Wennberg, P. O.: Kinetics and Products of the Reaction of the First-Generation Isoprene Hydroxy Hydroperoxide (ISOPOOH) with OH, *J. Phys. Chem. A*, 120, 1441–1451, doi:10.1021/acs.jpca.5b06532, 2015.
- Stavrou, T., Peeters, J., and Müller, J.-F.: Improved global modelling of HO<sub>x</sub> recycling in isoprene oxidation: evaluation against the GABRIEL and INTEX-A aircraft campaign measurements, *Atmos. Chem. Phys.*, 10, 9863–9878, doi:10.5194/acp-10-9863-2010, 2010.
- Toon, O. B., Maring, H., Dibb, J., Ferrare, R., Jacob, D. J., Jensen, E. J., Luo, Z. J., Mace, G. G., Pan, L. L., Pfister, L., and Rosenlof, K. H.: Planning, implementation, and scientific goals of the Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC<sup>4</sup>RS) field mission, *J. Geophys. Res.-Atmos.*, 121, 4967–5009, doi:10.1002/2015JD024297, 2016.
- Trainer, M., Parrish, D. D., Buhr, M. P., Norton, R. B., Fehsenfeld, F. C., Anlauf, K. G., Bottenheim, J. W., Tang, Y. Z., Wiebe, H. A., Roberts, J. M., Tanner, R. L., Newman, L., Bowersox, C., Meagher, J. F., Olszyna, K. J., Rodgers, M. O., Wang, T., Berresheim, H., Demerjian, K. L., and Roychowdhury, U. K.: Correlation of ozone with NO<sub>y</sub> in photochemically aged air, *J. Geophys. Res.*, 98, 2917–2925, 1993.

- Trainer, M., Parrish, D. D., Goldan, P. D., Roberts, J., and Fehsenfeld, F. C.: Review of observation-based analysis of the regional factors influencing ozone concentrations, *Atmos. Environ.*, 34, 2045–2061, 2000.
- Vinken, G. C. M., Boersma, K. F., Maasakkers, J. D., Adon, M., and Martin, R. V.: Worldwide biogenic soil  $\text{NO}_x$  emissions inferred from OMI  $\text{NO}_2$  observations, *Atmos. Chem. Phys.*, 14, 10363–10381, doi:10.5194/acp-14-10363-2014, 2014.
- Walker, T. W.: Applications of Adjoint Modeling in Chemical Composition: Studies of Tropospheric Ozone at Middle and High Northern Latitudes, Graduate Department of Physics, University of Toronto, 2014.
- Wang, Y., Jacob, D. J., and Logan, J. A.: Global simulation of tropospheric  $\text{O}_3$ - $\text{NO}_x$ -hydrocarbon chemistry, 1. Model formulation, *J. Geophys. Res.*, 103, 10727–10755, 1998.
- Wesely, M. L.: Parameterization of Surface Resistances to Gaseous Dry Deposition in Regional-Scale Numerical-Models, *Atmos. Environ.*, 23, 1293–1304, doi:10.1016/0004-6981(89)90153-4, 1989.
- Wolfe, G. M., Crounse, J. D., Parrish, J. D., St Clair, J. M., Beaver, M. R., Paulot, F., Yoon, T. P., Wennberg, P. O., and Keutsch, F. N.: Photolysis, OH reactivity and ozone reactivity of a proxy for isoprene-derived hydroperoxyenals (HPALDs), *Phys. Chem. Chem. Phys.*, 14, 7276–7286, doi:10.1039/c2cp40388a, 2012.
- Wolfe, G. M., Hanisco, T. F., Arkinson, H. L., Bui, T. P., Crounse, J. D., Dean-Day, J., Goldstein, A., Guenther, A., Hall, S. R., Huey, G., Jacob, D. J., Karl, T., Kim, P. S., Liu, X., Marvin, M. R., Mikoviny, T., Misztal, P. K., Nguyen, T. B., Peischl, J., Pollack, I., Ryerson, T., St. Clair, J. M., Teng, A., Travis, K. R., Ullman, K., Wennberg, P. O., and Wisthaler, A.: Quantifying Sources and Sinks of Reactive Gases in the Lower Atmosphere using Airborne Flux Observations, *Geophys. Res. Lett.*, 42, 8231–8240, doi:10.1002/2015GL065839, 2015.
- Xie, Y., Paulot, F., Carter, W. P. L., Nolte, C. G., Luecken, D. J., Hutzell, W. T., Wennberg, P. O., Cohen, R. C., and Pinder, R. W.: Understanding the impact of recent advances in isoprene photooxidation on simulations of regional air quality, *Atmos. Chem. Phys.*, 13, 8439–8455, doi:10.5194/acp-13-8439-2013, 2013.
- Yu, K., Jacob, D. J., Fisher, J. A., Kim, P. S., Marais, E. A., Miller, C. C., Travis, K. R., Zhu, L., Yantosca, R. M., Sulprizio, M. P., Cohen, R. C., Dibb, J. E., Fried, A., Mikoviny, T., Ryerson, T. B., Wennberg, P. O., and Wisthaler, A.: Sensitivity to grid resolution in the ability of a chemical transport model to simulate observed oxidant chemistry under high-isoprene conditions, *Atmos. Chem. Phys.*, 16, 4369–4378, doi:10.5194/acp-16-4369-2016, 2016.
- Zaveri, R. A.: Ozone production efficiency and  $\text{NO}_x$  depletion in an urban plume: Interpretation of field observations and implications for evaluating  $\text{O}_3$ - $\text{NO}_x$ -VOC sensitivity, *J. Geophys. Res.*, 108, 4436, doi:10.1029/2002jd003144, 2003.
- Zhang, L., Jacob, D. J., Yue, X., Downey, N. V., Wood, D. A., and Blewitt, D.: Sources contributing to background surface ozone in the US Intermountain West, *Atmos. Chem. Phys.*, 14, 5295–5309, doi:10.5194/acp-14-5295-2014, 2014.
- Zhou, X., Ye, C., Pu, D., Stutz, J., Festa, J., Spolaor, M., Weinheimer, A. J., Campos, T. L., Haggerty, J. A., Cantrell, C. A., Mauldin, L., Guenther, A. B., Hornbrook, R. S., Apel, E. C., and Jensen, J. B.: Tropospheric HONO Distribution and Chemistry in the Southeastern US, American Geophysical Union, Fall Meeting 2014, abstract #A31J-08, 2014.
- Zhu, L., Jacob, D. J., Kim, P. S., Fisher, J. A., Yu, K., Travis, K. R., Mickley, L. J., Yantosca, R. M., Sulprizio, M. P., De Smedt, I., Gonzalez Abad, G., Chance, K., Li, C., Ferrare, R., Fried, A., Hair, J. W., Hanisco, T. F., Richter, D., Scarino, A. J., Walega, J., Weibring, P., and Wolfe, G. M.: Observing atmospheric formaldehyde (HCHO) from space: validation and intercomparison of six retrievals from four satellites (OMI, GOME2A, GOME2B, OMPS) with SEAC<sup>4</sup>RS aircraft observations over the Southeast US, *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2016-162, in review, 2016.