The Sensitivity of Surface Ozone Formation as Inferred from OMI Formaldehyde and Nitrogen Dioxide Tropospheric Column Data

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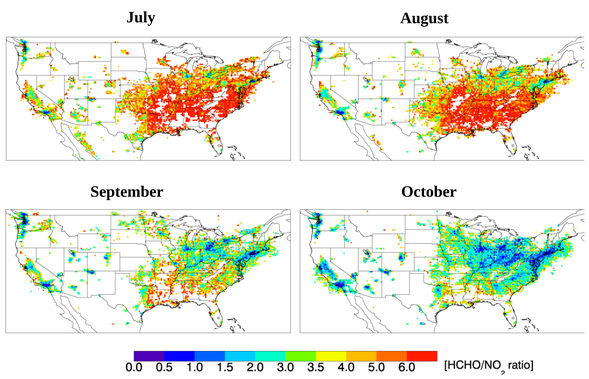
Abstract

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 (HCHO) 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 emissions 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 on reducing NO_x emissions, even in cities which have historically benefited from reductions in both NO_x and VOC emissions (e.g., Los Angeles, New York City).

$HCHO/NO_2$: Air Quality Indicator

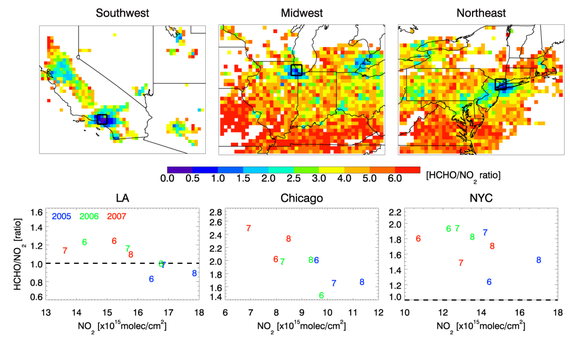
An air quality indicator indicates which ozone precursor species, volatile organic compounds (VOCs) or nitrogen oxides (NO_x), limits the instantaneous rate of ozone production. Sillman [1995] (*Sillman, S. The use of NO_y, H_2O_2 and HNO_3 as indicators for O_3-NO_x-ROG sensitivity in urban locations. J. Geophys. Res., 100, 14175-14188, 1995***) pioneered the use of ratios of *in situ* data (e.g., H_2O_2/HNO_3) to provide guidance on the development of emission control strategies with the intent to reduce unhealthy levels of surface ozone. Martin et al. [2004] (***Martin, R., A. Fiore, and A. Van Donkelaar, Space-based diagnosis of surface ozone sensitivity to anthropogenic emissions, Geophys. Res. Lett. 31, L06120, doi:10.1029/2004GL019416, 2004***) applied this concept to the ratio of the tropospheric columns of HCHO and NO_2 from the GOME instrument. Here we use the same ratio from the OMI, which has a finer horizontal resolution than GOME.**



The figure shows the ratio over the U.S. from July to October, 2006. During summer, the ratio over most of the U.S. is greater than one, indicating that the instantaneous ozone production rate is limited by the concentration of NO_x. However, in the transition from summer to fall, the ratio changes for the following reasons: 1) natural isoprene emissions, which dominate HCHO in much of the eastern U.S., decrease rapidly in September on average, and 2) NO_x partitioning favors NO_2 in fall, but less so in summer. The color scale is saturated above a ratio of 6.

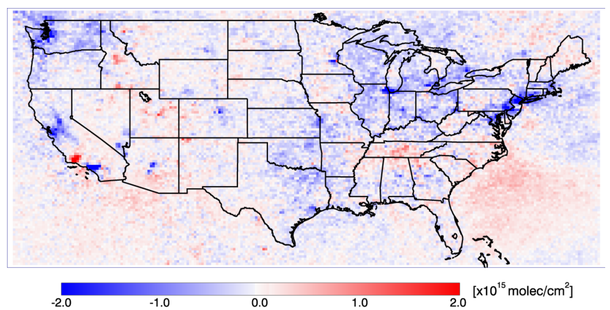
$HCHO/NO_2$: Variability from Variations in NO_x

The figure shows the monthly-average $HCHO/NO_2$ for the southwestern, Midwestern, and northeastern U.S for August 2006. Many urban areas (e.g., Los Angeles, Chicago, and New York City) have downtown ratios less than 1, indicating that the instantaneous ozone production rate is limited by the concentration of VOCs there.

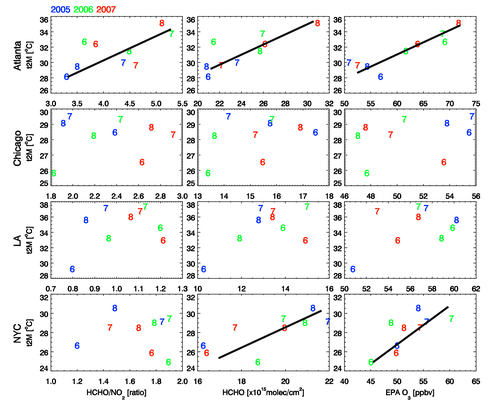


The bottom row of the figure shows the monthly $HCHO/NO_2$ vs. NO_2 concentration for June (6), July (7), and August (8) of 2005-2007 for the Los Angeles (LA), Chicago, and New York City (NYC) metropolitan areas, which are delineated by black boxes in the top row panels of the figure. The horizontal dashed line shows where the transition ($HCHO/NO_2 \sim 1$) occurs between NO_x-limited (above the line) and VOC-limited (below the line) regimes. The figure shows that decreasing NO_x concentrations from 2005 to 2007 increased the ratio, indicating that ozone production became more NO_x-limited.

NO_x emissions in the U.S. decreased from 2005 to 2007. Point source emissions were 10% lower in 2007 than 2005 due to controls imposed under the NO_x Budget Trading Program of EPA. Automobile emissions decreased due to controls imposed by the Tier 2 Vehicle and Gasoline Sulfur Program. This decrease can be seen in the OMI tropospheric NO_2 column, taken here as the average of June-August 2007 minus the same period in 2005. Increases in the western U.S. are associated with wildfires that occurred in 2007.

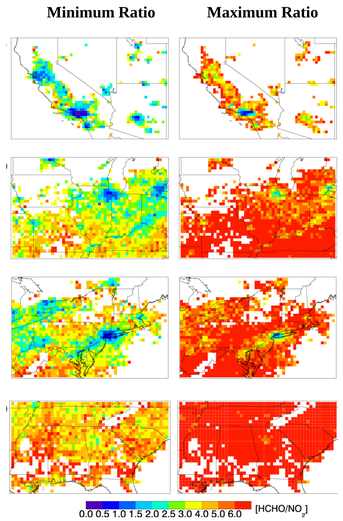


$HCHO/NO_2$: Variability from Variations in Isoprene



While there were no clear trends in HCHO during the summers of 2005-2007 (not shown), there was significant variation, mainly associated with the temperature dependence of emissions of biogenic isoprene. This implies that cities, which have isoprene contributing significantly to their total VOC reactivities, become more NO_x-limited during heat waves; this is important as high ozone episodes are more frequent during heatwaves than in cooler periods. This effect is most clearly seen in cities with high biogenic emissions (e.g., Atlanta and NYC).

$HCHO/NO_2$: Range of Ratios



The figure shows that there was a considerable range of monthly ratios during summer from 2005-7 (i.e., 9 months in all). The minimum monthly $HCHO/NO_2$ is shown in the left column and the maximum is shown in the right column.

While cities, such as Chicago, New York City, and Phoenix, exhibited both NO_x-limited (i.e., $HCHO/NO_2 > 1$) and VOC-limited (i.e., $HCHO/NO_2 < 1$) conditions during our study period, only downtown Los Angeles was consistently VOC-limited.