

## Application of OMI observations to a space-based indicator of NO<sub>x</sub> and VOC controls on surface ozone formation

Bryan N. Duncan<sup>a,\*</sup>, Yasuko Yoshida<sup>a,b</sup>, Jennifer R. Olson<sup>c</sup>, Sanford Sillman<sup>d</sup>, Randall V. Martin<sup>e,f</sup>, Lok Lamsal<sup>e</sup>, Yongtao Hu<sup>g</sup>, Kenneth E. Pickering<sup>a</sup>, Christian Retscher<sup>a,b</sup>, Dale J. Allen<sup>h</sup>, James H. Crawford<sup>c</sup>

<sup>a</sup>Atmospheric Chemistry and Dynamics Branch, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA

<sup>b</sup>Goddard Earth Sciences and Technology Center, University of Maryland, Baltimore, MD, USA

<sup>c</sup>Chemistry and Dynamics Branch, NASA Langley Research Center, Hampton, VA, USA

<sup>d</sup>Department of Atmospheric, Oceanic and Space Sciences, University of Michigan, Ann Arbor, MI, USA

<sup>e</sup>Department of Physics and Atmospheric Science, Dalhousie University, Halifax, NS, Canada

<sup>f</sup>Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA

<sup>g</sup>School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA, USA

<sup>h</sup>Department of Atmospheric and Oceanic Sciences, University of Maryland, College Park, MD, USA

### ARTICLE INFO

#### Article history:

Received 13 January 2010

Received in revised form

10 March 2010

Accepted 12 March 2010

#### Keywords:

Surface ozone

Air quality indicator

OMI

HCHO

NO<sub>2</sub>

### ABSTRACT

We investigated variations in the relative sensitivity of surface ozone formation in summer to precursor species concentrations of volatile organic compounds (VOCs) and nitrogen oxides (NO<sub>x</sub>) as inferred from the ratio of the tropospheric columns of formaldehyde to nitrogen dioxide (the "Ratio") from the Aura Ozone Monitoring Instrument (OMI). Our modeling study suggests that ozone formation decreases with reductions in VOCs at Ratios < 1 and NO<sub>x</sub> at Ratios > 2; both NO<sub>x</sub> and VOC reductions may decrease ozone formation for Ratios between 1 and 2. Using this criteria, the OMI data indicate that ozone formation became: 1. more sensitive to NO<sub>x</sub> over most of the United States from 2005 to 2007 because of the substantial decrease in NO<sub>x</sub> emissions, primarily from stationary sources, and the concomitant decrease in the tropospheric column of NO<sub>2</sub>, and 2. more sensitive to NO<sub>x</sub> with increasing temperature, in part because emissions of highly reactive, biogenic isoprene increase with temperature, thus increasing the total VOC reactivity. In cities with relatively low isoprene emissions (e.g., Chicago), the data clearly indicate that ozone formation became more sensitive to NO<sub>x</sub> from 2005 to 2007. In cities with relatively high isoprene emissions (e.g., Atlanta), we found that the increase in the Ratio due to decreasing NO<sub>x</sub> emissions was not obvious as this signal was convolved with variations in the Ratio associated with the temperature dependence of isoprene emissions and, consequently, the formaldehyde concentration.

Published by Elsevier Ltd.

### 1. Introduction

In polluted areas, unhealthy levels of ozone form from a complex series of reactions involving nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) and volatile organic compounds (VOCs) in the presence of sunlight (Haagen-Smit, 1952). Therefore, ozone formation can be controlled by reducing either emissions of NO<sub>x</sub> or VOCs, depending on which is in excess (Dodge, 1987). These two states are commonly referred to as NO<sub>x</sub>-limited and VOC-limited photochemical regimes. However, the VOC-limited regime is better described as the radical-limited regime, since ozone production first requires

the formation of the hydroxyl radical (OH) through the photolysis of ozone itself, and its subsequent oxidation of VOCs, forming peroxy radicals (e.g., Kleinman, 1994). In order to determine the regime, one must estimate the total reactivity with OH of the myriad of VOCs in the urban atmosphere, as reaction with OH is often the rate-limiting step of many oxidation pathways (Chameides et al., 1992). In the absence of such information, one can use the formaldehyde (HCHO) concentration as a proxy for VOC reactivity as it is a short-lived oxidation product of many VOCs and is positively correlated with peroxy radicals (Sillman, 1995). Sillman used correlations between the afternoon concentrations of various trace gases (e.g., HCHO and total reactive nitrogen (NO<sub>y</sub>)) to determine chemical sensitivity, which is considered NO<sub>x</sub>-limited when the ratio of HCHO to NO<sub>y</sub> is high and radical-limited when the ratio is low; in this way, HCHO and NO<sub>y</sub> are 'indicator species'.

\* Corresponding author. Tel.: +1 301 614 5994; fax: +1 301 614 5903.

E-mail address: [Bryan.N.Duncan@nasa.gov](mailto:Bryan.N.Duncan@nasa.gov) (B.N. Duncan).

Martin et al. (2004a) extended the technique of Sillman to space-based observations, using the ratio of the tropospheric columns of HCHO and nitrogen dioxide ( $\text{NO}_2$ ) (hereafter referred to as “the Ratio”) from the Global Ozone Monitoring Experiment (GOME) instrument to show that this diagnosis of ozone sensitivity is consistent with current understanding of surface photochemistry. The Ratio is an indicator of surface photochemistry as the bulk of the columns of both species are within the planetary boundary layer (PBL) over polluted regions and as the columns are closely related to  $\text{NO}_x$  and VOC emissions due to their short lifetimes (Abbot et al., 2003; Martin et al., 2003, 2004b). Satellite measurements of global tropospheric HCHO and  $\text{NO}_2$  columns have been widely used to infer surface emissions of VOCs and  $\text{NO}_x$ , respectively (e.g., Martin et al., 2003; Millet et al., 2006).

The Ratio reflects the sensitivity of local ozone production rather than the local ozone concentration. Using a numerical model, Martin et al. (2004a) estimated that the transition between the radical- and  $\text{NO}_x$ -limited regimes during summer occurs when the Ratio is  $\sim 1$ . The 3-d models from Sillman also show  $\text{NO}_x$ -limited conditions for Ratios  $> 1$ . However, local ozone production is also influenced by other factors, such as water vapor concentrations (e.g., Kleinman et al., 2005) and meteorological variables, so that the transition estimated by Martin et al. (2004a) would be expected to vary both geographically and temporally.

In this manuscript, we examine the chemical limitation of local ozone formation to its ambient precursor species concentrations in the United States (U.S.) for summer from 2005 to 2007 as inferred from the ratio of the tropospheric columns of HCHO to  $\text{NO}_2$  from the Ozone Monitoring Instrument (OMI). The OMI has a finer horizontal resolution ( $\sim 13 \times 24 \text{ km}^2$  at nadir) than the GOME instrument ( $\sim 40 \times 320 \text{ km}^2$ ), so the OMI provides information on spatial gradients, such as urban–rural ones, that other instruments cannot.

## 2. The OMI observations

The OMI is an UV/Vis imaging spectrometer on the Aura satellite, which crosses the equator at about 1338 local time. The OMI uses spectral windows from 405 to 465 nm for  $\text{NO}_2$  and from 327.5 to 356.5 nm for HCHO. We use tropospheric columns of  $\text{NO}_2$  from the Derivation of OMI tropospheric  $\text{NO}_2$  (DOMINO) product (Boersma et al., 2007) to which Lamsal et al. (2010) applied a stripe correction and  $\text{NO}_2$  profiles from a 3-d model of chemistry and transport (CTM), GEOS-Chem. We gridded the data to a horizontal resolution of  $0.25^\circ$  latitude by  $0.25^\circ$  longitude, using only data with cloud radiance fraction (Boersma et al., 2004) not exceeding 30%. The overall error in the vertical, tropospheric  $\text{NO}_2$  column data is 10–40% (Boersma et al., 2007). Comparisons with ground-based and in situ data suggest that the OMI tropospheric  $\text{NO}_2$  columns are biased low in summer by  $\sim 5\%$  (Lamsal et al., 2010).

The specifics of the HCHO algorithm are described in Chance (2002) and Kurosu et al. (2004). We use the level-2 gridded product (v003), which is a vertical column with a horizontal resolution of  $0.25^\circ$  latitude by  $0.25^\circ$  longitude. Millet et al. (2006) estimated that the overall error in the vertical, tropospheric HCHO column data is 25–31%. There is currently no estimate of the bias of OMI HCHO as there are sparse ground-based and in situ observations with which to compare.

Assuming that the overall errors in the OMI HCHO and  $\text{NO}_2$  data are uncorrelated, the combined uncertainty in the Ratio is 27–51% with a mean of 38% and half of the data points falling between 32 and 40%. However, uncertainties in clouds, aerosol, and surface reflectivity similarly affect the retrievals of HCHO and  $\text{NO}_2$ , so these

errors largely cancel in their ratio (Martin et al., 2004a). Therefore, this range of errors should be taken as an upper limit. Errors associated with the removal of the stratospheric portion of the total column of  $\text{NO}_2$  tend to be least important in polluted areas as the majority of the total column is in the PBL.

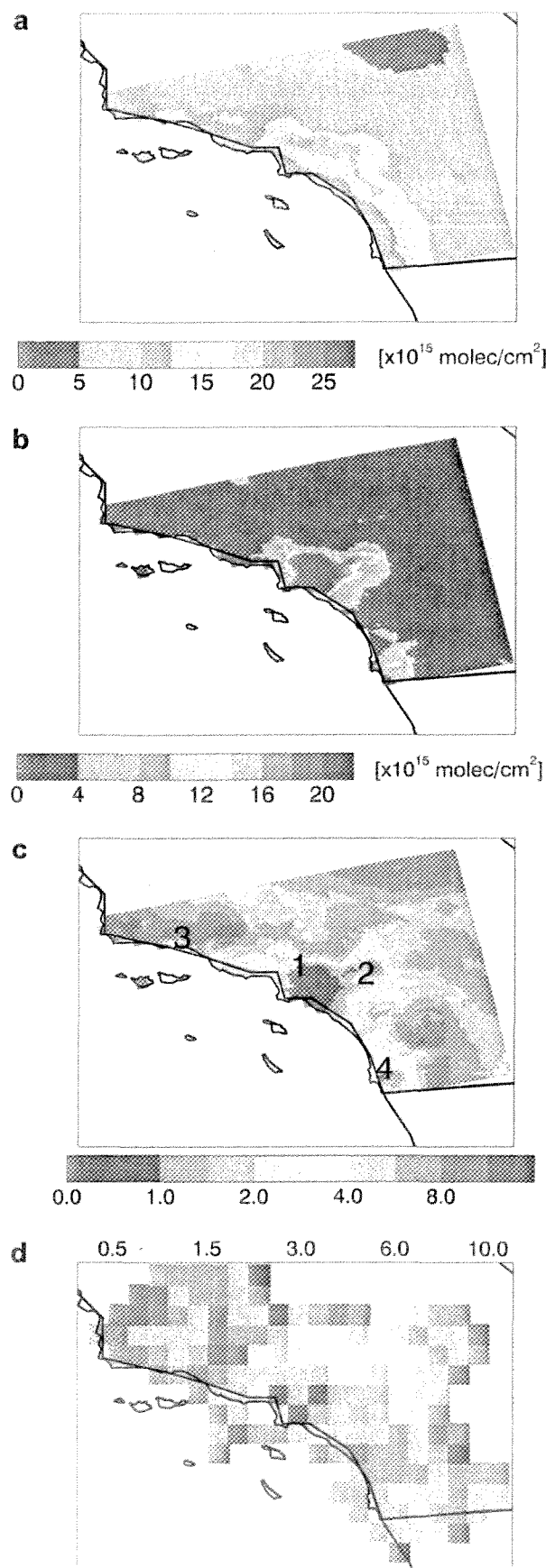
## 3. A modeling perspective of HCHO/ $\text{NO}_2$ as an air quality indicator

In this section, we present the results of a modeling study, discussing how to use the Ratio as an air quality indicator of the sensitivity of the instantaneous ozone production rate ( $\text{PO}_3$ ). To calculate  $\text{PO}_3$ , we used trace gas concentrations and other parameters from the Community Multiscale Air Quality Modeling System (CMAQ) model (Byun and Schere, 2006) as input to the NASA Langley Research Center (LaRC) time-dependent photochemical box model (Crawford et al., 1999; Olson et al., 2006). The box model was used to calculate information (such as some radical concentrations) that was not saved in the CMAQ runs to diagnose the  $\text{PO}_3$ . The CMAQ simulation covered southern California with a horizontal grid of  $4 \times 4 \text{ km}^2$  for July 1–4, 2007. The SAPRC-99 chemical mechanism (Carter, 2000) was used. The emissions inventory was projected from the U.S. National Emissions Inventory of 2002 (<http://www.epa.gov/ttn/chief/net/2002inventory.html>) to year 2007 using growth factors from the Economic Growth Analysis System (<http://www.epa.gov/ttnecas1/gfmodels.html>) and control factors for the federal control strategies that were in place in 2007 and integrated with monitored hourly  $\text{NO}_x$  and  $\text{SO}_2$  emissions for the Electricity Generating Utility sources from the U.S. EPA's Continuous Emissions Monitoring database (<http://camddataandmaps.epa.gov/gdm/index.cfm?fuseaction=emissions.prepacksmoke>). The predicted hourly ozone at the 4-km domain compared well to surface observations with mean normalized bias and error as 16.7% and 24.9% (with a 40 ppbv cutoff), respectively. As upper tropospheric  $\text{NO}_2$  is typically not well simulated in CMAQ (Napelenok et al., 2008), we replaced the free tropospheric  $\text{NO}_2$  and HCHO concentrations output from CMAQ with those from the NASA Global Modeling Initiative's (GMI) combined stratosphere–troposphere CTM (Duncan et al., 2007).

Fig. 1a–c shows the model's tropospheric columns over land of HCHO and  $\text{NO}_2$ , and Ratios, respectively. The spatial extent and magnitude of the July-average 2007 Ratios from OMI (Fig. 1d) compare reasonably well with the 4-day mean Ratios from CMAQ (Fig. 1c) despite the two different time periods.

Fig. 2a shows the average Ratio in the PBL from the CMAQ simulation versus the  $\text{PO}_3$  near the Aura overpass time for one day. About 32% of the total net production occurs at Ratios  $> 5$  (74% of horizontal domain), with the rest (68%) occurring at Ratios  $< 5$  (26% of horizontal domain). The highest  $\text{PO}_3$  occurs at Ratios  $< 3$ . Therefore, most net ozone production occurs in a geographically small portion of the model domain where Ratios are relatively low and  $\text{NO}_x$  emissions are high.

Fig. 2b and c shows the  $\text{PO}_3$  as a function of HCHO and  $\text{NO}_2$ , respectively, in the PBL. While it is well known that the  $\text{PO}_3$  increases with the ambient  $\text{NO}_x$  concentration (e.g., Liu et al., 1987; Lin et al., 1988), the  $\text{PO}_3$  also increases with increasing HCHO concentration partially due to the collocation of anthropogenic sources of  $\text{NO}_x$  and VOCs and the predominance of biogenic sources of VOCs along the populated coast. The  $\text{PO}_3$  is lower, approaching zero, at high concentrations of  $\text{NO}_2$  (Fig. 2c) because of the loss of  $\text{NO}_x$  to nitric acid and the titration of ozone by NO. In general,  $\text{PO}_3$  typically declines at  $\text{NO}_x$  concentrations  $> 1$  ppbv, depending on VOC composition and concentration, and other factors (Lin et al., 1988).



### 3.1. How representative is the tropospheric Ratio of the $\text{PO}_3$ within the PBL?

The Ratio is most useful when the majority of the tropospheric column resides in the PBL so that it is representative of ozone photochemistry near the surface. In this study, we used model HCHO and  $\text{NO}_2$  when at least 70% of the tropospheric columns of both gases were in the PBL; we refer to this quantity as %PBL. In Fig. 2, for instance, we used >75% of the columns over land in our analysis. However, there is typically less variability in these trace gases within the free troposphere (FT) than in the PBL, so that the Ratio should provide useful information in many cases even when % PBL is <70%.

For the entire CMAQ domain, the correlation was poor between the tropospheric Ratio and the PBL Ratio ( $R^2 = 0.34$ ) as the tropospheric column was not representative of the PBL column in many areas, particularly over the ocean and in nonpolluted regions (Martin et al., 2003, 2004b). Fig. 3 shows the PBL Ratios versus the tropospheric Ratios for those points over land with %PBL >70% for both HCHO and  $\text{NO}_2$ . The tropospheric Ratios are well correlated with the PBL Ratios ( $R^2 = 0.99$ ) and are almost always higher than the PBL Ratios as methane oxidation is a relatively major source of HCHO in the FT. Though this criterion of %PBL >70% limits us to a smaller geographical area, this area has a relatively high  $\text{PO}_3$  as discussed above.

We used the GMI CTM to estimate typical values of %PBL in summer over the U.S. This simulation has a relatively coarse horizontal resolution ( $2^\circ$  latitude  $\times$   $2.5^\circ$  longitude), so that the strong gradients in  $\text{NO}_2$  and, consequently, the wide range of Ratios observed by OMI are not captured. Nevertheless, the GMI simulation provides us with a general picture of the spatial and temporal variability of %PBL for three summers, 2005–2007. On average, % PBL was ~60–90% for HCHO in the eastern U.S., with the highest values in regions with high isoprene emissions. However, there was more variability (~40–90%) in the western U.S., with the highest values in portions of California (e.g., the Central Valley and Los Angeles (LA)) where isoprene emissions were relatively high. In the eastern U.S., the highest %PBL for  $\text{NO}_2$  (~90%) occurred where surface emissions were highest, though most values were >70%. In the western U.S., %PBL typically ranged from 50 to 90%, with the highest values in polluted areas.

Lightning is an episodic source of  $\text{NO}_x$  in the FT, particularly in the eastern U.S. (e.g., Hudman et al., 2007). We used GMI CTM sensitivity simulations with and without lightning (Allen et al., submitted for publication) to assess the relative contribution of lightning in the FT to the tropospheric  $\text{NO}_2$  column on average during summer. This contribution is high in rural areas and is small in more polluted regions. For instance, it is typically <10% in the polluted eastern U.S. and 10–30% in the central U.S., similar to the findings of Martin et al. (2007).

Of the portion of the tropospheric column within the FT, lightning contributes from ~25 to 70% with the lower contributions over polluted regions in the eastern U.S. and much of California. In these polluted regions, up to 65% of the  $\text{NO}_2$  column in the FT is associated with pollution lofted from the PBL (e.g., by convection) and a minor contribution from aircraft emissions. Therefore, the relative contribution of  $\text{NO}_2$  from lightning to the column in the FT is smaller than the  $\text{NO}_2$  lofted from the PBL in polluted regions. The converse is true in nonpolluted regions.

Fig. 1. Four-day mean (July 1–4, 2007) for tropospheric a) HCHO columns ( $\times 10^{15}$  molec  $\text{cm}^{-2}$ ; to 200 hPa), b)  $\text{NO}_2$  columns ( $\times 10^{15}$  molec  $\text{cm}^{-2}$ ), and c) Ratios from the CMAQ simulation near the Aura overpass time. d) OMI Ratios for July 2007. White areas in d. indicate locations where HCHO data are below the detection limit and/or  $\text{NO}_2$  data are  $<1.5 \times 10^{15}$  molec  $\text{cm}^{-2}$ .

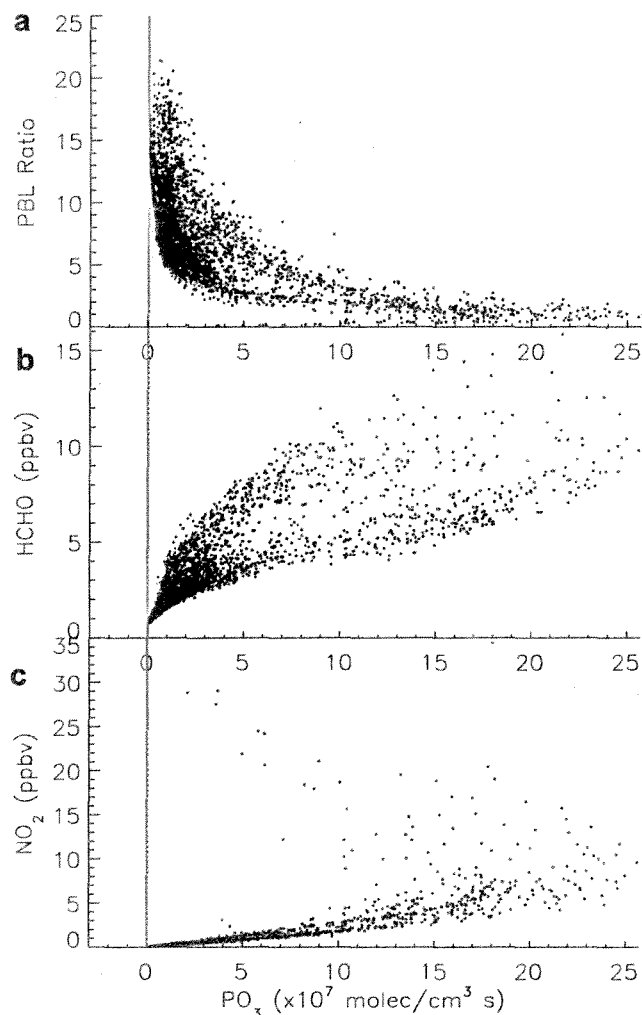


Fig. 2. The PBL  $\text{PO}_3$  ( $\times 10^7 \text{ molec cm}^{-3} \text{ s}^{-1}$ ) versus a) PBL Ratio, b) PBL HCHO (ppbv), and c) PBL  $\text{NO}_2$  (ppbv) from the CMAQ simulation. The vertical line indicates where  $\text{PO}_3 = 0$ .

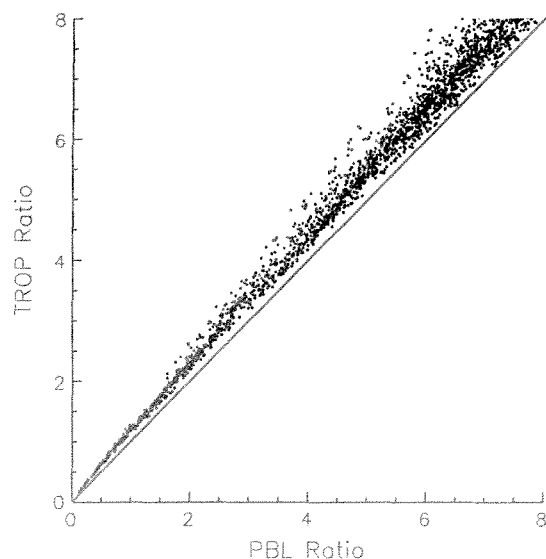


Fig. 3. PBL Ratio versus tropospheric Ratio from the CMAQ simulation. The line is 1:1.

As discussed above, we are interested in the Ratio representing the  $\text{PO}_3$  in the PBL. Fortunately, the partitioning of  $\text{NO}_x$  into  $\text{NO}_2$  and  $\text{NO}$  favors  $\text{NO}_2$  near the surface ( $\sim 90\%$ ), but is less ( $< 50\%$ ) at higher altitudes where most  $\text{NO}$  from lightning is emitted. Consequently, the contributions of  $\text{NO}_x$  1. from lightning, and 2. lofted to the FT, to the tropospheric  $\text{NO}_2$  column are somewhat muted. Filtering model output when %PBL for either HCHO or  $\text{NO}_2$  is  $< 70\%$  removes columns significantly impacted by deep convection and lightning.

### 3.2. The transition between regimes

Martin et al. (2004a) estimated that the transition between the  $\text{NO}_x$ - and radical-limited regimes occurs when the tropospheric Ratio is  $\sim 1$ , using the GEOS-Chem CTM with  $2.5^\circ$  longitude  $\times$   $2^\circ$  latitude horizontal resolution. We found that this transition occurs over a range of values, using the CMAQ model with higher spatial resolution (i.e.,  $4 \times 4 \text{ km}^2$ ). We used the ratio of the formation of  $\text{H}_2\text{O}_2$  and organic peroxides (i.e., a radical sink) to the formation of  $\text{HNO}_3$  (i.e., a  $\text{NO}_x$  sink) as an indicator of the chemical sensitivity of the  $\text{PO}_3$ ; we refer to this quantity as  $L_{\text{HO}_x}/L_{\text{NO}_x}$ . These formation rates were calculated using species concentrations from CMAQ, except for the formation of higher organic peroxides which involves species not retained in the CMAQ run. These values were obtained using the LaRC box model, as described earlier.  $L_{\text{HO}_x}/L_{\text{NO}_x}$  has been shown to correlate strongly with the  $\text{NO}_x$ -VOC sensitivity of the  $\text{PO}_3$ , with  $\text{NO}_x$ -limited conditions corresponding to high  $L_{\text{HO}_x}/L_{\text{NO}_x}$  (Sillman et al., 1990; Kleinman, 1994). We assume that the transition in the Ratio occurs when  $L_{\text{HO}_x}/L_{\text{NO}_x}$  is one. Fig. 4

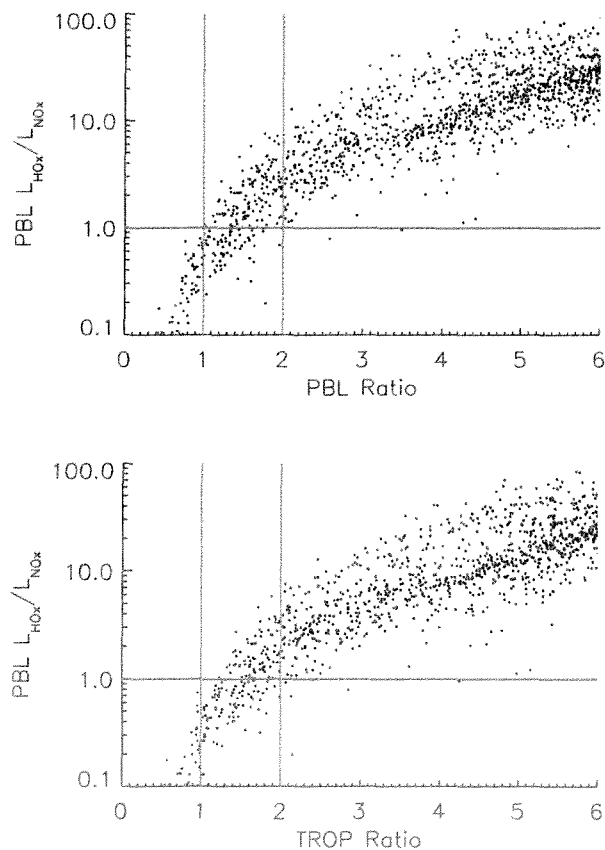


Fig. 4. Modeled PBL Ratio versus PBL  $L_{\text{HO}_x}/L_{\text{NO}_x}$  (top) and tropospheric Ratio versus PBL  $L_{\text{HO}_x}/L_{\text{NO}_x}$  (bottom). The horizontal line indicates where  $L_{\text{HO}_x}/L_{\text{NO}_x} = 1$  and the vertical lines indicate the range of Ratios when  $L_{\text{HO}_x}/L_{\text{NO}_x} = 1$ .

shows the PBL  $L_{\text{HCHO}}/L_{\text{NO}_x}$  versus the PBL Ratio for the CMAQ domain. The transition occurs over a range of PBL Ratios,  $\sim 1$ – $2$ . The range of tropospheric Ratios for the transition is similar when comparing to the PBL  $L_{\text{HCHO}}/L_{\text{NO}_x}$  (Fig. 4). Our approach needs to be applied to other urban areas in order to know if the transition is regionally dependent.

We performed a similar analysis on a second CMAQ simulation for the same time period, but with  $36 \times 36 \text{ km}^2$  for the full continental U.S. In general, we found similar results as in the run with the finer horizontal resolution, though the transition between regimes occurred over a range of both higher PBL and tropospheric Ratios,  $\sim 1.5$ – $2.5$ . Of the model boxes used in the analysis, only 4% had Ratios  $<3$  due to spatial averaging which effectively dilutes sharp gradients in  $\text{NO}_x$  emissions. In contrast, 78% of the model boxes used in the analysis of the simulation with finer resolution had Ratios  $<3$ ; there are  $81 \times 4 \times 4 \text{ km}^2$  boxes within one  $36 \times 36 \text{ km}^2$  box. Therefore, the results of the finer resolution simulation are more statistically significant.

The modeling study indicates that radical-limited conditions should occur when the OMI tropospheric Ratio is  $<1$  and  $\text{NO}_x$ -limited conditions should occur when the Ratio is  $>2$ . The Ratios between 1 and 2 reflect the transition between regimes, where both reductions in  $\text{NO}_x$  and VOCs may reduce the  $\text{PO}_3$ . This transition regime is relatively broad as the  $\text{PO}_3$  is also a function of other variables, such as the water vapor concentration, sunlight, etc.

It is well known that many urban areas start the day in the radical-limited or transition regime because of low levels of sunlight, moving to the  $\text{NO}_x$ -limited regime by late morning or early afternoon (e.g., Milford et al., 1989, 1994). Fig. 5 shows the hourly tropospheric Ratios from the CMAQ simulation for four cities in southern California. The Ratios are typically  $<1$  in the more polluted regions near sunrise, rising slowly into the transition regime by mid-morning, except in downtown LA which only enters the transition regime for a short time in early afternoon. Only Santa Barbara is clearly in the  $\text{NO}_x$ -limited regime for most of the day. The total ozone produced each day at any given location may have occurred under one, two, or all three photochemical regimes. Therefore, the use of OMI data as a space-based indicator of the  $\text{PO}_3$  is currently limited by having only one daylight overpass each day.

#### 4. OMI HCHO/ $\text{NO}_2$

Fig. 6 shows the average tropospheric columns of HCHO and  $\text{NO}_2$ , and Ratios, respectively, in August 2006. Most of the U.S. was clearly  $\text{NO}_x$ -limited as the Ratios were  $>3$ . In the southeastern U.S., Ratios were  $>6$  as natural VOCs (e.g., isoprene) contribute

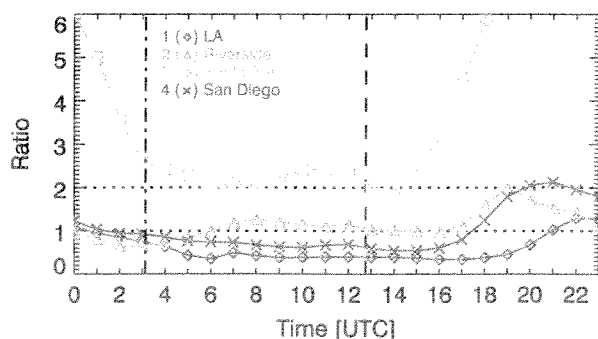


Fig. 5. Hourly tropospheric Ratios as a 4-day mean (July 1–4, 2007) in the CMAQ simulation for four cities (locations shown in Fig. 1c). The area between the dotted horizontal lines represents the transition regime. The dashed vertical line represents local sunrise and the dashed-dotted vertical line represents sunset.

significantly to total VOC reactivity (Chameides et al., 1992). The importance of isoprene generally decreases with increasing latitude in the eastern U.S. because of the spatial distribution of high isoprene emitting vegetation and the temperature dependence of isoprene emissions (Guenther et al., 2006). Parts of the Midwest and northeastern U.S. had Ratios  $<4$ , although heavily forested regions in Massachusetts, Pennsylvania and Michigan had Ratios comparable to the southeastern U.S. In all regions, the lowest Ratios were found in urban centers with higher Ratios in the surrounding suburbs. The western U.S. typically had lower Ratios than the eastern U.S. in both rural and urban areas because of lower isoprene emissions. Overall, the OMI Ratios have similar spatial distributions as the GOME ones presented in Martin et al. (2004a).

Fig. 7 shows the range of monthly tropospheric Ratios during our study period. Most cities and regions exhibited a wide range of Ratios. In the northwestern U.S., Seattle had minimum Ratios  $<1$  and Portland had Ratios  $<2$ . In the southwestern U.S., Phoenix, San Francisco and LA had rather low minimum Ratios ( $<2$ ), with the lowest in LA ( $<1$ ). In the Midwest, Chicago and Detroit had minimum Ratios from 1 to 2, and other urban areas (e.g., St. Louis and Indianapolis) from 1 to 4. In the northeastern U.S., New York City (NYC) had minimum Ratios from 0.5 to 1.5, while other urban areas had Ratios from 1 to 3. In the southeastern U.S., all urban centers had Ratios  $>3$ . Almost all areas in the U.S., including urban centers, had maximum Ratios  $>2$ , except for downtown LA.

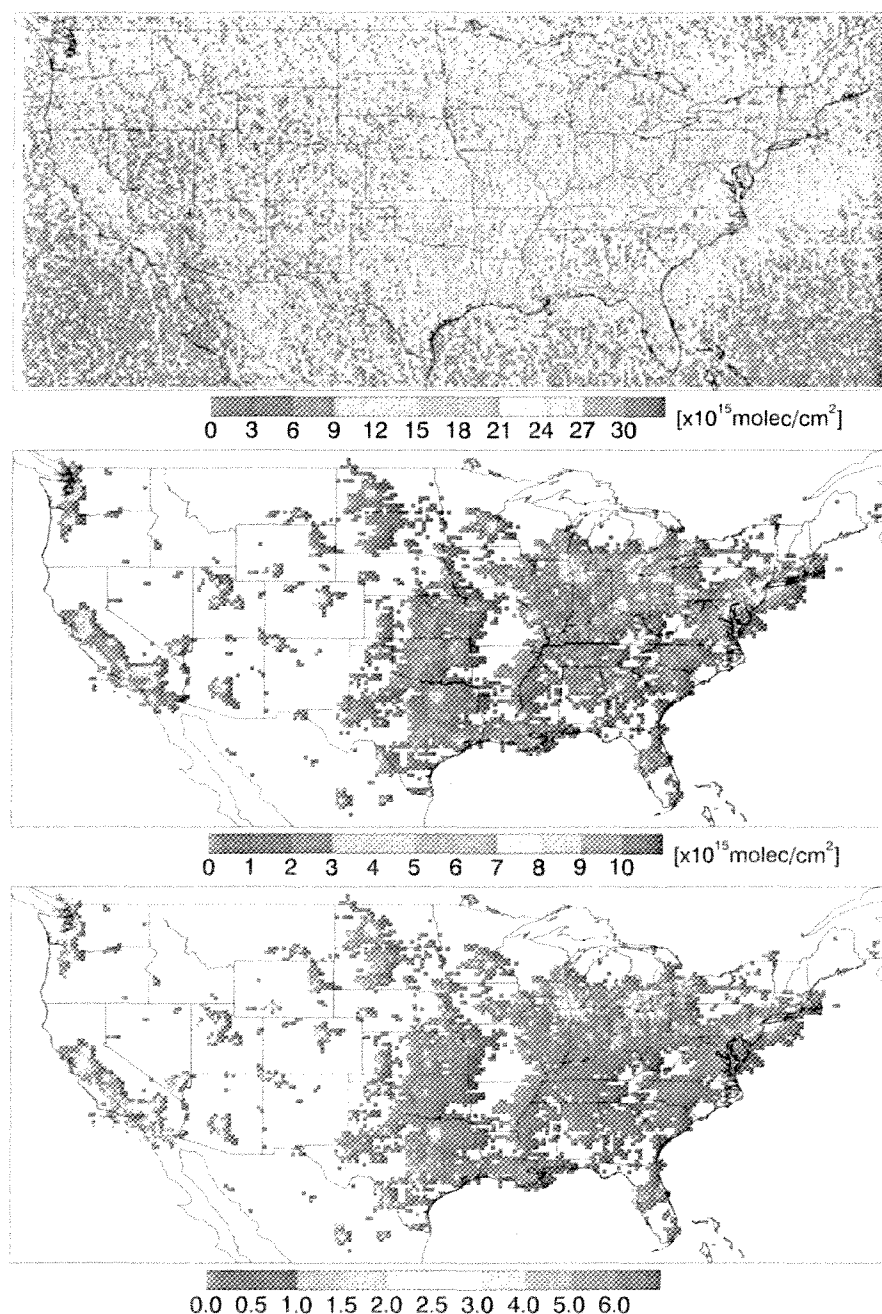
#### 4.1. Variations in $\text{NO}_2$

Fig. 8 shows the difference in the OMI tropospheric  $\text{NO}_2$  columns between 2007 and 2005 over land. There were substantial decreases in most areas, which is consistent with emission controls mandated by the federal government. Emissions from large stationary sources (e.g., power plants) decreased by more than 10% in the eastern U.S. from 2005 to 2007 under the  $\text{NO}_x$  Budget Trading Program (NBTP) of the Environmental Protection Agency (EPA) (EPA, 2008a). Additional decreases in automobile emissions occurred under the Tier 2 Vehicle and Gasoline Sulfur Program. Areas of the western U.S. had higher  $\text{NO}_2$  in 2007 than 2005 because of widespread fires (Grossi, 2008). For instance, the Zaca wildfire, which burned north of LA, was one of the largest in California's history. The increases in the southeastern U.S. (e.g., central Tennessee) may be partly a data artifact due to surface albedo differences between the two years. For instance, the area of increase in OMI  $\text{NO}_2$  in central Tennessee is predominantly pastureland in which the grass would have been greener in 2005 when conditions were wetter than during the historic drought in 2007; this issue needs further investigation.

Fig. 9 shows the metropolitan-average Ratios as a function of the tropospheric  $\text{NO}_2$  columns during the summers of 2005–2007 for Atlanta, NYC, Chicago, and LA. In these cities, there was a general decrease in  $\text{NO}_2$  with a concomitant increase in the Ratios from 2005 to 2007, except in Atlanta. While NYC was predominantly  $\text{NO}_x$ -limited, it became more so by 2007. Chicago may have recently crossed from the transition to the  $\text{NO}_x$ -limited regime and LA may have crossed from the radical-limited to the transition regime. The decrease in  $\text{NO}_2$  and the concomitant increase in the Ratio are less obvious in cities with high HCHO (e.g., Atlanta) as discussed below.

#### 4.2. Variations in HCHO

There was significant variation in OMI HCHO during the summers of 2005–2007, mainly associated with the strong, linear temperature dependence of isoprene emissions (Duncan et al., 2009). Duncan et al. estimated that the regional-average variation

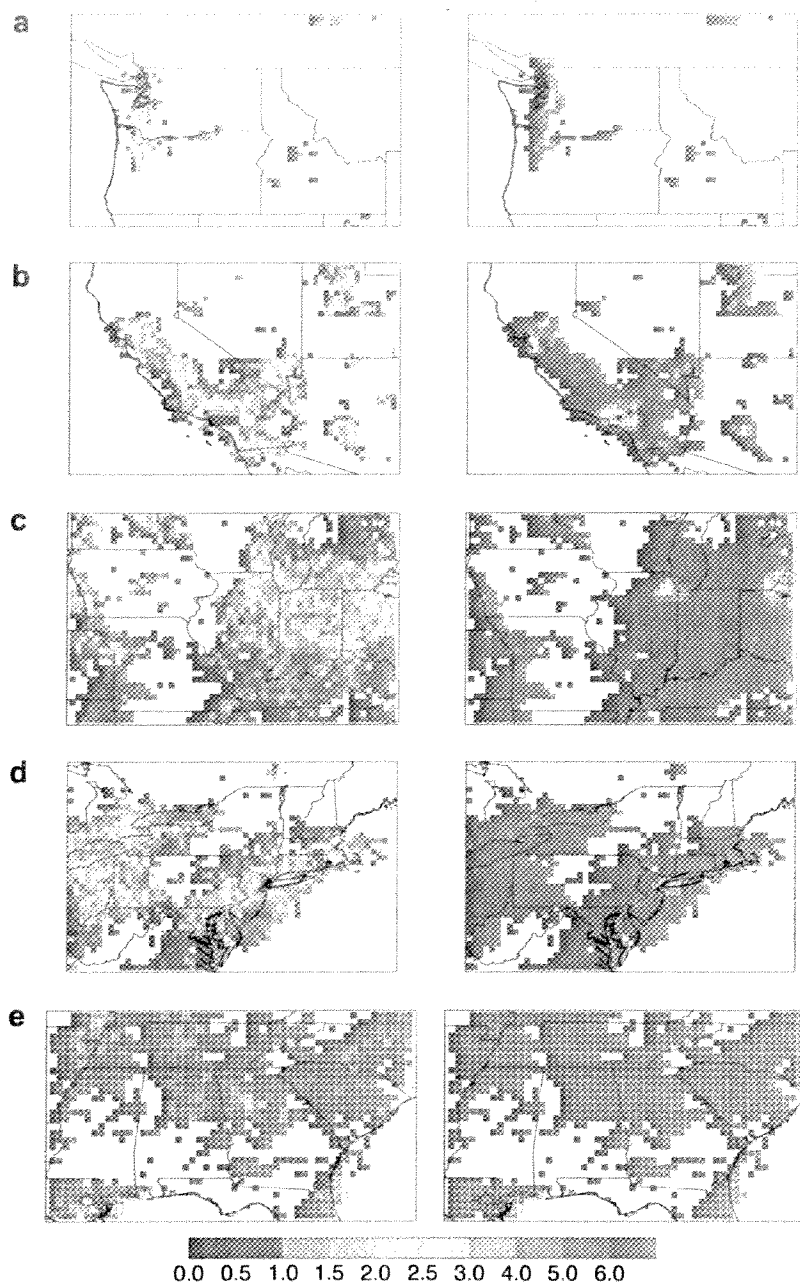


**Fig. 6.** OMI HCHO (top), NO<sub>2</sub> (middle), and Ratios (bottom) for August 2006. White areas indicate where HCHO data are below the detection limit and/or NO<sub>2</sub> data are  $< 1.5 \times 10^{15}$  molec cm<sup>-2</sup>. The color scale is saturated above a Ratio of 6. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

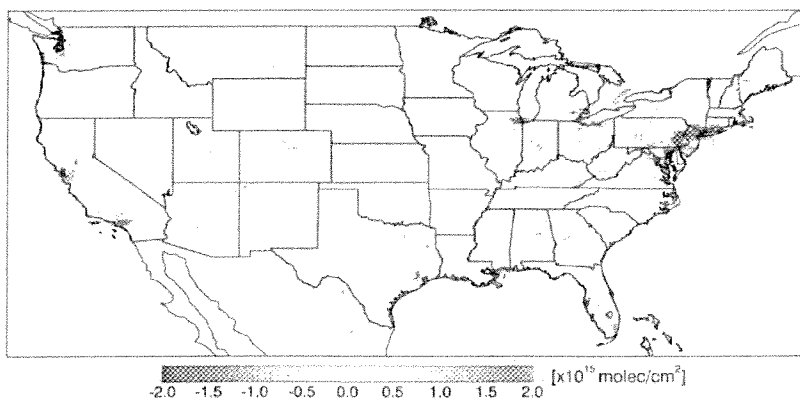
in the southeastern U.S. was ~22% for 2005–2007, but could be much higher locally. Fig. 10 (middle column) shows that the monthly-average HCHO in some cities appears to be linearly correlated with temperature, particularly in Atlanta. This is consistent with cities that have isoprene contributing significantly to their total VOC reactivities, becoming more NO<sub>x</sub>-limited with increasing temperature; this is important as high ozone episodes are more frequent during heatwaves (Fig. 10; right column).

There is a correlation of the Ratio with surface temperature in most cities in the southeastern U.S. where isoprene emissions are typically high (e.g., Atlanta in Fig. 10, left column). In these cities,

the variability in isoprene emissions dominates the variability in the Ratio. In NYC where isoprene emissions are lower, HCHO appears to be correlated with temperature, but the Ratio is not correlated with temperature as the correlation is complicated by the downward trend in NO<sub>x</sub> emissions (Fig. 9). In cities where isoprene emissions are lower still (e.g., Chicago), the temperature dependence of HCHO and the Ratio are not apparent. The temperature dependence of the Ratio is also influenced by the temperature dependence of anthropogenic VOC emissions (e.g., evaporative emissions), peroxyacetylnitrate (PAN) formation and other factors (Sillman and Samson, 1995), though the temperature



**Fig. 7.** (left) Minimum OMI Ratios of 9 months (i.e., June–August 2005–2007). (right) Maximum OMI Ratios of the same period. a) northwestern U.S., b) southwestern U.S., c) Midwest, d) northeastern U.S., and e) southeastern U.S.



**Fig. 8.** June–August average OMI  $\text{NO}_2$  ( $\times 10^{15} \text{ molec cm}^{-2}$ ) over land for 2007 minus the same period in 2005.



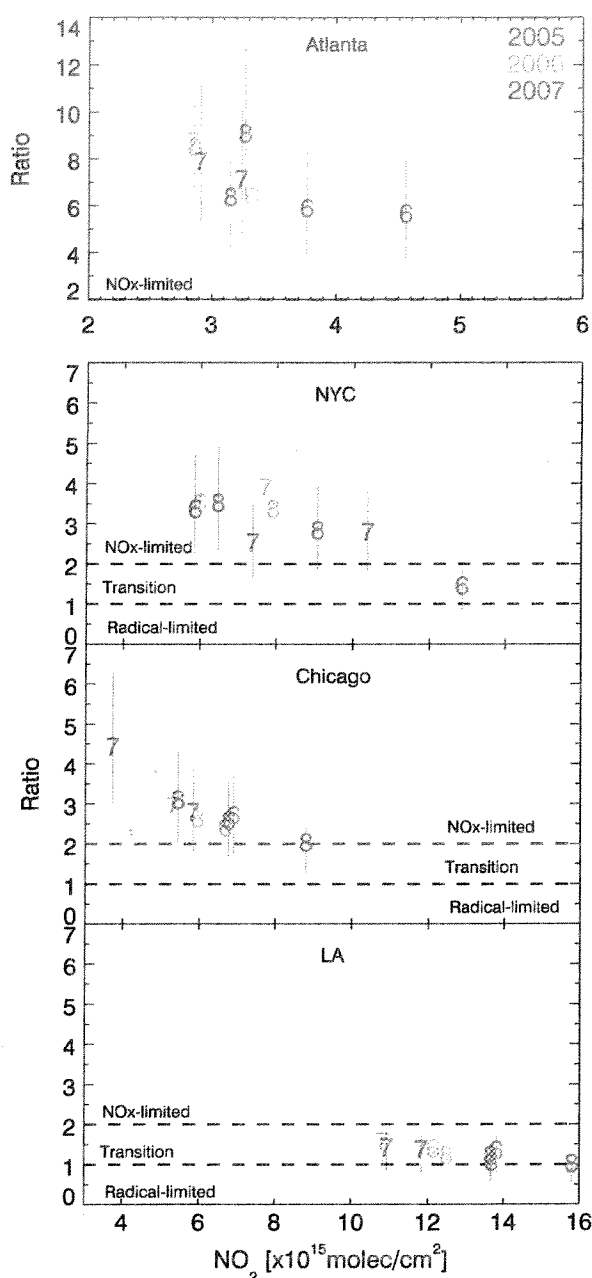


Fig. 9. OMI Ratios versus  $\text{NO}_2$  for June (6), July (7), and August (8) of 2005–2007 for Atlanta, NYC, Chicago, and LA. Data are averages of nine  $0.25^\circ \times 0.25^\circ$  gridboxes for each metropolitan area. Vertical lines indicate uncertainties assuming a combined error of 35%. Note that the axes ranges for the top panel differ from those of the lowest three panels.

dependence of isoprene emissions is likely to be the most important factor affecting the Ratio in the eastern U.S. in summer.

#### 4.3. Daily variations in $\text{NO}_x$ emissions

For many metropolitan areas, the daily-average Ratios are typically higher during the weekend, especially Sunday, and lower during the week as shown in Fig. 11 because of changes in  $\text{NO}_x$  emissions (e.g., Beirle et al., 2003; Kaynak et al., 2009). This indicates that these areas are more  $\text{NO}_x$ -limited on weekends than

weekdays. The Ratios on weekdays in LA are in the transition regime, but they are well within the  $\text{NO}_x$ -limited regime on weekends. NYC and Chicago are  $\text{NO}_x$ -limited every day on average, but are more so on the weekends. Sunday has the highest Ratios in all three cities. The average day-to-day variation of HCHO is smaller ( $\sim 20\%$  during summer) than the variation for  $\text{NO}_2$  (typically  $> 40\%$ ) with the lowest  $\text{NO}_2$  columns occurring on weekends. Blanchard et al. (2008) found that weekday versus weekend differences in ozone are not statistically significant for most urban sites (83%) despite the large decreases in emissions on weekends. The issue is complicated by the degree of titration of ozone by NO (e.g., in LA), which can cause ozone on weekends to be higher than weekdays (e.g., Yarwood et al., 2008).

#### 5. Consistency of OMI Ratio with in situ observations

The implied ozone-precursor sensitivity from the Ratio reported here is broadly consistent with results from studies using models and in situ data to understand the dependence of ozone on  $\text{NO}_x$  and VOCs. Ozone formation in LA is strongly radical-limited (e.g., Milford et al., 1989; Harley et al., 1993) and primarily radical-limited in the San Francisco area (Steiner et al., 2006) and in Phoenix (Kleinman et al., 2005). NYC is typically radical-limited (Kleinman et al., 2000), although the urban plume likely becomes  $\text{NO}_x$ -limited at some point downwind (Sillman, 1995; Daum et al., 1996). Philadelphia and Houston appear to be in the transition regime (Daum et al., 2004; Kleinman et al., 2005), while Atlanta is primarily  $\text{NO}_x$ -limited (Cardelino and Chameides, 1995; Sillman et al., 1995). Significant ozone production occurs in rural and suburban regions in the eastern U.S., which is predominantly  $\text{NO}_x$ -limited (Trainer et al., 1987; Pierce et al., 1998). In all regions there is a tendency towards more radical-limited conditions in urban centers and more  $\text{NO}_x$ -limited conditions elsewhere (Milford et al., 1989, 1994).

If the OMI Ratio  $< 1$  indicates radical-limited chemistry, then our results suggest that only downtown LA is exclusively radical-limited. Even the LA suburbs may be  $\text{NO}_x$ -limited at times (Fig. 7), which is consistent with Milford et al. (1989). After LA, the next lowest Ratios are in Seattle, Portland, Phoenix, Detroit, Chicago and NYC, suggesting the transition regime. Somewhat higher Ratios are found in other urban centers. The highest Ratios, suggesting strongly  $\text{NO}_x$ -limited conditions, are in rural areas in the eastern U.S. and Midwest. In all these cases the relative ordering of locations (from lowest to highest Ratios) is consistent with the relative ordering based on in situ studies (from radical- to  $\text{NO}_x$ -limited). The implied result from the OMI Ratios tends to be somewhat more  $\text{NO}_x$ -limited than in the in situ studies. It is possible that recent reductions in  $\text{NO}_x$  emissions have caused more  $\text{NO}_x$ -limited conditions than indicated by the earlier studies.

One would expect  $\text{PO}_3$  and, subsequently, the summertime ozone to be lower in 2007 than 2005 in most areas because of the significant reductions in  $\text{NO}_x$  emissions (e.g., Frost et al., 2006; G  go et al., 2007; Bloomer et al., 2009). In the eastern U.S., however, the observed surface ozone increased from 2005 to 2007. When adjusted for weather, there was a slight decrease,  $\sim 1\%$ . The average observed surface ozone in the U.S. decreased by 1% from 2001 to 2007 during the ozone season. When adjusted for weather, the decrease was 8% (EPA, 2008b), largely because of emission controls on  $\text{NO}_x$  emissions as discussed above. Therefore, local ozone is not only dependent on its chemical precursors, but also on several important factors, such as variations in temperature as discussed above (Fig. 10) and variations in the transport of ozone (e.g., Camalier et al., 2007; Zheng et al., 2007).



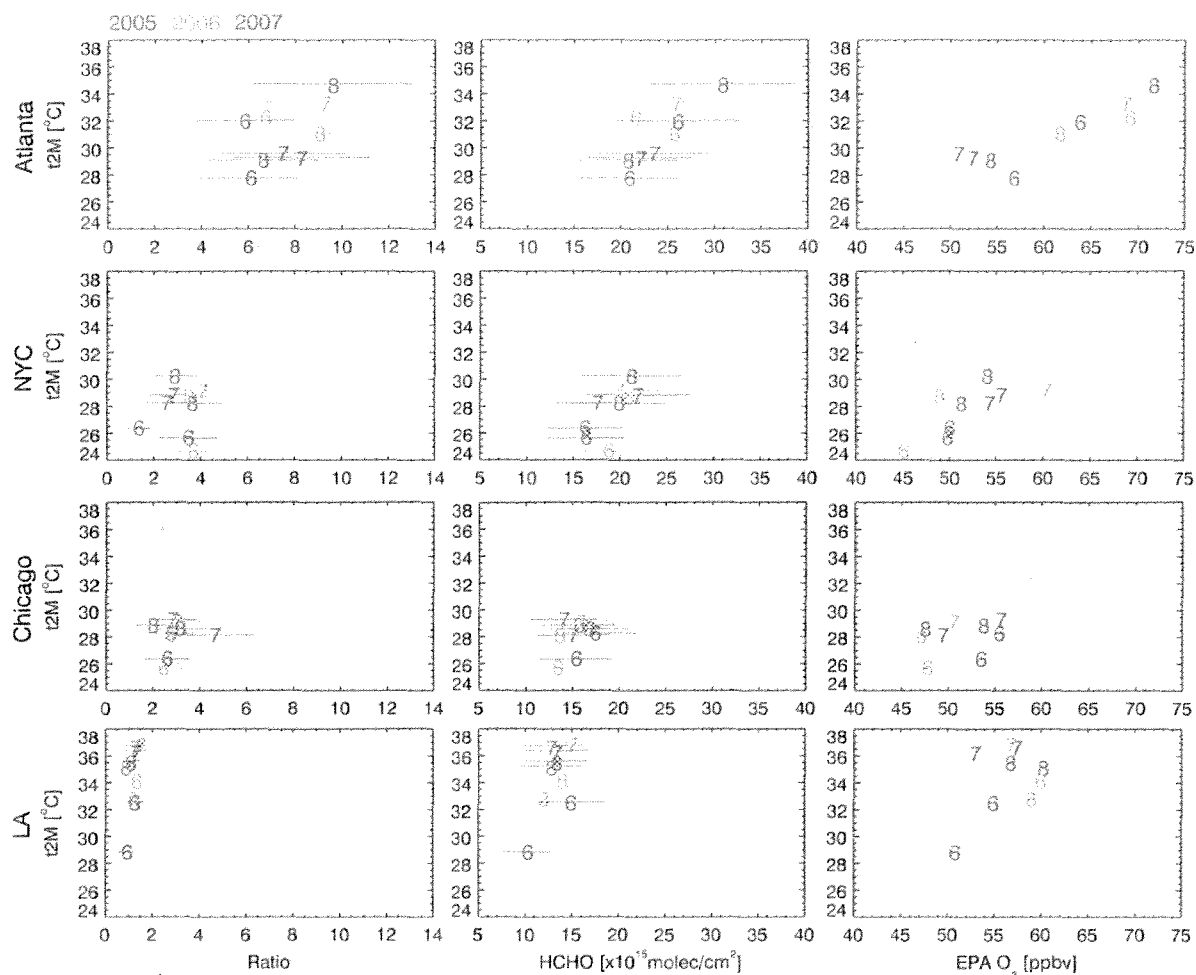


Fig. 10. Monthly-averaged surface temperature ( $^{\circ}\text{C}$ ) at 2 m versus (left) OMI Ratio, (middle) OMI HCHO ( $\times 10^{15}$  molec  $\text{cm}^{-2}$ ), and (right) measured ozone (ppbv) from the EPA for Atlanta, NYC, Chicago, and LA. Horizontal lines indicate uncertainties assuming a combined error of 35% for the Ratio and 25% for HCHO.

## 6. Summary

We presented a space-based assessment of the chemical limitation of surface ozone formation in summer using the ratio of the OMI tropospheric columns of HCHO and  $\text{NO}_2$  (i.e., the “Ratio”) as an air quality indicator. We used an air quality model and a photochemical box model to better quantify the use of the tropospheric Ratio as an indicator of  $\text{NO}_x$ - and radical-limited ozone production. We found that Ratios  $<1$  indicate radical-limited chemistry and Ratios  $>2$  indicate  $\text{NO}_x$ -limited chemistry, though there may be some regional dependence of these definitions. The area between the  $\text{NO}_x$ - and radical-limited regimes is a transition regime where the instantaneous ozone production (i.e., “ $\text{PO}_3$ ”) may respond to changes in both  $\text{NO}_x$  and VOC emissions.

We found that there was a general increase in the OMI Ratio that was associated with the decrease in anthropogenic  $\text{NO}_x$  emissions that occurred from 2005 to 2007. While there are uncertainties in the link between the Ratio and ozone-precursor sensitivity, the change in the Ratio suggests that ozone formation became more sensitive to  $\text{NO}_x$  over much of the U.S. This may have important policy implications for urban areas, such as LA and NYC, where both  $\text{NO}_x$  and anthropogenic VOC emission controls are in place. In addition, there was significant variability in HCHO associated with biogenic isoprene and its dependence on temperature; this result

implies that urban areas, where isoprene contributes to total VOC reactivity, become more  $\text{NO}_x$ -limited with increasing ambient temperature. This finding is important as peak ozone formation typically occurs during heatwaves.

The fine horizontal resolution of the OMI data allows us to discern the gradients in the Ratio from urban centers to suburbs to rural areas. Therefore, the data provide a basis for evaluating the accuracy of air quality models, particularly in areas with sparse in situ observations, as HCHO and  $\text{NO}_2$  are closely linked to ozone-precursor sensitivity as estimated from in situ measurements. However, the  $\text{PO}_3$  for a given location varies throughout the day and from day to day because of changes in sunlight and precursor emissions (e.g., Beirle et al., 2003; Kaynak et al., 2009). Consequently, space-based air quality monitoring would benefit from a geo-stationary platform. In addition, an instrument on a geo-stationary platform will have a longer sampling time which will increase the ratio of signal-to-noise as compared to the OMI.

While the Ratio has the potential to provide important information to air quality planners, the Ratio gives information on the  $\text{PO}_3$ , not the ozone concentration. Therefore, it should be treated as an additional piece of information to help formulate ozone attainment strategies. The usefulness of the Ratio is currently limited by the uncertainties associated with the OMI HCHO and  $\text{NO}_2$  data. Errors are introduced during the conversion of

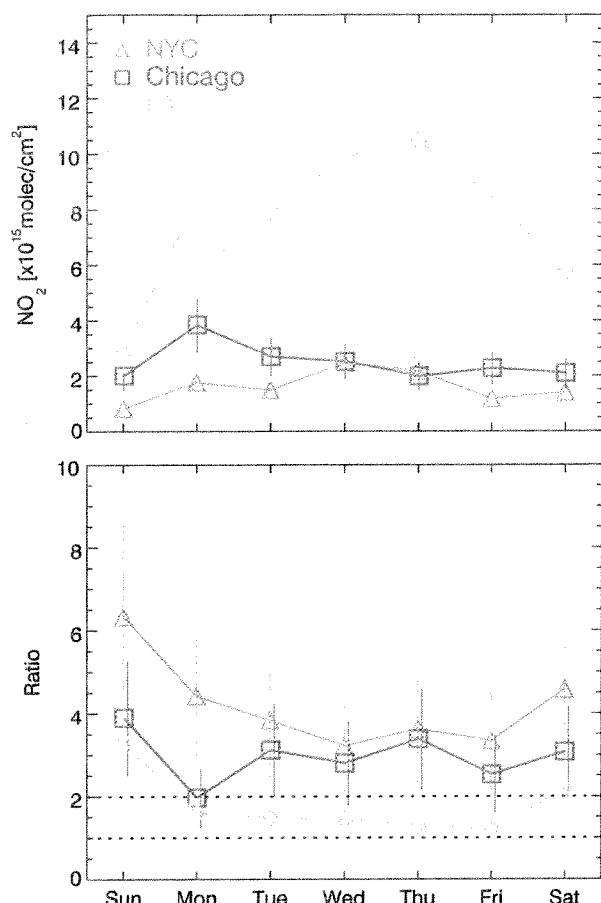


Fig. 11. (top) Daily-average OMI NO<sub>2</sub> ( $\times 10^{15}$  molec cm<sup>-2</sup>) in summer (i.e., June–August) from 2005 to 2007 in NYC, Chicago, and LA. (bottom) Daily-average OMI Ratios for the same period. Dashed horizontal lines represent the transition regime. Vertical lines indicate uncertainties assuming an error of 25% for NO<sub>2</sub> and a combined error of 35% for the Ratio.

atmospheric slant columns to tropospheric vertical columns (Martin et al., 2002; Boersma et al., 2004). Therefore, work is ongoing by members of the OMI science team to reduce this source of error, which includes, for instance, examining the effects of the assumed trace gas profiles on the OMI retrievals.

## Acknowledgement

This work was supported by the NASA's Earth Science Research Program.

## References

- Abbot, D., Palmer, P., Martin, R., Chance, K., Jacob, D., Guenther, A., 2003. Seasonal and interannual variability of isoprene emissions as determined by formaldehyde column measurements from space. *Geophysical Research Letters* 30, 1886. doi:10.1029/2003GL017336.
- Allen, D., Pickering, K., Rodriguez, J., Duncan, B., Strahan, S., Damon, M. Impact of lightning-NO emissions on North American photochemistry as determined using the GMI model. *Journal of Geophysical Research*, submitted for publication.
- Beirle, S., Platt, U., Wenig, M., Wagner, T., 2003. Weekly cycle of NO<sub>2</sub> by GOME measurements: a signature of anthropogenic sources. *Atmospheric Chemistry and Physics* 3, 2225–2232.
- Blanchard, C., Tanenbaum, S., Lawson, D., 2008. Differences between weekday and weekend air pollutant levels in Atlanta; Baltimore; Chicago; Dallas-Fort Worth; Denver; Houston; New York; Phoenix; Washington, DC; and surrounding areas. *Journal of the Air & Waste Management Association* 58 (12), 1598–1615.
- Bloomer, B., Stehr, J., Piety, C., Salawitch, R., Dickerson, R., 2009. Observed relationships of ozone air pollution with temperature and emissions. *Geophysical Research Letters* 36, L09803. doi:10.1029/2009GL037308.
- Boersma, K., Eskes, H., Brinkma, E., 2004. Error analysis for tropospheric NO<sub>2</sub> retrieval from space. *Journal of Geophysical Research* 109. doi:10.1029/2003JD003962.
- Boersma, K., Eskes, H., Veefkind, J., Brinkma, E., van der A, R., Sneep, M., van den Oord, G.H.J., Levelt, P., Stammes, P., Gleason, J., Bucsela, E., 2007. Near-real time retrieval of tropospheric NO<sub>2</sub> from OMI. *Atmospheric Chemistry and Physics* 7, 2103–2118.
- Byun, D., Schere, K., 2006. Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multiscale Air Quality (CMAQ) modeling system. *Applied Mechanics Reviews* 59 (2), 51–77.
- Camalier, L., Cox, W., Dolwick, P., 2007. The effects of meteorology on ozone in urban areas and their use in assessing ozone trends. *Atmospheric Environment* 41, 7127–7137.
- Cardelino, C., Chameides, W., 1995. An observation-based model for analyzing ozone-precursor relationships in the urban atmosphere. *Journal of the Air & Waste Management Association* 45, 161–180.
- Carter, W., 2000. Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment. Edited. California Air Resources Board. Contract No. 92-329 and 95-308.
- Chameides, W., Fehsenfeld, F., Rodgers, M., Cardelino, C., Martinez, J., Parrish, D., Lonneman, W., Lawson, D., Rasmussen, R., Zimmerman, P., Greenberg, J., Middleton, P., Wang, T., 1992. Ozone precursor relationships in the ambient atmosphere. *Journal of Geophysical Research* 97, 6037–6056.
- Chance, K., 2002. OMI Algorithm Theoretical Basis Document, vol. IV. OMI Trace Gas Algorithms, OMI-ATBD-VOL4, ATBD-OMI-04, Version 2.0.
- Crawford, J., Davis, D., Olson, J., Chen, G., Liu, S., Gregory, G., Barrick, J., Sachse, G., Sandholm, S., Heikes, B., Singh, H., Blake, D., 1999. Assessment of upper tropospheric HO<sub>x</sub> sources over the tropical Pacific based on NASA GTE/PEM data: net effect on HO<sub>x</sub> and other photochemical parameters. *Journal of Geophysical Research* 104, 16255–16273.
- Daum, P., Kleinman, L., Newman, L., Luke, W., Weinstein-Lloyd, J., Berkowitz, C., Busness, K., 1996. Chemical and physical properties of anthropogenic pollutants transported over the North Atlantic during NARE. *Journal of Geophysical Research* 101, 29029–29042.
- Daum, P., Kleinman, L., Springston, S., Nunnermacker, L., Lee, Y.-N., Weinstein-Lloyd, J., Zheng, J., Berkowitz, C., 2004. Origin and properties of plumes of high ozone observed during the Texas 2000 Air Quality Study (TexAQS 2000). *Journal of Geophysical Research* 109, D17306. doi:10.1029/2003JD004311.
- Dodge, M., 1987. Chemistry of Oxidant Formation: Implications for Designing Effective Control Strategies. U.S. Environmental Protection Agency, Washington, D.C. EPA/600/D-87/114 (NTIS PB87179990).
- Duncan, B., Strahan, S., Yoshida, Y., Steenrod, S., Livesey, N., 2007. Model study of the cross-tropopause transport of biomass burning pollution. *Atmospheric Chemistry and Physics* 7, 3713–3736.
- Duncan, B., Yoshida, Y., Damon, M., Douglass, A., Witte, J., 2009. Temperature dependence of factors controlling isoprene emissions. *Geophysical Research Letters* 36, L05813. doi:10.1029/2008GL037090.
- EPA, 2008a. NO<sub>x</sub> Budget Trading Program, Compliance and Environmental Results. U.S. Environmental Protection Agency. EPA-430-R-08-008.
- EPA, 2008b. National Air Quality Status and Trends through 2007. November 2008. U.S. Environmental Protection Agency. EPA-454/R-08-006.
- Frost, G., McKeen, S., Trainer, M., Ryerson, T., Neuman, J., Roberts, J., Swanson, A., Holloway, J., Sueper, D., Fortin, T., Parrish, D., Fehsenfeld, F., Flocke, F., Peckham, S., Grell, G., Kowal, D., Cartwright, J., Auerbach, N., Habermann, T., 2006. Effects of changing power plant NO<sub>x</sub> emissions on ozone in the eastern United States: proof of concept. *Journal of Geophysical Research* 111, D12306. doi:10.1029/2005JD006354.
- Gégo, E., Porter, P., Gilliland, A., Rao, S., 2007. Observation-based assessment of the impact of nitrogen oxides emissions reductions on ozone air quality over the eastern United States. *Journal of Applied Meteorology and Climatology* 46, 994–1008.
- Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P., Geron, C., 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmospheric Chemistry and Physics* 6, 3181–3210.
- Grossi, P., 2008. The 2007 U.S. Wildfire Season: Lessons from Southern California. Risk Management Solutions, Inc., Newark, CA.
- Haagen-Smit, A., 1952. Chemistry and physiology of Los Angeles smog. *Industrial & Engineering Chemistry* 44, 1342–1346.
- Harley, R., Russell, A., McRae, G., Cass, G., Seinfeld, J., 1993. Photochemical modeling of the Southern California Air Quality Study. *Environmental Science & Technology* 27, 378–388.
- Hudman, R., Jacob, D., Turquety, S., Leibensperger, E., Murray, L., Wu, S., Gilliland, A., Avery, M., Bertram, T., Brune, W., Cohen, R., Dibb, J., Flocke, F., Fried, A., Holloway, J., Neuman, J., Orville, R., Perring, A., Ren, X., Sachse, G., Singh, H., Swanson, A., Wooldridge, P., 2007. Surface and lightning sources of nitrogen oxides over the United States: magnitudes, chemical evolution, and outflow. *Journal of Geophysical Research* 112, D12505. doi:10.1029/2006JD007912.
- Kaynak, B., Hu, Y., Martin, R., Sioris, C., Russell, A., 2009. Comparison of weekly cycle of NO<sub>2</sub> satellite retrievals and NO<sub>x</sub> emission inventories for the continental United States. *Journal of Geophysical Research* 114, D05302. doi:10.1029/2008JD010714.

- Kleinman, L., 1994. Low and high  $\text{NO}_x$  tropospheric photochemistry. *Journal of Geophysical Research* 99, 16831–16838.
- Kleinman, L., Daum, P., Imre, D., Lee, J., Lee, Y.-N., Nunnermacker, L., Springston, S., Weinstein-Lloyd, J., Newman, L., 2000. Ozone production in the New York City urban plume. *Journal of Geophysical Research* 105, 14495–14511.
- Kleinman, L., Daum, P., Lee, Y.-N., Nunnermacker, L., Springston, S., Weinstein-Lloyd, J., Rudolph, J., 2005. A comparative study of ozone production in five U.S. metropolitan areas. *Journal of Geophysical Research* 110, D02301. doi:10.1029/2004JD005096.
- Kurosu, T., Chance, K., Sioris, C., 2004. "Preliminary results for HCHO and BrO from the EOS-Aura Ozone Monitoring Instrument", in passive optical remote sensing of the atmosphere and clouds IV. *Proceedings of SPIE* 5652. doi:10.1117/12.578606.
- Lamsal, L., Martin, R., van Donkelaar, A., Celarier, E., Bucsela, E., Boersma, K., Dirksen, R., Luo, C., Wang, Y., 2010. Indirect validation of tropospheric nitrogen dioxide retrieved from the OMI satellite instrument: insight into the seasonal variation of nitrogen oxides at northern midlatitudes. *Journal of Geophysical Research* 115, D5. doi:10.1029/2009JD013351.
- Lin, X., Trainer, M., Liu, S., 1988. On the nonlinearity of the tropospheric ozone production. *Journal of Geophysical Research* 93 (D12), 15879–15888.
- Liu, S., Trainer, M., Fehsenfeld, F., Parrish, D., Williams, E., Fahey, D., Hübler, G., Murphy, P., 1987. Ozone production in the rural troposphere and the implications for regional and global ozone distributions. *Journal of Geophysical Research* 92 (D4), 4191–4207.
- Martin, R., Chance, K., Jacob, D., Kurosu, T., Spurr, R., Bucsela, E., Gleason, J., Palmer, P., Bey, I., Fiore, A., Li, Q., Yantosca, R., Koelemeijer, R., 2002. An improved retrieval of tropospheric nitrogen dioxide from GOME. *Journal of Geophysical Research* 107 (D20), 4437. doi:10.1029/2001JD001027.
- Martin, R., Jacob, D., Chance, K., Kurosu, T., Palmer, P., Evans, M., 2003. Global inventory of nitrogen dioxide emissions constrained by space-based observations of  $\text{NO}_2$  columns. *Journal of Geophysical Research* 108, 4537. doi:10.1029/2003JD003453.
- Martin, R., Fiore, A., Van Donkelaar, A., 2004a. Space-based diagnosis of surface ozone sensitivity to anthropogenic emissions. *Geophysical Research Letters* 31, L06120. doi:10.1029/2004GL019416.
- Martin, R., Parrish, D., Ryerson, T., Nicks, D., Chance, K., Kurosu, T., Jacob, D., Sturges, E., Fried, A., Wert, B., 2004b. Evaluation of GOME satellite measurements of tropospheric  $\text{NO}_2$  and HCHO using regional data from aircraft campaigns in the southeastern United States. *Journal of Geophysical Research* 109, D24307. doi:10.1029/2004JD004869.
- Martin, R., Sauvage, B., Folkens, I., Sioris, C., Boone, C., Bernath, P., Ziemke, J., 2007. Space-based constraints on the production of nitric oxide by lightning. *Journal of Geophysical Research* 112, D09309. doi:10.1029/2006JD007831.
- Milford, J., Russell, A., McRae, G., 1989. A new approach to photochemical pollution control: implications of spatial patterns in pollutant responses to reductions in nitrogen oxides and reactive organic gas emissions. *Environmental Science & Technology* 23, 1290–1301.
- Milford, J., Gao, D., Sillman, S., Blosser, P., Russell, A., 1994. Total reactive nitrogen ( $\text{NO}_y$ ) as an indicator for the sensitivity of ozone to  $\text{NO}_x$  and hydrocarbons. *Journal of Geophysical Research* 99, 3533–3542.
- Millet, D., Jacob, D., Turquety, S., Hudman, R., Wu, S., Fried, A., Walega, J., Heikes, B., Blake, D., Singh, H., Anderson, B., Clarke, A., 2006. Formaldehyde distribution over North America: implications for satellite retrievals of formaldehyde columns and isoprene emissions. *Journal of Geophysical Research* 111, D24502. doi:10.1029/2005JD006853.
- Napelenok, S., Pinder, R., Gilliland, A., Martin, R., 2008. A method for evaluating spatially-resolved  $\text{NO}_x$  emissions using Kalman filter inversion, direct sensitivities, and space-based  $\text{NO}_2$  observations. *Atmospheric Chemistry and Physics* 8, 5603–5614.
- Olson, J., Crawford, J., Chen, G., Brune, W., Faloona, I., Tan, D., Harder, H., Martinez, M., 2006. A reevaluation of airborne  $\text{HO}_x$  observations from NASA field campaigns. *Journal of Geophysical Research* 111, D10301. doi:10.1029/2005JD006617.
- Pierce, T., Geron, C., Bender, L., Dennis, R., Tonnesen, G., Guenther, A., 1998. Influence of increased isoprene emissions on regional ozone modeling. *Journal of Geophysical Research* 103, 25611–25630.
- Sillman, S., Logan, J., Wofsy, S., 1990. The sensitivity of ozone to nitrogen oxides and hydrocarbons in regional ozone episodes. *Journal of Geophysical Research* 95, 1837–1851.
- Sillman, S., 1995. The use of  $\text{NO}_y$ ,  $\text{H}_2\text{O}_2$ , and  $\text{HNO}_3$  as indicators for ozone- $\text{NO}_x$ -hydrocarbon sensitivity in urban locations. *Journal of Geophysical Research* 100, 14175–14188.
- Sillman, S., Al-Wali, K., Marsik, F., Nowacki, P., Samson, P., Rodgers, M., Garland, L., Martinez, J., Stoneking, C., Imhoff, R., Lee, J., Newman, L., Weinstein-Lloyd, J., Aneja, V., 1995. Photochemistry of ozone formation in Atlanta, GA: models and measurements. *Atmospheric Environment* 29, 3055–3066.
- Sillman, S., Samson, P., 1995. Impact of temperature on oxidant photochemistry in urban, polluted rural and remote environments. *Journal of Geophysical Research* 100, 11497–11508.
- Steiner, A., Tonne, S., Cohen, R., Goldstein, A., Harley, R., 2006. Influence of future climate and emissions on regional air quality in California. *Journal of Geophysical Research* 111, D18303. doi:10.1029/2005JD006935.
- Trainer, M., Williams, E., Parrish, D., Buhr, M., Allwine, E., Westberg, H., Fehsenfeld, F., Liu, S., 1987. Models and observations of the impact of natural hydrocarbons on rural ozone. *Nature* 329 (6141), 705–707.
- Yarwood, G., Grant, J., Koo, B., Dunker, A., 2008. Modeling weekday to weekend changes in emissions and ozone in the Los Angeles basin for 1997 and 2010. *Atmospheric Environment* 42, 3765–3779. doi:10.1016/j.atmosenv.2007.12.074.
- Zheng, J., Swall, J., Cox, W., Davis, J., 2007. Interannual variation in meteorologically adjusted ozone levels in the eastern United States: a comparison of two approaches. *Atmospheric Environment* 41 (4), 705–716.