Application of OMI observations to a space-based indicator of NO_x and VOC controls on surface ozone formation

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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_x) 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_x at Ratios > 2; both NO_x 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_x over most of the United States from 2005 to 2007 because of the substantial decrease in NO_x emissions, primarily from stationary sources, and the concomitant decrease in the tropospheric column of NO_2, and 2. more sensitive to NO_x 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_x 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_x 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.

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1. Introduction

In polluted areas, unhealthy levels of ozone form from a complex series of reactions involving nitrogen oxides ($NO_x = NO + NO_2$) 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_x or VOCs, depending on which is in excess (Dodge, 1987). These two states are commonly referred to as NO_x-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_y)) to determine chemical sensitivity, which is considered NO_x-limited when the ratio of HCHO to NO_y is high and radical-limited when the ratio is low; in this way, HCHO and NO_y are 'indicator species'.

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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 (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 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 NO_2 columns have been widely used to infer surface emissions of VOCs and 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 NO_x-limited regimes during summer occurs when the Ratio is ~1. The 3-d models from Sillman also show 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 NO_2 from the Ozone Monitoring Instrument (OMI). The OMI has a finer horizontal resolution ($\sim 13 \times 24$ km^2 at nadir) than the GOME instrument ($\sim 40 \times 320$ 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 NO_2 and from 327.5 to 356.5 nm for HCHO. We use tropospheric columns of NO_2 from the Derivation of OMI tropospheric NO_2 (DOMINO) product (Boersma et al., 2007) to which Lamsal et al. (2010) applied a stripe correction and 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° latitude by 0.25° longitude, using only data with cloud radiance fraction (Boersma et al., 2004) not exceeding 30%. The overall error in the vertical, tropospheric NO_2 column data is 10–40% (Boersma et al., 2007). Comparisons with ground-based and in situ data suggest that the OMI tropospheric NO_2 columns are biased low in summer by ~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° latitude by 0.25° 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 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 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 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/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 (PO_3). To calculate 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 PO_3. The CMAQ simulation covered southern California with a horizontal grid of 4×4 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 NO_x and 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 NO_2 is typically not well simulated in CMAQ (Napelenok et al., 2008), we replaced the free tropospheric 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 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 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 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 NO_x emissions are high.

Fig. 2b and c shows the PO_3 as a function of HCHO and NO_2, respectively, in the PBL. While it is well known that the PO_3 increases with the ambient NO_x concentration (e.g., Liu et al., 1987; Lin et al., 1988), the PO_3 also increases with increasing HCHO concentration partially due to the colocation of anthropogenic sources of NO_x and VOCs and the predominance of biogenic sources of VOCs along the populated coast. The PO_3 is lower, approaching zero, at high concentrations of NO_2 (Fig. 2c) because of the loss of NO_x to nitric acid and the titration of ozone by NO. In general, PO_3 typically declines at NO_x concentrations >1 ppbv, depending on VOC composition and concentration, and other factors (Lin et al., 1988).
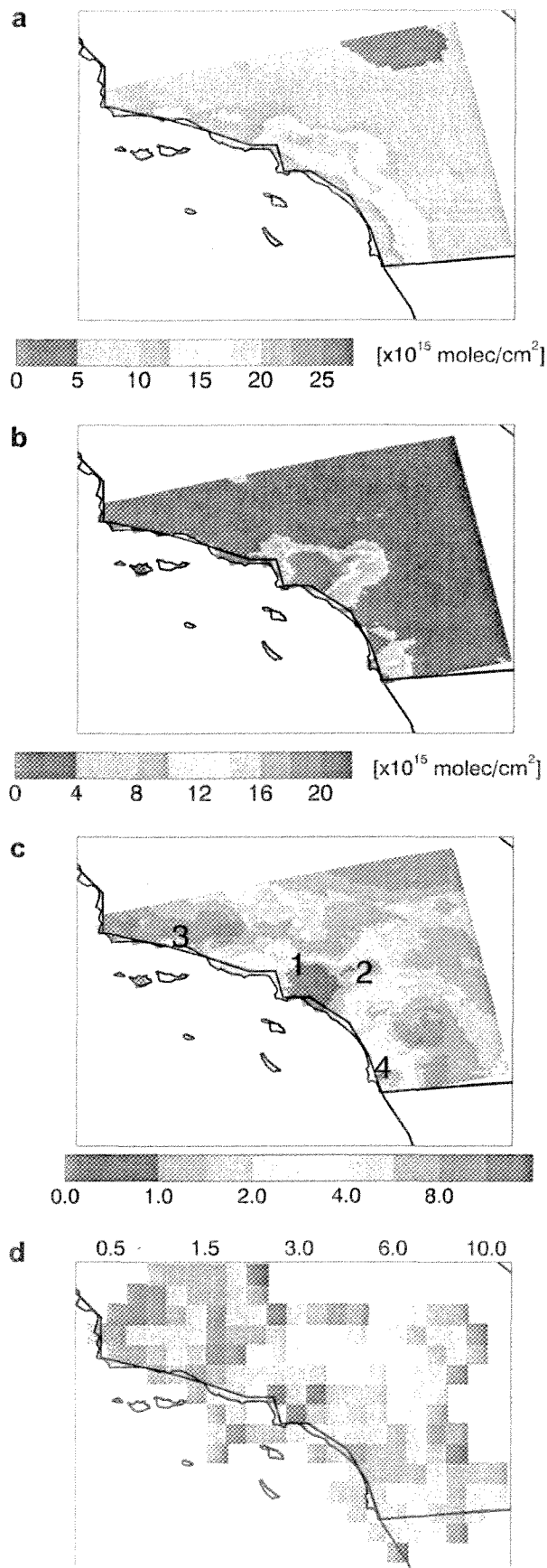
3.1. How representative is the tropospheric Ratio of the PO_3 within the PBL?

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 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 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 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 ($2°$ latitude $\times$ $2.5°$ longitude), so that the strong gradients in 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 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 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 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 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 NO_2 from lightning to the column in the FT is smaller than the 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 cm^{-2}; to 200 hPa), b) NO_2 columns ($\times 10^{15}$ molec 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 NO_2 data are $<1.5 \times 10^{15}$ molec cm^{-2}.
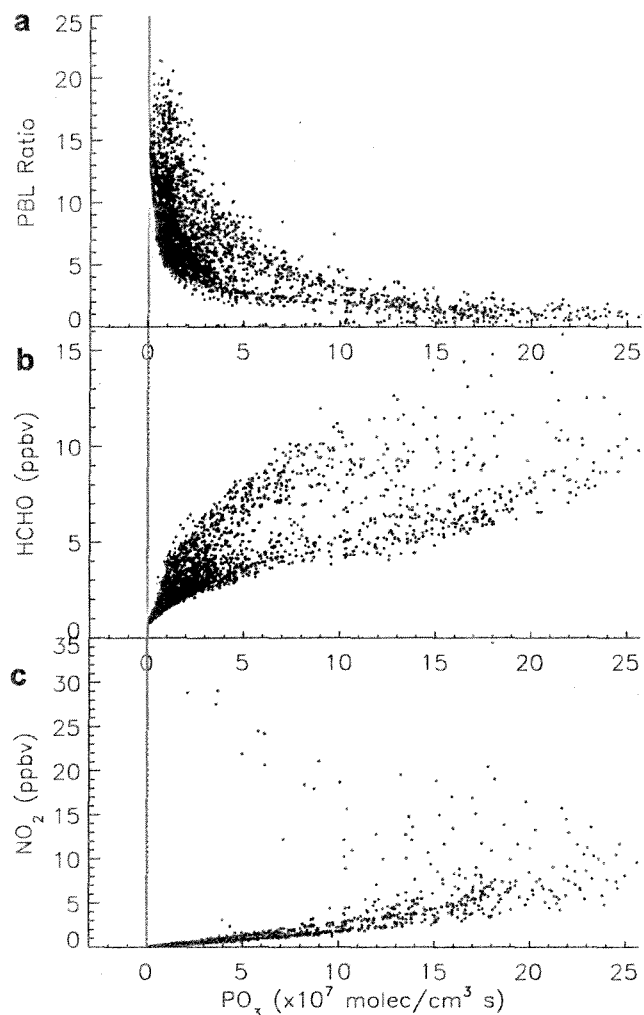
Fig. 2. The PBL PO_3 ($\times 10^7$ molec cm^{-3} s^{-1}) versus a) PBL Ratio, b) PBL HCHO (ppbv), and c) PBL NO_2 (ppbv) from the CMAQ simulation. The vertical line indicates where $PO_3 = 0$.
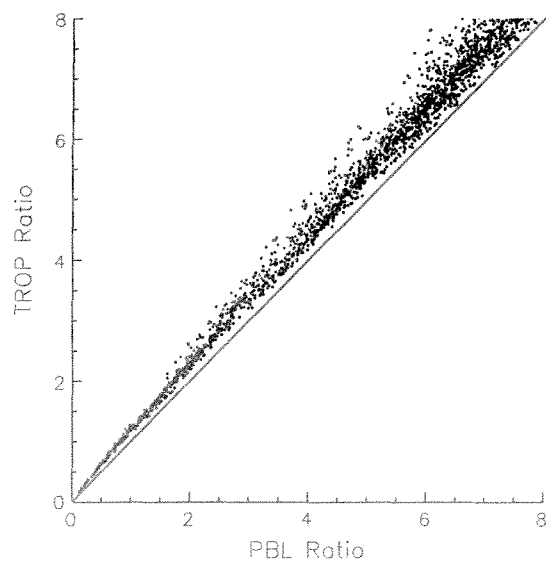

Fig. 3. PBL Ratio versus tropospheric Ratio from the CMAQ simulation. The line is 1:1.

As discussed above, we are interested in the Ratio representing the PO_3 in the PBL. Fortunately, the partitioning of NO_x into NO_2 and NO favors NO_2 near the surface (~90%), but is less (<50%) at higher altitudes where most NO from lightning is emitted. Consequently, the contributions of NO_x 1. from lightning, and 2. lofted to the FT, to the tropospheric NO_2 column are somewhat muted. Filtering model output when %PBL for either HCHO or 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 NO_x- and radical-limited regimes occurs when the tropospheric Ratio is ~1, using the GEOS-Chem CTM with 2.5° longitude × 2° 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 × 4 km^2). We used the ratio of the formation of H_2O_2 and organic peroxides (i.e., a radical sink) to the formation of HNO_3 (i.e., a NO_x sink) as an indicator of the chemical sensitivity of the PO_3; we refer to this quantity as L_{HO_x}/L_{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_{HO_x}/L_{NO_x} has been shown to correlate strongly with the NO_x-VOC sensitivity of the PO_3, with NO_x-limited conditions corresponding to high L_{HO_x}/L_{NO_x} (Sillman et al., 1990; Kleinman, 1994). We assume that the transition in the Ratio occurs when L_{HO_x}/L_{NO_x} is one. Fig. 4
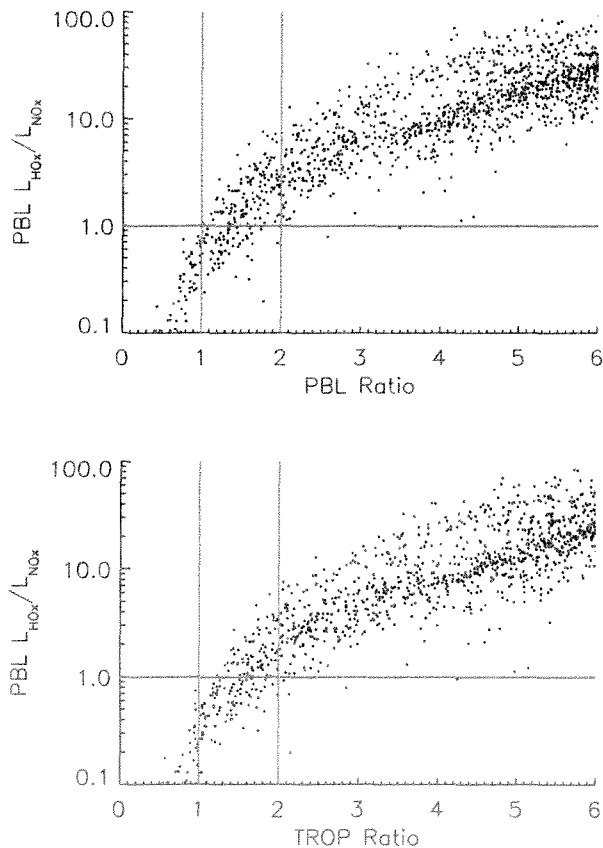

Fig. 4. Modeled PBL Ratio versus PBL L_{HO_x}/L_{NO_x} (top) and tropospheric Ratio versus PBL L_{HO_x}/L_{NO_x} (bottom). The horizontal line indicates where $L_{HO_x}/L_{NO_x} = 1$ and the vertical lines indicate the range of Ratios when $L_{HO_x}/L_{NO_x} = 1$.

shows the PBL L_{HO_x}/L_{NO_x} versus the PBL Ratio for the CMAQ domain. The transition occurs over a range of PBL Ratios, ~1–2. The range of tropospheric Ratios for the transition is similar when comparing to the PBL L_{HO_x}/L_{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 36×36 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, ~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 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 4×4 km^2 boxes within one 36×36 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 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 NO_x and VOCs may reduce the PO$_3$. This transition regime is relatively broad as the 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 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 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 PO$_3$ is currently limited by having only one daylight overpass each day.

4. OMI HCHO/NO$_2$

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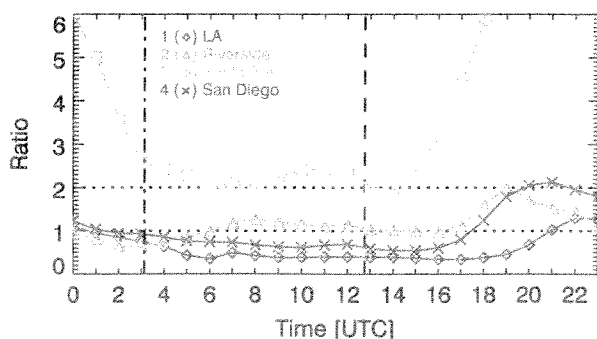

Fig. 5. Hourly tropospheric Ratios as a 4-day mean (July 1–4, 2007) in the CMAQ simulation for four cities (locations shown in Fig. 1c). The area between the dotted horizontal lines represents the transition regime. The dashed vertical line represents local sunrise and the dashed-dotted vertical line 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 NO$_2$

Fig. 8 shows the difference in the OMI tropospheric 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 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 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 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 NO$_2$ columns during the summers of 2005–2007 for Atlanta, NYC, Chicago, and LA. In these cities, there was a general decrease in NO$_2$ with a concomitant increase in the Ratios from 2005 to 2007, except in Atlanta. While NYC was predominantly NO_x-limited, it became more so by 2007. Chicago may have recently crossed from the transition to the NO_x-limited regime and LA may have crossed from the radical-limited to the transition regime. The decrease in 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
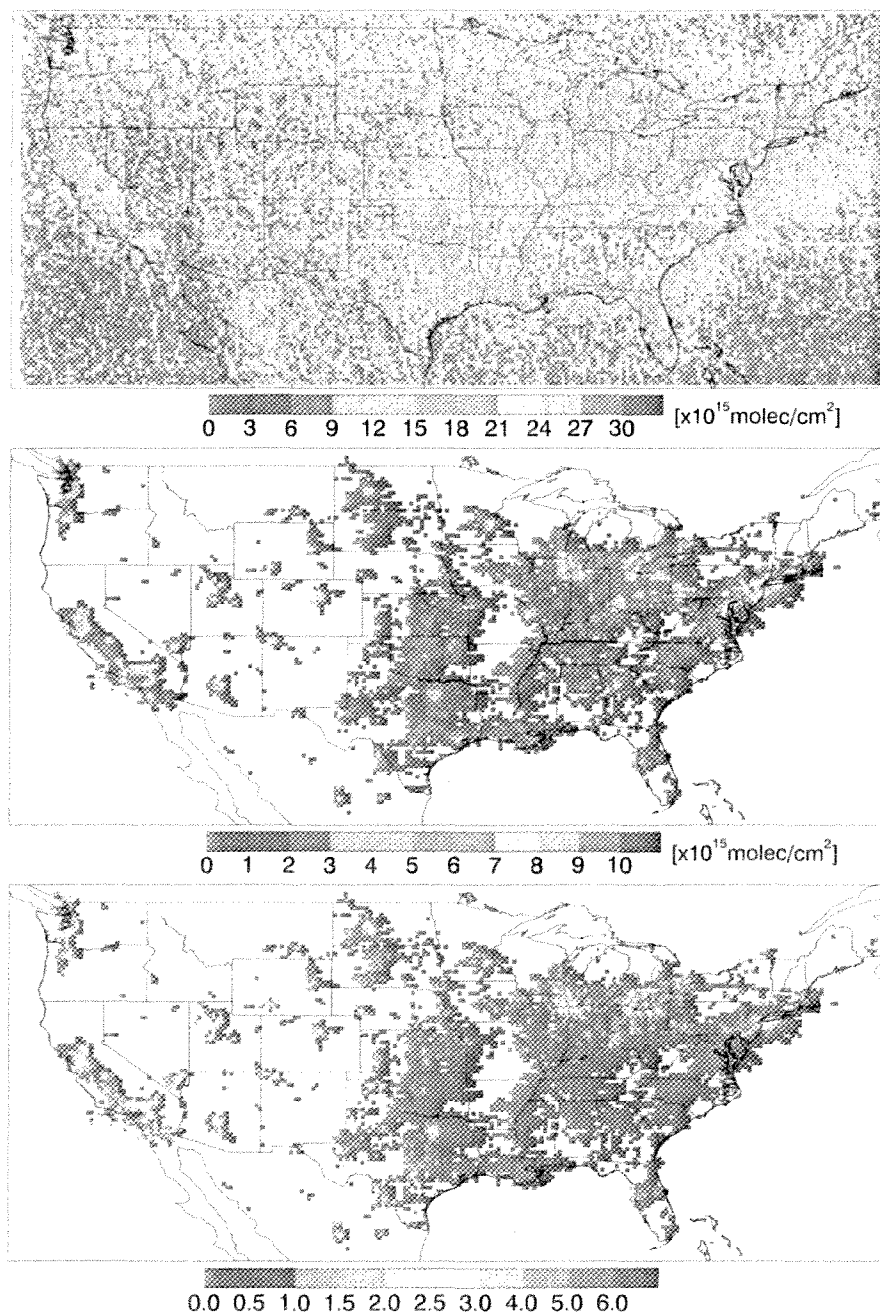
Fig. 6. OMI HCHO (top), NO$_2$ (middle), and Ratios (bottom) for August 2006. White areas indicate where HCHO data are below the detection limit and/or NO$_2$ data are $< 1.5 \times 10^{15}$ molec cm^{-2}. The color scale is saturated above a Ratio of 6. (For interpretation of the references to color 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$_x$-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$_x$ 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
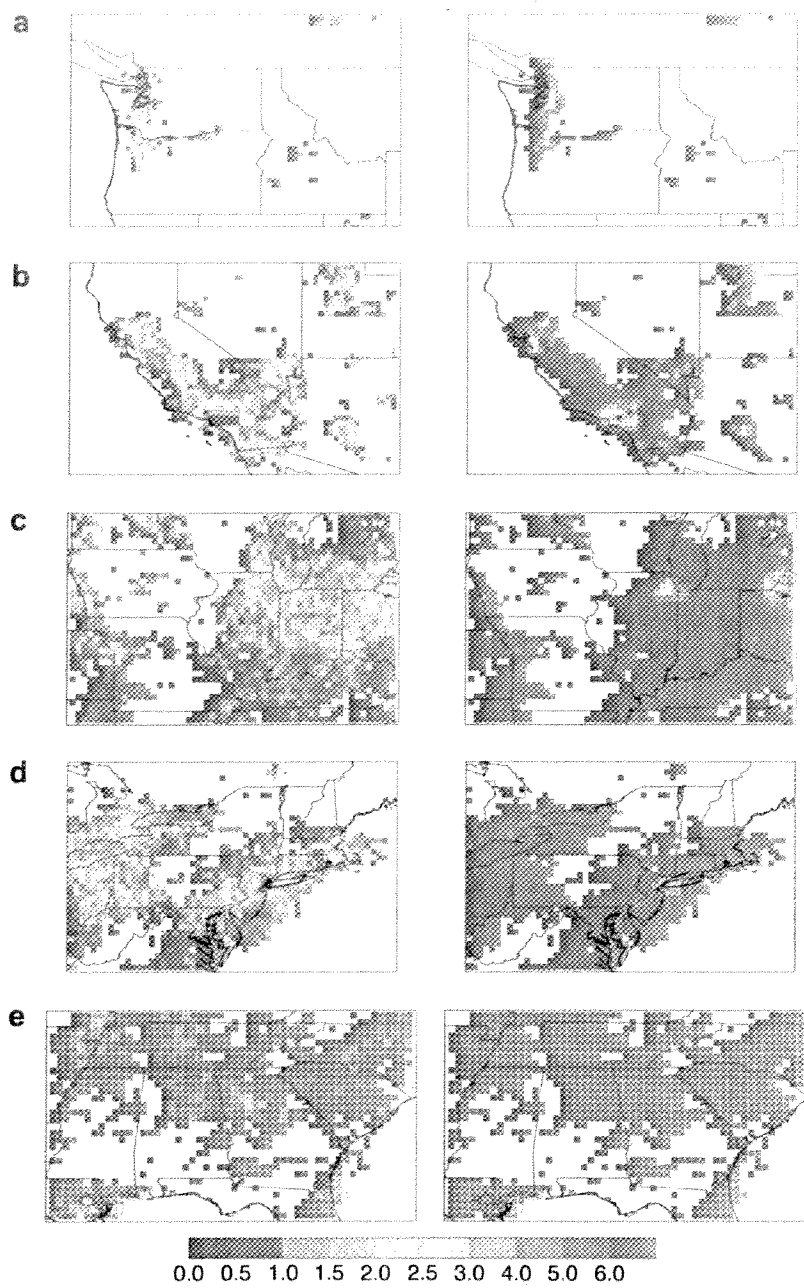
Fig. 7. (left) Minimum OMI Ratios of 9 months (i.e., June–August 2005–2007). (right) Maximum OMI Ratios of the same period. a) northwestern U.S., b) southwestern U.S., c) Midwest, d) northeastern U.S., and e) southeastern U.S.
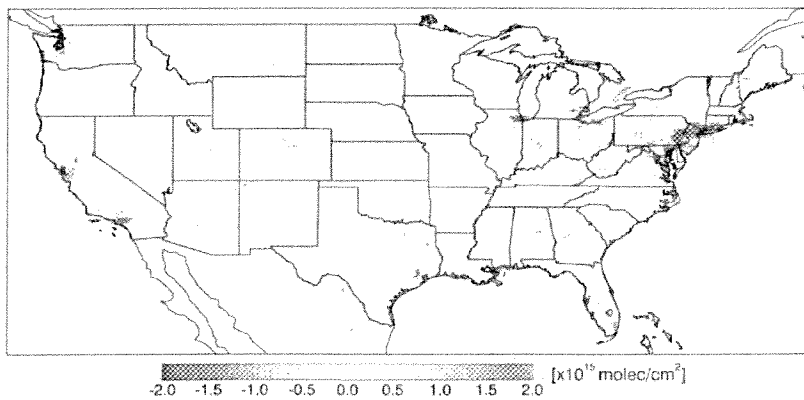

Fig. 8. June–August average OMI NO$_2$ ($\times 10^{15}$ molec cm^{-2}) over land for 2007 minus the same period in 2005.
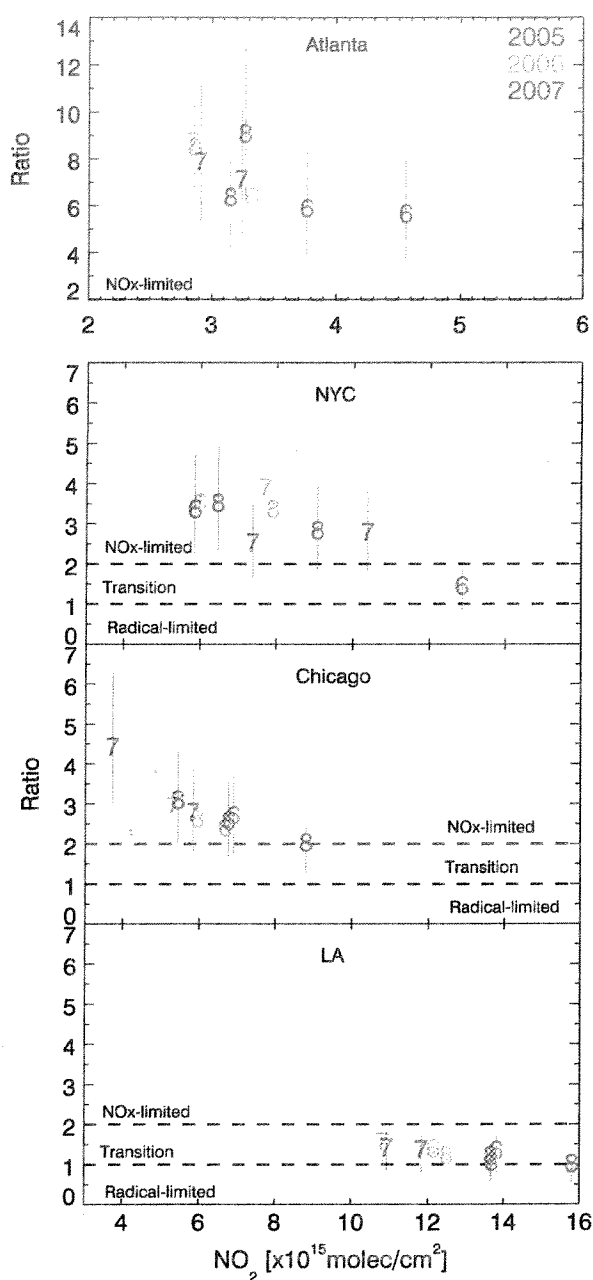
Fig. 9. OMI Ratios versus NO_2 for June (6), July (7), and August (8) of 2005–2007 for Atlanta, NYC, Chicago, and LA. Data are averages of nine 0.25° × 0.25° gridboxes for each metropolitan area. Vertical lines indicate uncertainties assuming a combined error of 35%. Note that the axes ranges for the 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 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 NO_x emissions (e.g., Beirle et al., 2003; Kaynak et al., 2009). This indicates that these areas are more NO_x-limited on weekends than

weekdays. The Ratios on weekdays in LA are in the transition regime, but they are well within the NO_x-limited regime on weekends. NYC and Chicago are 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 (~20% during summer) than the variation for NO_2 (typically >40%) with the lowest 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 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 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 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 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 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 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 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 NO_x-limited). The implied result from the OMI Ratios tends to be somewhat more NO_x-limited than in the in situ studies. It is possible that recent reductions in NO_x emissions have caused more NO_x-limited conditions than indicated by the earlier studies.

One would expect PO_3 and, subsequently, the summertime ozone to be lower in 2007 than 2005 in most areas because of the significant reductions in NO_x emissions (e.g., Frost et al., 2006; Gégo 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, ~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 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).
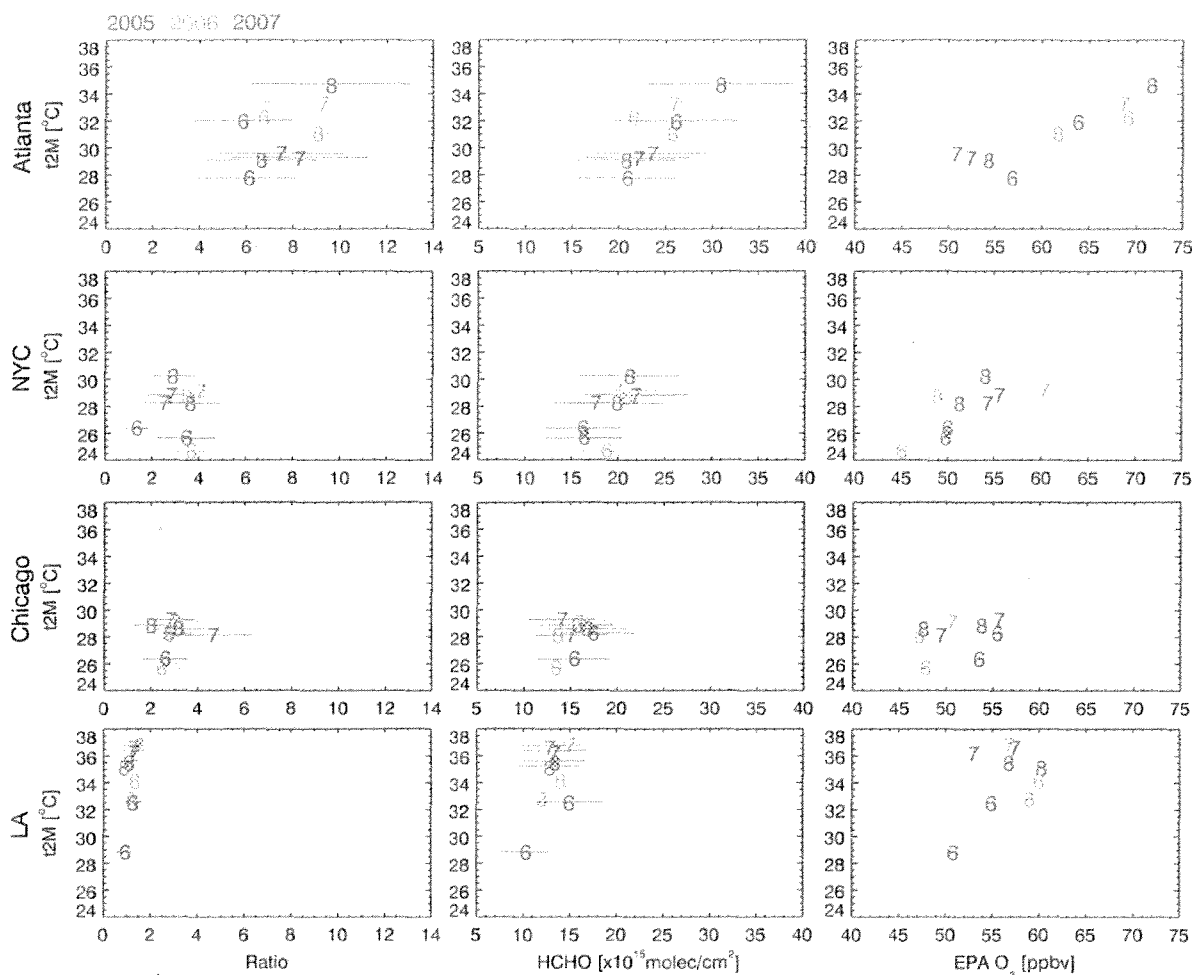
Fig. 10. Monthly-averaged surface temperature (°C) at 2 m versus (left) OMI Ratio, (middle) OMI HCHO ($\times 10^{15}$ molec cm^{-2}), and (right) measured ozone (ppbv) from the EPA for Atlanta, NYC, Chicago, and LA. Horizontal lines indicate uncertainties assuming a combined error of 35% for the Ratio 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 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 NO_x- and radical-limited ozone production. We found that Ratios <1 indicate radical-limited chemistry and Ratios >2 indicate NO_x-limited chemistry, though there may be some regional dependence of these definitions. The area between the NO_x- and radical-limited regimes is a transition regime where the instantaneous ozone production (i.e., "PO_3") may respond to changes in both 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 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 NO_x over much of the U.S. This may have important policy implications for urban areas, such as LA and NYC, where both 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 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 NO_2 are closely linked to ozone-precursor sensitivity as estimated from in situ measurements. However, the 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 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 NO_2 data. Errors are introduced during the conversion of
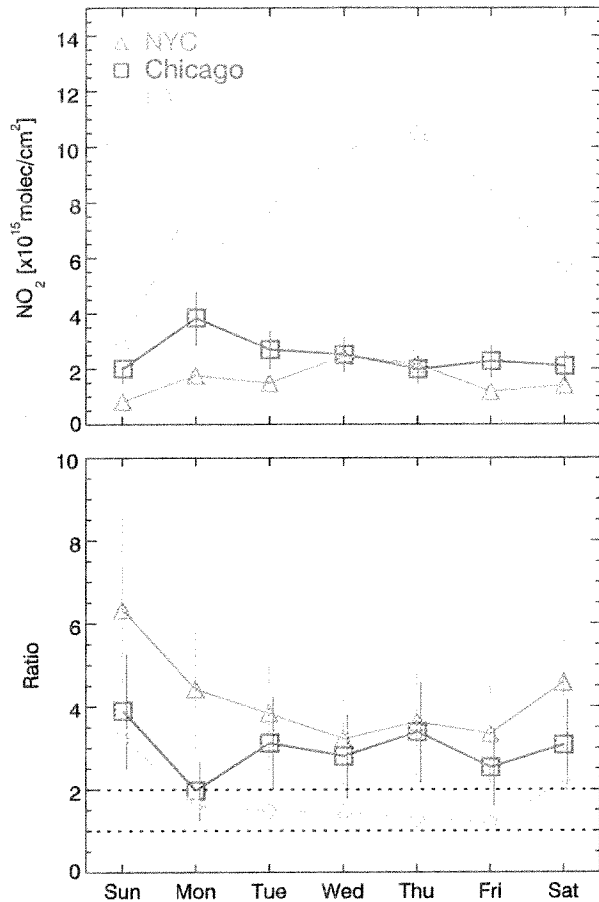
Fig. 11. (top) Daily-average OMI NO_2 ($\times 10^{15}$ molec cm^{-2}) in summer (i.e., June–August) from 2005 to 2007 in NYC, Chicago, and LA. (bottom) Daily-average OMI Ratios for the same period. Dashed horizontal lines represent the transition regime. Vertical lines indicate uncertainties assuming an error of 25% for NO_2 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.

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