

## THE SENSITIVITY OF U.S. SURFACE OZONE FORMATION TO NO<sub>x</sub> AND VOCS AS VIEWED FROM SPACE

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### 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 the limiting reagent (*Dodge*, 1987). These two states are commonly referred to as NO<sub>x</sub>-limited and VOC-limited (or sometimes NO<sub>x</sub>-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<sub>y</sub>)) to determine the chemical sensitivity of the atmosphere, 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.

*Martin et al.* (2004a) extended the technique of *Sillman* to space-based observations, using

tropospheric column amounts of HCHO and nitrogen dioxide (NO<sub>2</sub>) 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<sub>x</sub> 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<sub>2</sub> columns have been widely used to infer surface emissions of VOCs and NO<sub>x</sub>, respectively (*e.g.*, *Martin et al.* (2003); *Palmer et al.* (2003); *Millet et al.* (2006); *Boersma et al.* (2008)).

Using a numerical model, *Martin et al.* (2004a) estimated that the transition between the radical and NO<sub>x</sub>-limited regimes during summer occurs when HCHO/NO<sub>2</sub> is ~1. The 3-d models from *Sillman* also show NO<sub>x</sub>-limited conditions for HCHO/NO<sub>2</sub> >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<sub>x</sub>-limited conditions). The HCHO/NO<sub>2</sub> 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.

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<sub>2</sub> from the Ozone Monitoring Instrument (OMI) (*Levelt et al.*, 2006). The OMI has a finer horizontal resolution

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(~13x24 km<sup>2</sup> at nadir) than the GOME instrument (~40x320 km<sup>2</sup>), so the OMI provides information on spatial gradients, such as urban-rural ones, of the HCHO/NO<sub>2</sub> ratio that other instruments, including GOME, 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. We use tropospheric column amounts of NO<sub>2</sub> 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<sub>2</sub> is described by Bucseles *et al.* (2006) and Celarier *et al.* (2008). NO<sub>2</sub> fitting was performed in the spectral window 405-465 nm. Comparisons with ground-based and *in situ* data suggest that the OMI tropospheric NO<sub>2</sub> 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 1σ 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<sub>2</sub>, so these errors largely cancel in their ratio (Martin *et al.*, 2004a). Uncertainties associated with the removal of the stratospheric portion of the total column of NO<sub>2</sub> tend to be smallest in urban areas as the majority of the total column is near the surface.

## 3. HCHO/NO<sub>2</sub>

Figure 1 shows the monthly average ratios of the OMI HCHO and NO<sub>2</sub> in August 2006. Most of the U.S. was clearly NO<sub>x</sub>-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).

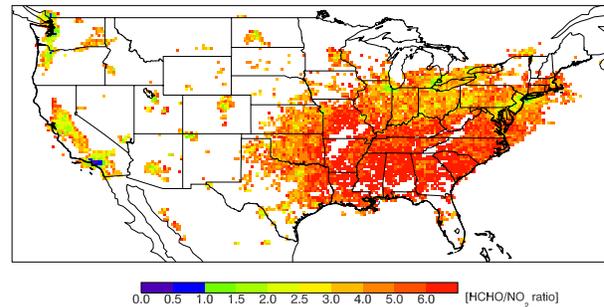


Fig. 1. The monthly-average OMI HCHO/NO<sub>2</sub> for August 2006. White areas in the figure indicate where the HCHO data values are below the detection limit and/or the NO<sub>2</sub> data values are < 2.5×10<sup>15</sup> molecules cm<sup>-2</sup>. The color scale is saturated above a ratio of 6.

Most cities and regions exhibited a wide range of monthly ratios during our study period. 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.

### 3.1 Variations in NO<sub>x</sub>

OMI NO<sub>2</sub> indicates that most areas of the U.S. show a substantial decrease between 2007 and 2005, 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<sub>x</sub> Budget Trading Program (NBTP) of the Environmental Protection Agency (EPA, 2008a). Additional decreases in automobile emissions occurred under the Tier 2 Vehicle and Gasoline Sulfur Program. Areas of

the West had higher NO<sub>2</sub> in 2007 than 2005 because of widespread fires (Grossi, 2008). For instance, the Zaca wildfire, which burned north of Los Angeles, was one of the largest in California's history.

### 3.2 Variations in HCHO

There was significant variation in HCHO during the summers of 2005-2007, 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<sub>x</sub>-limited with increasing temperature; this is important as high ozone episodes are more frequent during heatwaves.

### 3.3 Variations in HCHO/NO<sub>2</sub>

There is a clear correlation of both the ratio and HCHO with temperature in most cities in the eastern U.S. where isoprene emissions are typically high, particularly in the southeastern U.S. (e.g., Atlanta). In these cities, the variability in isoprene emissions dominates the variability in the ratio. In cities where isoprene emissions are lower, the temperature dependence of the ratio is muddled by the downward trend in NO<sub>x</sub> emissions. For instance in Chicago, the 2007 ratios were higher than the 2005 ones because of the downward trend in NO<sub>x</sub> emissions (Figure 2).

### 3.4 Variations in Ozone

Average observed surface ozone in the U.S. during the ozone season decreased by 1% from 2001-2007, but it is well known that ozone formation is temperature dependent (e.g., Camalier, Cox and Dolwich (2007) and references therein). When adjusted for weather, the surface ozone decreased by 8% (EPA (2008b)) during the same period, largely because of emission controls on NO<sub>x</sub> emissions as discussed above. In the eastern U.S., the observed surface ozone increased from 2005 to 2007, but when adjusted for weather, there was a slight decrease, ~1%.

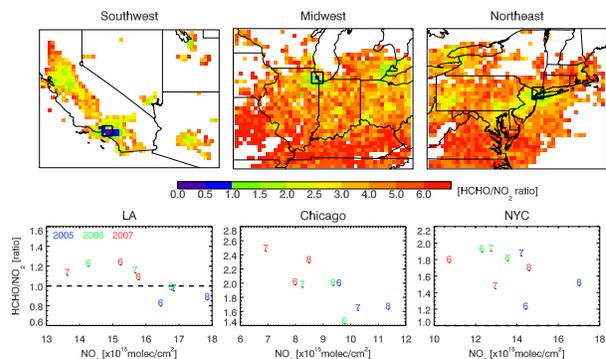


Fig. 2. (top) The monthly-average OMI HCHO/NO<sub>2</sub> for the Southwest, Midwest, and Northeast for August 2006. The color scale is saturated above a ratio of 6. (bottom) Metropolitan-average HCHO/NO<sub>2</sub> vs. NO<sub>2</sub> for June (6), July (7), and August (8) of 2005-2007 for Los Angeles (LA), Chicago, and New York (NYC). The HCHO/NO<sub>2</sub> and NO<sub>2</sub> 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.

## 4. IMPLICATIONS FOR OZONE CHEMISTRY

The implied ozone-precursor sensitivity from the OMI HCHO/NO<sub>2</sub> reported here is broadly consistent with results from studies using models and *in situ* data to understand the dependence of ozone on NO<sub>x</sub> 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<sub>x</sub>-limited at some point downwind (Sillman, 1995; Daum *et al.*, 1996). Philadelphia and Houston appear to have mixed NO<sub>x</sub>-radical-limitations (Daum *et al.*, 2004; Kleinman *et al.*, 2005), while Atlanta is primarily NO<sub>x</sub>-limited (Cardelino and Chameides, 1995; Sillman *et al.*, 1995). The OMI HCHO/NO<sub>2</sub> 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<sub>x</sub>-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<sub>x</sub>-limited conditions elsewhere (Milford *et al.*, 1989, 1994).

If the OMI HCHO/NO<sub>2</sub> < 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<sub>x</sub>-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<sub>x</sub>-radical limitations. Somewhat higher ratios are found in other urban centers. The highest ratios, suggesting strongly NO<sub>x</sub>-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<sub>2</sub>) is consistent with the relative ordering based on *in situ* studies (from radical-limited to NO<sub>x</sub>-limited).

The implied result from HCHO/NO<sub>2</sub> tends to be somewhat more NO<sub>x</sub>-limited than in the *in situ* studies. It is possible that recent reductions in NO<sub>x</sub> emissions have caused more NO<sub>x</sub>-limited conditions than indicated by the earlier studies. Figure 2 shows the metropolitan-average ratios as a function of the tropospheric NO<sub>2</sub> 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<sub>2</sub> columns with a concomitant increase in the ratios from 2005 to 2007. Reducing the positive summertime bias in the OMI NO<sub>2</sub> would imply even more NO<sub>x</sub>-limited conditions.

## 5. SUMMARY

We presented a space-based assessment of the sensitivity of surface ozone formation in summer using the OMI HCHO and NO<sub>2</sub> data. We found that there was a general increase in the ratio of HCHO to NO<sub>2</sub> that was associated with the decrease in anthropogenic NO<sub>x</sub> emissions that occurred from 2005 to 2007. While there are uncertainties in the link between ambient HCHO/NO<sub>2</sub> and ozone-precursor sensitivity, the change in HCHO/NO<sub>2</sub> suggests that ozone formation became more sensitive to NO<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub>-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<sub>2</sub> 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<sub>2</sub> column ratio from NO<sub>x</sub>- to radical-limited conditions, and examine the effects of the assumed trace gas profiles on the OMI retrievals.

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