The Sensitivity of U.S. Surface Ozone Formation to NO_x and VOCs as Viewed from Space

Bryan N. Duncan[1], Yasuko Yoshida[1,2], Sanford Sillman[3], Christian Retscher[1,2], Kenneth E. Pickering[1], Randall V. Martin[4], and Edward A. Celarier[1,2]

[1]Atmospheric Chemistry and Dynamics Branch, NASA Goddard Space Flight Center, Greenbelt, MD, USA.
[2]Goddard Earth Sciences and Technology Center, University of Maryland Baltimore County, Baltimore, MD, USA.
[3]Department of Atmospheric, Oceanic and Space Sciences, University of Michigan, Ann Arbor, MI, USA.
[4]Department of Physics and Atmospheric Science, Dalhousie University, Halifax, NS, Canada.

Abstract. We investigated variations in the 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 tropospheric columns of formaldehyde and nitrogen dioxide from the Aura Ozone Monitoring Instrument (OMI). The data indicate that ozone formation became: 1. more sensitive to NO_x over most of the U.S. from 2005 to 2007 because of substantial decreases in NO_x emissions primarily from stationary sources, 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. Based on our interpretation of the data, current strategies implemented to reduce unhealthy levels of surface ozone should focus more on reducing NO_x emissions, except in some downtown areas which have historically benefited from reductions in VOC emissions.

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 the limiting reagent [*Dodge*, 1987]. These two states are commonly referred to as NO_x-limited and VOC-limited (or sometimes NO_x-saturated) 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 the chemical sensitivity of the atmosphere, which is considered NO_x-limited when the ratio of HCHO to NO_y is high and radical-limited when the ratio is low.

Martin et al. [2004a] extended the technique of *Sillman* to space-based observations, using tropospheric column amounts of HCHO and nitrogen dioxide (NO_2) 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 of these two gases is an indicator of surface photochemistry as the bulk of their columns are within the lower mixed layer 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; *Martin et al.,* 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]; *Palmer et al.* [2003]).

Using a numerical model, *Martin et al.* [2004a] estimated that the transition between the radical and NO_x-limited regimes during summer occurs when $HCHO/NO_2$ is ~1. The 3-d models from *Sillman* also show NO_x-limited conditions for $HCHO/NO_2$ >1, but with some exceptions. The exceptions were associated with transport situations in which ozone may have been formed at an upwind location with different chemistry (e.g., within an urban center under radical-limited conditions and then transported downwind to an area with NO_x-limited conditions). The $HCHO/NO_2$ reflects the sensitivity of local ozone production rather than transport. In addition, local ozone production is dependent on 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] may vary.

In this manuscript, we examine the chemical sensitivity of ozone formation in the United States (U.S.) for summer from 2005-2007 as inferred from the ratio of the tropospheric columns of HCHO and NO_2 from the Ozone Monitoring Instrument (OMI) [*Levelt et al.,* 2006]. The OMI has a finer horizontal resolution (~13x24 km^2 at nadir) than the GOME instrument (~40x320 km^2), so OMI provides more information on the spatial gradients.

2. OMI Observations

The OMI is an UV/Vis imaging spectrometer on the Aura satellite, which crosses the equator at about 1338 local time. We use tropospheric column amounts of NO_2 from the collection 3 standard product, gridded to a horizontal resolution of 0.25° latitude by 0.25° longitude using only data with effective geometric cloud fractions < 30% [*Acarreta et al.,* 2004]. The algorithm for the retrieval of total column and tropospheric NO_2 is described by *Bucsela et al.* [2006] and *Celarier et al.* [2008]. NO_2 fitting was performed in the spectral window 405-465 nm. Comparisons with ground-based and *in situ* data suggest that OMI tropospheric NO_2 columns are biased low by 15-30% [e.g., *Celarier et al.*, 2008] with a positive bias in summer [*Lamsal et al.*, 2008]. The specifics of the HCHO algorithm are described in *Chance* [2002] and *Kurosu et al.* [2004]. HCHO fitting was performed in the spectral window 327.5-356.5 nm. 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. The overall 1 **?** error in HCHO column retrievals is 25-27% [*Millet et al.,* 2006]. 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].

3. $HCHO/NO_2$

Figure 1 shows the monthly average ratios of OMI HCHO and NO_2 in August 2006. Most of the U.S. was clearly NO_x-limited as the ratios were > 3. In the Southeast, ratios were > 6 as natural VOCs (e.g., isoprene) contribute significantly to total VOC reactivity [*Chameides et al.*, 1992]. The importance of isoprene generally decreases with increasing latitude in the East because of the spatial distribution of high isoprene emitting vegetation and the temperature dependence of isoprene emissions [*Guenther et al.*, 2006]. Much of the Midwest and Northeast had ratios < 4, although heavily forested regions in Massachusetts, Pennsylvania and Michigan had ratios comparable to the Southeast. In all regions, the lowest ratios were found in urban centers with higher ratios in the surrounding suburbs. The West typically had lower ratios than the East in both rural and urban areas, including in the Pacific Northwest. Overall, the OMI ratios have similar spatial distributions as the GOME ones presented in *Martin et al.* [2004a].

Figure 2 shows the range of monthly ratios during our study period. Most cities and regions exhibited a wide range of ratios. In the Northwest, Seattle and Portland had minimum ratios < 1. In the Southwest, the Phoenix, San Francisco and Los Angeles metropolitan areas had rather low minimum ratios (< 2), with the lowest in downtown Los Angeles (0.5-1.5). In the Midwest, the Chicago metropolitan area had minimum ratios from 0.5-2, Detroit from 1-2, and other urban areas (e.g., St. Louis and Indianapolis) from 1-4. In the Northeast, the New York metropolitan area had minimum ratios from 0.5-1.5, while the other urban areas had ratios from 1-3. In the Southeast, all urban centers had ratios > 1.5. Almost all areas in the U.S., including urban centers, had maximum ratios >2.5.

Variations in NO_2. Figure 3 shows the difference in OMI NO_2 between 2007 and 2005. Most areas show a substantial decrease, which is consistent with emission controls mandated by the federal government. Emissions in the East from large stationary sources (e.g., power plants) decreased by more than 10% from 2005 to 2007 under the NO_x Budget Trading Program (NBTP) of the Environmental Protection Agency [*EPA*, 2008]. Additional decreases in automobile emissions occurred under the Tier 2 Vehicle and Gasoline Sulfur Program. Areas of the West had higher NO_2 in 2007 than 2005 because of widespread fires [*Grossi*, 2008]. For instance, the Zaca wildfire, which burned north of Los Angeles, was the second largest in California's history.

Variations in HCHO. There was significant variation in HCHO during the summers of 2005-2007 (not shown), mainly associated with the temperature dependence of isoprene emissions. *Duncan et al.* [2009] estimated that the average variation in the Southeast was about 22% for 2005-2007, but could be much higher locally. This implies that cities that have isoprene contributing significantly to their total VOC reactivities, become more NO_x-limited with increasing temperature; this is important as high ozone episodes are more frequent during heatwaves.

4. Implications for Ozone Chemistry

The implied ozone-precursor sensitivity from the OMI $HCHO/NO_2$ 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 in polluted regions in the U.S. Ozone formation in Los Angeles 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]. New York 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 have mixed NO_x-radical-limitations [*Daum et al.*, 2004; *Kleinman et al.*, 2005], while Atlanta is primarily NO_x-limited [*Cardelino and Chameides*, 1995; *Sillman et al.*, 1995]. The OMI $HCHO/NO_2$ over Houston deserves further study in light of the relationship between anthropogenic VOCs and ozone inferred from *in situ* observations (e.g., Kleinman et al. [2002]). Significant ozone production occurs in rural and suburban regions in the East, 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 OMI $HCHO/NO_2 < 1$ indicates radical-limited chemistry, then our results suggest that only downtown Los Angeles is exclusively radical-limited. Even the Los Angeles suburbs may be NO_x-limited at times (Figure 2), which is consistent with *Milford et al.* [1989]. After Los Angeles, the next lowest ratios are in Seattle, Portland, Phoenix, Chicago and New York, suggesting mixed NO_x-radical limitations. Somewhat higher ratios are found in other urban centers. The highest ratios, suggesting strongly NO_x-limited conditions, are in rural areas in the East and Midwest. In all these cases the relative ordering of locations (from lowest to highest $HCHO/NO_2$) is consistent with the relative ordering based on *in situ* studies (from radical-limited to NO_x-limited).

The implied result from $HCHO/NO_2$ 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. Figure 4 shows the metropolitan-average ratios as a function of the tropospheric NO_2 columns during the summers of 2005-2007 for Los Angeles, Chicago, and New York. In these cities, there was a general decrease in the NO_2 columns with a concomitant increase in the ratios from 2005 to 2007. Reducing the positive summertime bias in OMI NO_2 would imply even more NO_x-limited conditions.

5. Summary

We presented a space-based assessment of the sensitivity of surface ozone formation in summer using OMI HCHO and NO_2 data. We found that there was a general increase in the ratio of HCHO to NO_2 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 ambient $HCHO/NO_2$ and ozone-precursor sensitivity, the change in $HCHO/NO_2$ 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 Los Angeles and New York, 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 OMI data provide a basis for evaluating the accuracy of air quality models, including 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 sensitivity of ozone formation for a region varies throughout the day and from day to day because of changes in sunlight, precursor emissions, and meteorology (e.g., *Duncan et al.* [1998]). Therefore, space-based air quality monitoring would benefit from a geo-stationary platform, which would provide information on the temporal variation of the sensitivity of ozone formation.

Future work should use a high spatial resolution model to examine the transition in the $HCHO/NO_2$ column ratio from NO_x- to radical-limited conditions, and examine the effects of the assumed trace gas profiles on the OMI retrievals.

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

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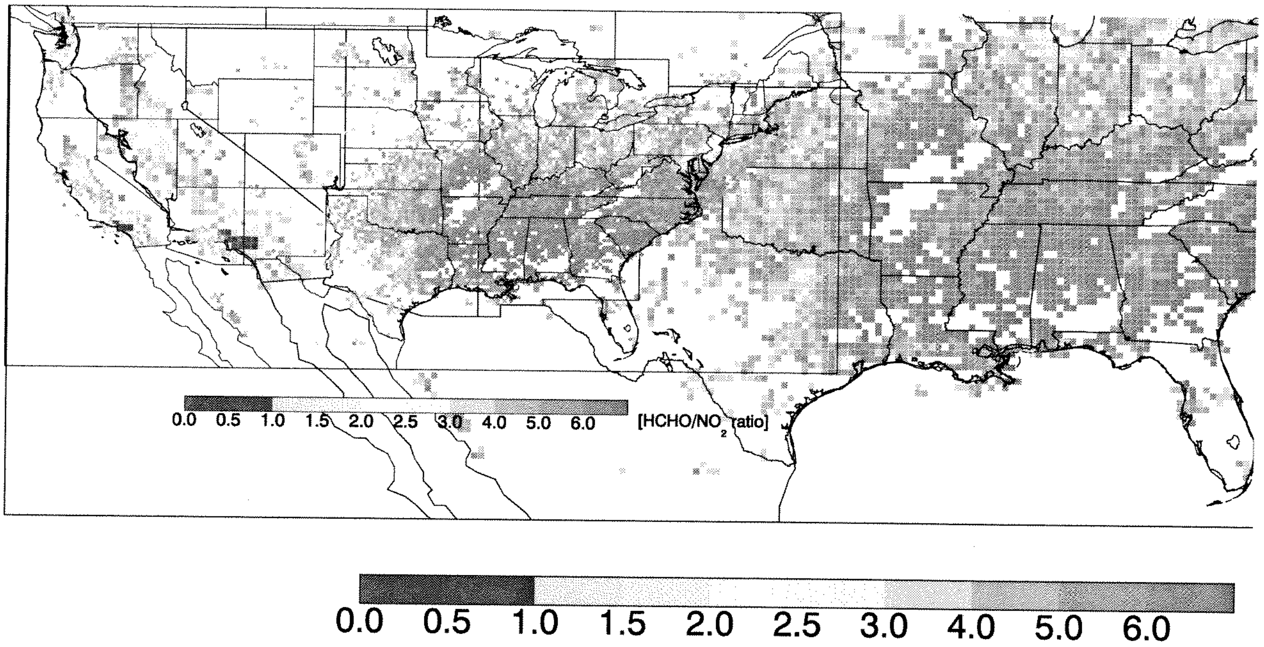

Figure 1. Monthly-average HCHO/NO$_2$ for August 2006. White areas in the figure indicate where the HCHO data values are below the detection limit and/or the NO$_2$ data values are < 2.5×10^{15} molecules cm^{-2}. The color scale is saturated above a ratio of 6.

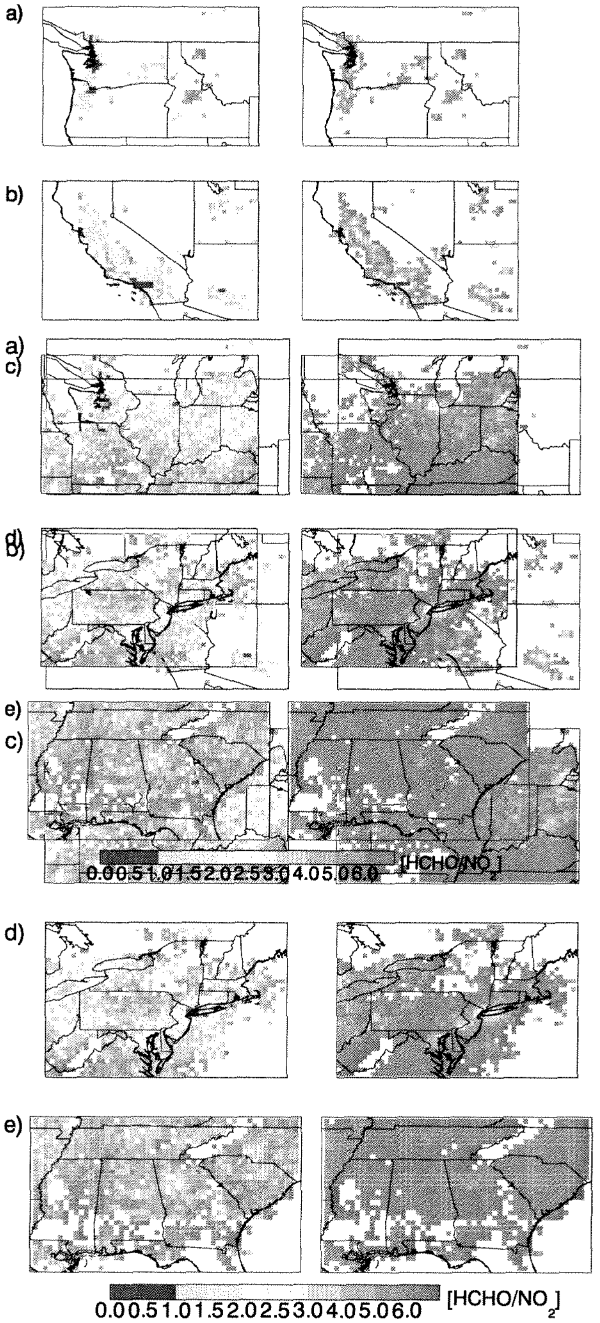

Figure 2. (left) The minimum monthly HCHO/NO$_2$ of 9 months (i.e., June-August 2005-2007). (right) The maximum ratio in the same period. a) Northwest, b) Southwest, c) Midwest, d) Northeast, and e) Southeast. The color scale is saturated above a ratio of 6.

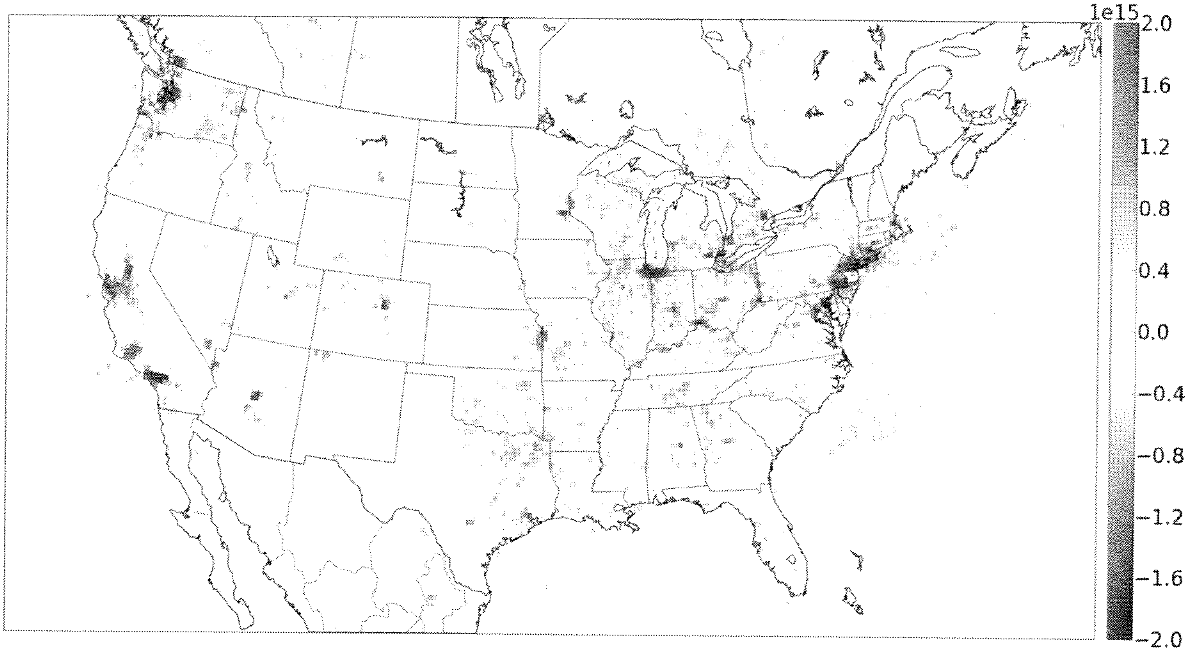

Figure 3. The June-August average OMI NO_2 for 2007 minus the same period in 2005.

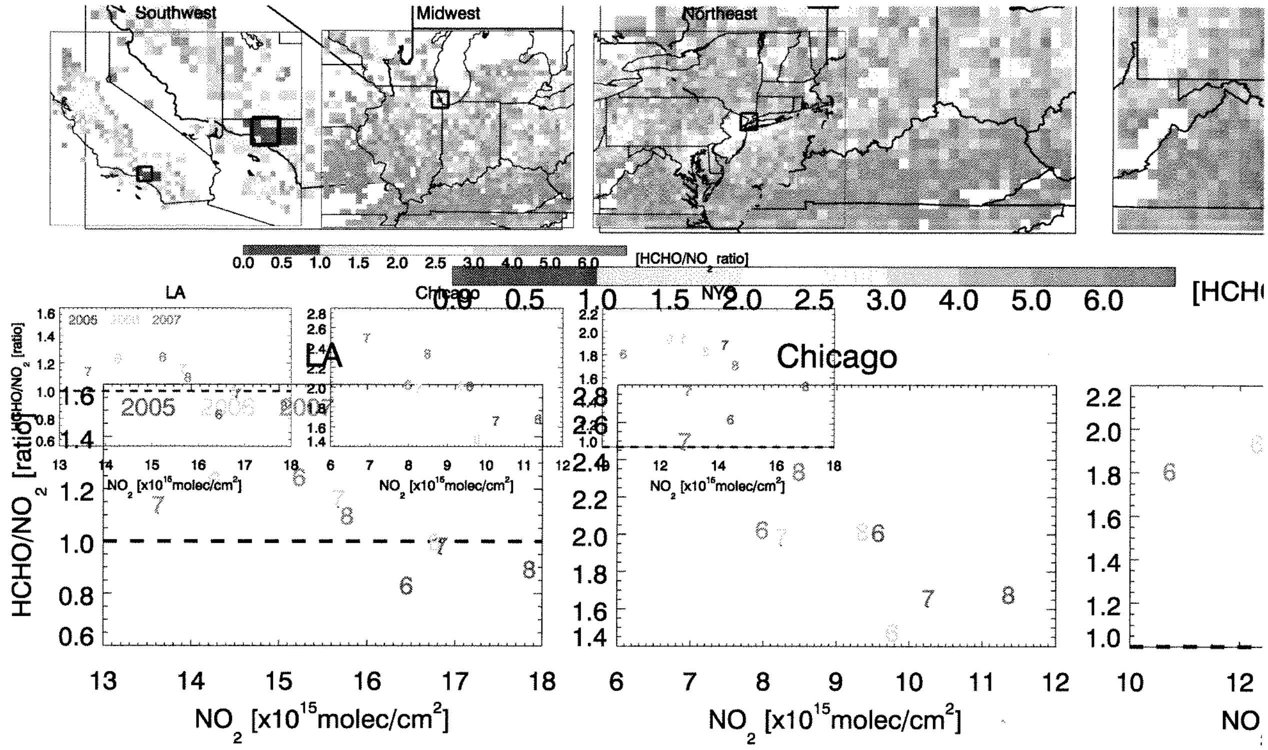

Figure 4. (top) Monthly-average HCHO/NO$_2$ for the Southwest, Midwest, and Northeast for August 2006. The color scale is saturated above a ratio of 6. (bottom) Metropolitan-average HCHO/NO$_2$ vs. NO$_2$ for June (6), July (7), and August (8) of 2005-2007 for Los Angeles (LA), Chicago, and New York (NYC). The HCHO/NO$_2$ and NO$_2$ values are averages of nine 0.25°x0.25° gridboxes for each metropolitan area, which is delineated by a box in the top panel. The horizontal dashed line represents the transition between photochemical regimes.