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Article

Inferring Changes in Summertime Surface Ozone–NO_x–VOC Chemistry over U.S. Urban Areas from Two Decades of Satellite and Ground-Based Observations

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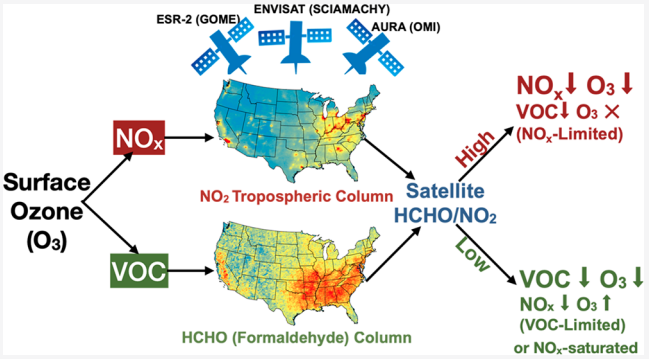
ABSTRACT: Urban ozone (O_3) formation can be limited by NO_x, VOCs, or both, complicating the design of effective O_3 abatement plans. A satellite-retrieved ratio of formaldehyde to NO_2 ($HCHO/NO_2$), developed from theory and modeling, has previously been used to indicate O_3 formation chemistry. Here, we connect this space-based indicator to spatiotemporal variations in O_3 recorded by on-the-ground monitors over major U.S. cities. High-O_3 events vary nonlinearly with OMI HCHO and NO_2, and the transition from VOC-limited to NO_x-limited O_3 formation regimes occurs at higher $HCHO/NO_2$ value (3 to 4) than previously determined from models, with slight intercity variations. To extend satellite records back to 1996, we develop an approach to harmonize observations from GOME and SCIAMACHY that accounts for differences in spatial resolution and overpass time. Two-decade (1996–2016) multisatellite $HCHO/NO_2$ captures the timing and location of the transition from VOC-limited to NO_x-limited O_3 production regimes in major U.S. cities, which aligns with the observed long-term changes in urban–rural gradient of O_3 and the reversal of O_3 weekend effect. Our findings suggest promise for applying space-based $HCHO/NO_2$ to interpret local O_3 chemistry, particularly with the new-generation satellite instruments that offer finer spatial and temporal resolution.



INTRODUCTION

Human exposure to ground-level ozone (O_3) is associated with increased risk of cardiovascular and respiratory diseases, and has been linked to 250 000 O_3-related premature deaths in 2015 globally,[1] and 11 700 deaths over the United States (U.S.).[2] In the troposphere, O_3 is produced from photochemical reactions involving its precursors: nitrogen oxides (NO_x: NO + NO_2) and volatile organic compounds (VOCs). It is well established that O_3 formation throughout much of the troposphere is largely controlled by the availability of NO_x (NO_x-limited), but in regions with high NO_x emissions, such as metropolitan areas, O_3 formation can be VOC-limited or in transition between these regimes.[3,4] Identifying the most effective emissions control strategy to lower the O_3 exposure of a densely populated metropolitan area requires knowledge of the local O_3 formation chemistry.

While current satellite-based spectrometers do not retrieve ground-level O_3 abundances, they have provided continuous global observations for two species indicative of O_3 precursors, namely nitrogen dioxide (NO_2) for NO_x,[5−7] and formaldehyde (HCHO) for VOC,[8−13] for over two decades. In theory, the ratio of HCHO to NO_2 ($HCHO/NO_2$) reflects the relative availability of NO_x and total organic reactivity to hydroxyl radicals.[14,15] We build here upon earlier work proposing this satellite-based $HCHO/NO_2$ as an indicator of O_3 sensitivity to its NO_x versus VOC precursors.[16−19] All of these prior studies use theory as represented in models to link column-based $HCHO/NO_2$ with surface O_3 sensitivity.[16−19] Models, however, can be biased,[20] and airborne measurements suggest large uncertainty in the $HCHO/NO_2$ threshold values between O_3 production regimes.[21] Also, modeled and satellite retrieved HCHO and NO_2 often disagree,[19,22,23] and the difference varies by satellite retrievals.[19,24] To overcome these limitations, we derive the threshold values marking transitions in O_3 formation regimes entirely from observations by directly connecting space-based $HCHO/NO_2$ with ground-based measurements of O_3.

Over the U.S., nationwide anthropogenic NO_x emissions are estimated to have declined by 31% from 1997 to 2016.[25] Correspondingly, satellite-retrieved NO_2 tropospheric columns are declining,[7,26,27] although relating NO_2 columns directly to

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NO_x emissions requires accounting for lifetime changes,[28] and accurate partitioning between anthropogenic versus background sources of NO_2.[22,29] Despite the widespread decrease of NO_x emissions, observed O_3 trends are heterogeneous in space and time: decreasing in summer over less urbanized areas, and increasing in winter, night, and urban cores, due to the nonlinear relationship between O_3 production and NO_x.[30−33] As NO_x emissions continue to decline, O_3 formation over VOC-limited urban areas is transitioning toward the NO_x-limited regime,[19,34−36] but the observed long-term O_3 trends may also reflect changes in VOC reactivity,[37] as well as meteorology.[38] U.S. anthropogenic VOC emissions from vehicles and industry are estimated to have declined by 22% from 1997 to 2016,[25] while volatile chemical product emissions may be growing.[39] Regionally, summertime U.S. VOC emissions are dominated by biogenic sources, particularly highly reactive isoprene, that vary with meteorology and vegetation density.[40]

A key policy-relevant metric is the turning point between VOC-limited and NO_x-limited O_3 formation regimes. It remains uncertain as to which (and whether) U.S. cities have reached this turning point, and how closely long-term changes in O_3 follow transitions in O_3 production regimes, particularly in light of the strong sensitivity of O_3 to meteorological variability.[41,42] Previous studies used observations of HCHO/NO_2 from single satellite instrument, such as Ozone Monitoring Instrument (OMI), which dates back to 2005.[17−19] The newly developed, consistently retrieved multisatellite HCHO and NO_2 products, available from the EU FP7-project Quality Assurance for Essential Climate Variables (QA4ECV),[43−49] offer a new opportunity to extend the record back by a decade to 1996. We first assess if space-based HCHO/NO_2 captures the nonlinearity of O_3 chemistry by matching daily OMI observation with ground-based O_3 measurements over polluted areas. We find a robust relationship between space-based HCHO/NO_2 and the O_3 response patterns that is qualitatively similar but quantitatively distinct across cities. Next, we link the long-term changes in the harmonized multisatellite HCHO/NO_2 to changes in urban−rural O_3 gradients and the O_3 weekend effect from 1996 to 2016. We show that this multisatellite HCHO/NO_2 complements ground-based networks by providing insights into spatial heterogeneity and long-term evolution of O_3 formation regimes, which could be valuable for future applications over regions lacking dense ground-based monitors.

MATERIALS AND METHODS

Multisatellite Observations of O_3 Precursors. We use 21-year (1996−2016) multisatellite products of tropospheric NO_2 (Ω_{NO2}) and HCHO (Ω_{HCHO}) vertical columns developed under the QA4ECV project that retrieves products consistently from three satellite instruments: Global Ozone Monitoring Experiment (GOME), SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) and OMI.[43−49] The nadir resolution is 24 × 13 km^2 for OMI, 60 × 30 km^2 for SCIAMACHY and 320 × 40 km^2 for GOME. The overpass time is around 1:30 PM local time for OMI, 10:00 AM for SCIAMACHY, and 10:30 AM for GOME. The a priori vertical profiles used for QA4ECV products are obtained from the same chemical transport model (TM5-MP),[50] which are better suited for analyzing space-based HCHO/NO_2 than products developed with different prior profiles. The retrieval algorithms are briefly described in the Supporting Information (SI, S1). We select daily Level-2 observations with (1) no processing error; (2) less than 10% snow or ice coverage; (3) solar zenith angle less than 80° for NO_2, and 70° for HCHO; (4) cloud radiance fractions <0.5. For OMI, we exclude the first and last five rows, which contain large pixels retrieved on the swath edges, and select the rows 5 to 23, which are unaffected by row anomalies throughout the study period.[51] We grid Level-2 swaths by calculating area weighted averages (S2).

Seasonal Harmonization of GOME, SCIAMACHY, and OMI. To study the long-term changes in HCHO, NO_2, and HCHO/NO_2, we construct seasonal average Ω_{HCHO} and Ω_{NO2} from the three satellites by calculating the area-weighted averages from 1996 to 2016. The long-term satellite records are based on OMI observations for the years after 2005, the harmonized SCIAMACHY observations for 2002−2004, and harmonized GOME observations before 2002. Even with the consistent algorithms for retrieving NO_2 and HCHO under the QA4ECV project, multisatellite retrievals still need to be harmonized to account for differences in horizontal resolution, overpass time, and any instrumental offsets. We adjust SCIAMACHY and GOME HCHO and NO_2 data with reference to OMI, because OMI has the finest spatial resolution, and the satellites are best able to capture chemical conditions controlling O_3 production during the OMI afternoon overpass, when mixing depths and O_3 production rates are closest to their daily maxima. We first adjust SCIAMACHY Ω_{NO2} by decomposing the instrumental differences between SCIAMACHY and OMI into two factors: (1) those associated with different overpass timing or instrumental offsets, which we estimate as the difference in OMI Ω_{NO2} and SCIAMACHY Ω_{NO2} during the overlap period (2005−2011) at a coarse resolution at which we assume the difference is independent of the instrumental resolution ($\overline{\Delta\Omega_{NO2\_Coarse}}$, Figure S1); (2) those caused by resolution (RC_{NO2}, Figure S2), which we estimate as the relative change in OMI Ω_{NO2} at a fine-resolution (0.125°× 0.125°) versus a coarse-resolution (2° × 0.5°) grid that is close to the nadir resolution of GOME (RC_{NO2_OMI}, S3). While previous studies assumed constant resolution correction factors,[27,52] we find that RC_{NO2} varies with time, especially over urban areas, and the spatial gradients in Ω_{NO2} are larger when Ω_{NO2} is higher earlier in the record (Figure S3). Assuming a time-invariant RC_{NO2} may thus underestimate the steepness of spatial gradients at high Ω_{NO2}. We apply the relative temporal variability estimated from RC_{NO2_SCIA} to the long-term summertime average RC_{NO2_OMI} ($\overline{RC_{NO2\_OMI}}$). RC_{NO2_OMI} and RC_{NO2_SCIA} correlate well in time (Figure S4), though their absolute values differ. Combining these factors, the adjusted SCIAMACHY Ω_{NO2} (Ω_{NO2_adj}) at year yr season m (we focus on summer, June−July−August) and grid cell x is estimated as follows:

$$\Omega_{NO2\_adj}(x_f, yr, m) = (\Omega_{NO2\_coarse}(x_c, yr, m) + \overline{\Delta\Omega_{NO2\_Coarse}}(x_c, m)) \times RC_{NO2}(x_f, x_c, yr, m) \quad (1)$$

where $\overline{\Delta\Omega_{NO2\_Coarse}}(x_c, m)$ is the difference between OMI Ω_{NO2} and SCIAMACHY Ω_{NO2} at coarse resolution averaged during the overlap period (n years):

$$\overline{\Delta\Omega_{NO2\_Coarse}}(x_c, m) = \frac{1}{n}\sum_{yr=2005}^{yr=2011}(\Omega_{NO2\_OMI\_coarse}(x_c, yr, m) - \Omega_{NO2\_SCIA\_coarse}(x_c, yr, m)) \quad (2)$$

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where RC_{NO2} (x_f, x_c, yr, m) is the resolution correction factor, x_f is the grid cell at fine resolution, and x_c is the coarse grid cell where x_f falls.

$$RC_{NO2}(x_f, x_c, yr, m) = \overline{RC_{NO2\_OMI}}(x_f, x_c, m) \times \frac{RC_{NO2\_SCIA}(x_f, x_c, yr, m)}{\overline{RC_{NO2\_SCIA}}(x_f, x_c, m)} \quad (3)$$

$$\overline{RC_{NO2\_OMI}}(x_f, x_c, m) = \frac{1}{n}\sum_{yr=2005}^{yr=2016} \frac{\Omega_{NO2\_OMI\_fine}(x_f, yr, m)}{\Omega_{NO2\_OMI\_coarse}(x_c, yr, m)} \quad (4)$$

$$RC_{NO2\_SCIA}(x_f, x_c, yr, m) = \frac{\Omega_{NO2\_SCIA\_fine}(x_f, yr, m)}{\Omega_{NO2\_SCIA\_coarse}(x_c, yr, m)} \quad (5)$$

$$\overline{RC_{NO2\_SCIA}}(x_f, x_c, m) = \frac{1}{n}\sum_{yr=2002}^{yr=2012} RC_{NO2\_SCIA}(x_f, x_c, yr, m) \quad (6)$$

To harmonize GOME Ω_{NO2}, we apply the same correction factors that we applied to SCIAMACHY except that the temporal variability in RC_{NO2} is driven by the variability in RC_{NO2} of GOME. We do not adjust for any systematic differences between GOME and SCIAMACHY at coarse resolution, because the overpass time is close, and the overlap period (August 2002 to June 2003) does not cover an entire summer.

We similarly decompose the instrumental differences in Ω_{HCHO} to differences caused by resolution (RC_{HCHO_OMI}) versus overpass time ($\Delta\Omega_{HCHO\_Coarse}$). We find that RC_{HCHO_OMI} is much smaller than $\Delta\Omega_{HCHO\_Coarse}$, and the spatial pattern of RC_{HCHO_OMI} tends to be noisy (Figure S5). We find little resolution dependence of the difference between OMI Ω_{HCHO} and SCIAMACHY Ω_{HCHO}, likely due to widespread summertime isoprene emissions, the dominant summertime precursor to HCHO over the U.S., as well as HCHO produced during oxidation of longer-lived VOCs.[51] Therefore, we do not apply a resolution correction to SCIAMACHY Ω_{HCHO} or GOME Ω_{HCHO}. We calculate the climatology of the systematic difference ($\overline{\Delta\Omega_{HCHO}}$) between OMI Ω_{HCHO} and SCIAMACHY Ω_{HCHO} at 0.25°× 0.25° resolution, and adjust Ω_{HCHO} (Ω_{HCHO_adj}) by applying these differences to the original SCIAMACHY and GOME Ω_{HCHO}(Ω_{HCHO_Ori}) for the years without OMI observations:

$$\Omega_{HCHO\_adj}(x, yr, m) = \Omega_{HCHO\_Ori}(x, yr, m) + \overline{\Delta\Omega_{HCHO}}(x, m) \quad (7)$$

$$\overline{\Delta\Omega_{HCHO}}(x, m) = \frac{1}{n}\sum_{yr=2005}^{yr=2011} (\Omega_{HCHO\_OMI}(x, yr, m) - \Omega_{HCHO\_SCIA}(x, yr, m)) \quad (8)$$

The systematic difference is mainly attributed to the diel cycle in HCHO.[54] As we adjust the morning retrieval of HCHO with respect to the afternoon retrieval, upward adjustment is expected due to the diel cycle in temperature, which controls biogenic VOC emissions, and in OH, which controls HCHO production from its parent VOCs (Figure S5).[40,55]

Connecting Satellite HCHO/NO_2 with Ground-Based O_3 Observations. We use observations of hourly O_3 from the U.S. Air Quality System (AQS) from 1996 to 2016. We first aggregate daily OMI data (used in Figure 1) by sampling the gridded daily OMI Ω_{HCHO} and Ω_{NO2} (0.125° × 0.125°) coincident with ground-based observations of O_3. Retrievals from SCIAMACHY and GOME are not used for daily analysis because harmonization at the daily time scale is unrealistic. We average hourly O_3 measurements at 1 PM and 2 PM local time to match the OMI overpass time. We first select 1221 O_3 monitors located in polluted regions, defined as summertime 2005−2016 average OMI $\Omega_{NO2} > 1.5 \times 10^{15}$ molecules/cm^2. OMI retrieved Ω_{NO2} and Ω_{HCHO} are sampled daily over AQS O_3 sites for the warm season (May to October) from 2005 to 2016, yielding over 700 000 paired observations, and we calculate the probability of O_3 exceeding 70 ppb from this data set. Next, we focus on seven metropolitan areas to evaluate the satellite-based HCHO/NO_2 and study the long-term evolution of O_3 production regimes from 1996 to 2016, as the resolution of the harmonized satellite products (~10 km) is more suitable for studying cities spanning larger areas. We first select Los Angeles, New York, and Chicago, the three most populous cities in the U.S.A. We then include four additional cities: Washington, DC. Pittsburgh, Atlanta, and Houston, where long-term ground-based observations of O_3 and NO_x are available, and which also cover different U.S. climate regions. To assess if satellite HCHO/NO_2 captures the long-term changes in O_3 production regimes, we include ground-based measurements of O_3 from 1996 to 2016 in each of the seven cities and their surrounding rural areas, from which we analyze the changes in urban−rural O_3 gradients, and the weekday-to-weekend differences defined as weekend (Saturday−Sunday) O_3 − weekday (Tuesday−Friday) O_3.

RESULTS AND DISCUSSION

Nonlinear O_3 Chemistry Captured by Satellite-Based HCHO/NO_2. We first evaluate if satellite-based HCHO/NO_2 can capture the well-established nonlinearities in O_3 chemistry. Pusede et al.[56] proposed a conceptual framework that uses the observed O_3 exceedance probability to interpret the nonlinear dependence of O_3 production on precursor emissions. This framework assumes stagnant meteorology so that measured O_3 is sensitive to its local chemical production, and the local changes in chemical or depositional loss are insignificant on average. We follow this approach by calculating the probability that surface O_3 exceeds 70 ppbv (high-O_3 probability) at OMI overpass, given the OMI Ω_{NO2} and Ω_{HCHO} (Figure 1a). Figure 1a, derived solely from observations, resembles O_3 isopleths that are typically generated with analytical models.[4,57] Consistent with O_3 isopleths, three regimes can be roughly identified from Figure 1a: (1) high Ω_{NO2} and low Ω_{HCHO}, where high O_3 events become more likely at lower NO_x, indicating NO_x-saturated (or VOC-limited) chemistry; (2) low Ω_{NO2} and relatively high Ω_{HCHO}, where the probability of high O_3 events increases with Ω_{NO2}, indicating NO_x-limited chemistry; and (3) high Ω_{NO2} and high Ω_{HCHO}, where the probability of high-O_3 events peaks, and increases with both Ω_{NO2} and Ω_{HCHO}. While Figure 1a resembles this overall O_3−NO_x−VOC chemistry, the high O_3 probabilities span a broad range, with an uncertain, blurry transition between NO_x-limited and VOC-limited regimes. The lack of sharp transitions between O_3 production regimes in Figure 1a likely reflects the influence from other factors such as varying meteorology, chemical and depositional loss of O_3, noisy satellite retrievals, the spatial mismatch between the area satellite observations and the point measurements of surface O_3, and in some cases, small sample size that lacks statistical power to calculate high-

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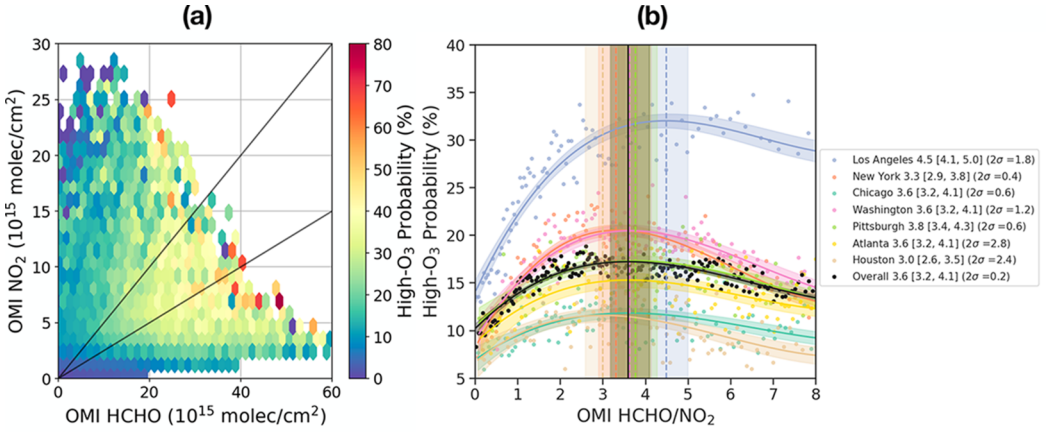

Figure 1. (a) Probability of O_3 exceeding 70 ppbv (high-O_3 probability) as a function of OMI Ω_{NO2} and Ω_{HCHO}. All ground-based hourly O_3 observations (averaged at 1 PM and 2 PM local time) in the warm season (May to October) from 2005 to 2016 are aggregated based on corresponding daily OMI Ω_{NO2} and Ω_{HCHO} (interval: 0.5×10^{15} molecules/cm^2). We only include sites over polluted regions (defined as long-term average OMI $\Omega_{NO2} > 1.5 \times 10^{15}$ molecules/cm^2). The probability is the number of observations with O_3 higher than 70 ppbv divided by the total number of observations at given OMI Ω_{NO2} and Ω_{HCHO}. The black lines delineate OMI HCHO/NO_2 values of 2 and 4. (b) Probability of O_3 exceeding 70 ppbv as a function of OMI HCHO/NO_2 for all selected sites (black) and seven cities individually. High-O_3 probability is calculated by first matching hourly O_3 observations with daily OMI HCHO/NO_2, dividing these paired observations to 100 (200 for black dots) bins based on OMI HCHO/NO_2, and then calculating the high-O_3 probability (y axis) for each OMI HCHO/NO_2 bin (x axis, labeled as a dot). The solid lines are fitted third order polynomial curves, and the shading indicates 95% confidence intervals. The vertical lines indicate the maximum of the fitted curve (labeled in the legend), and the vertical shading represents the range over the top 10% of the fitted curve (regime transition). The uncertainty is two standard deviation (2σ or 95% confidence interval) of the derived peaks using statistical bootstrapping by iteratively running the model on 50 randomly selected subsets of 30 data pairs.

O_3 probability. Despite these uncertainties, Figure 1a qualitatively illustrates the nonlinear relationship between the occurrence probability of high-O_3 events and the HCHO and NO_2 proxies for precursor VOC and NO_x, respectively.

Having established this qualitative approach, we next derive quantitative relationships by calculating high-O_3 probabilities at given OMI HCHO/NO_2 and examining their statistical relationship across different U.S. cities. We investigate three possible empirical relationships by applying moving average, second-order polynomial and third-order polynomial models to observations over seven U.S. cities (Figure S6). The third-order polynomial model is used to derive the maximum high-O_3 probability (the peak of the curve in Figure 1b), because it best fits the data, with the smallest uncertainty (estimated with statistical bootstrapping, Figure S6) and higher correlation coefficient (R) than the second-order model. Assuming that the peak of the curve marks the transition from VOC-limited to NO_x-limited regime,[56] we define the transitional regime as the range of HCHO/NO_2 spanning the top 10% of the high-O_3 probability distribution.

Aggregating over all available observations used in Figure 1a, we find that the high-O_3 probability peaks at HCHO/NO_2 = 3.6, with the transitional regime ranging from 3.2 to 4.1, hereafter denoted as [3.2, 4.1]. Evaluating the relationship for the seven cities individually, we find robust nonlinear relationships between the high-O_3 probability and OMI HCHO/NO_2, despite differences in the overall high-O_3 probability, which reflect other factors such as emissions, meteorology, and transport. The HCHO/NO_2 marking the regime transition varies slightly among these cities, which is highest for LA (4.5 [4.1, 5.0]), and lowest for Houston (3.0 [2.6, 3.5]). We evaluate the uncertainty in the derived peaks using statistical bootstrapping by iteratively applying the model to 50 randomly selected subsets of the data. We define the uncertainty as two standard deviations (2σ or 95% confidence interval) from the derived maxima. The uncertainty is generally within 2 except for Atlanta (2σ = 2.8) and Houston (2σ = 2.4), where the fitted curve is relatively flat. Separating the observations into two periods (before and after 2009), the derived thresholds are slightly higher in the later period, which may reflect more high HCHO/NO_2 values in the recent period, driving the curve to move toward a higher turning point, but the uncertainty also increases as we halve the number of observations (Figure S7).

The HCHO/NO_2 thresholds derived in Figure 1b are higher than previously reported model-based values,[16,17,19] implying that at the same HCHO/NO_2, our observation-based approach suggests O_3 production is more VOC-limited. The difference originates from the distinct approaches used to link HCHO/NO_2 with O_3 production regimes. Previous modeling studies derive the threshold by simulating the response of surface O_3 to an overall reduction in NO_x or NMVOC emissions with coarse resolution models, which best capture regional as opposed to local O_3−NO_x−VOC sensitivity.[16,19] Our thresholds derived with in situ observations should be more indicative of the local O_3 chemistry, including the effect of NO_x titration over urban areas. Schroeder et al.[21] also found VOC-limited chemistry occurring at high HCHO/NO_2 (1.3−5.0) in their analysis of column HCHO/NO_2 from aircraft measurements.

Declining NO_2 Over Time. Figure 2a shows summertime average Ω_{NO2} over seven metropolitan areas in 1996−2000 versus 2013−2016 produced from the harmonized multi-satellite data. NO_2 is concentrated over urban areas and near combustion sources. Applying the resolution corrections to GOME NO_2 reveals spatial gradients not detected directly with the coarse resolution of GOME (Figure S8). We find the largest urban−rural gradients in NYC and LA, where Ω_{NO2} varies by a factor of 10 within their core-based statistical areas (CBSA, outlined in Figure 2). Satellite observations show large

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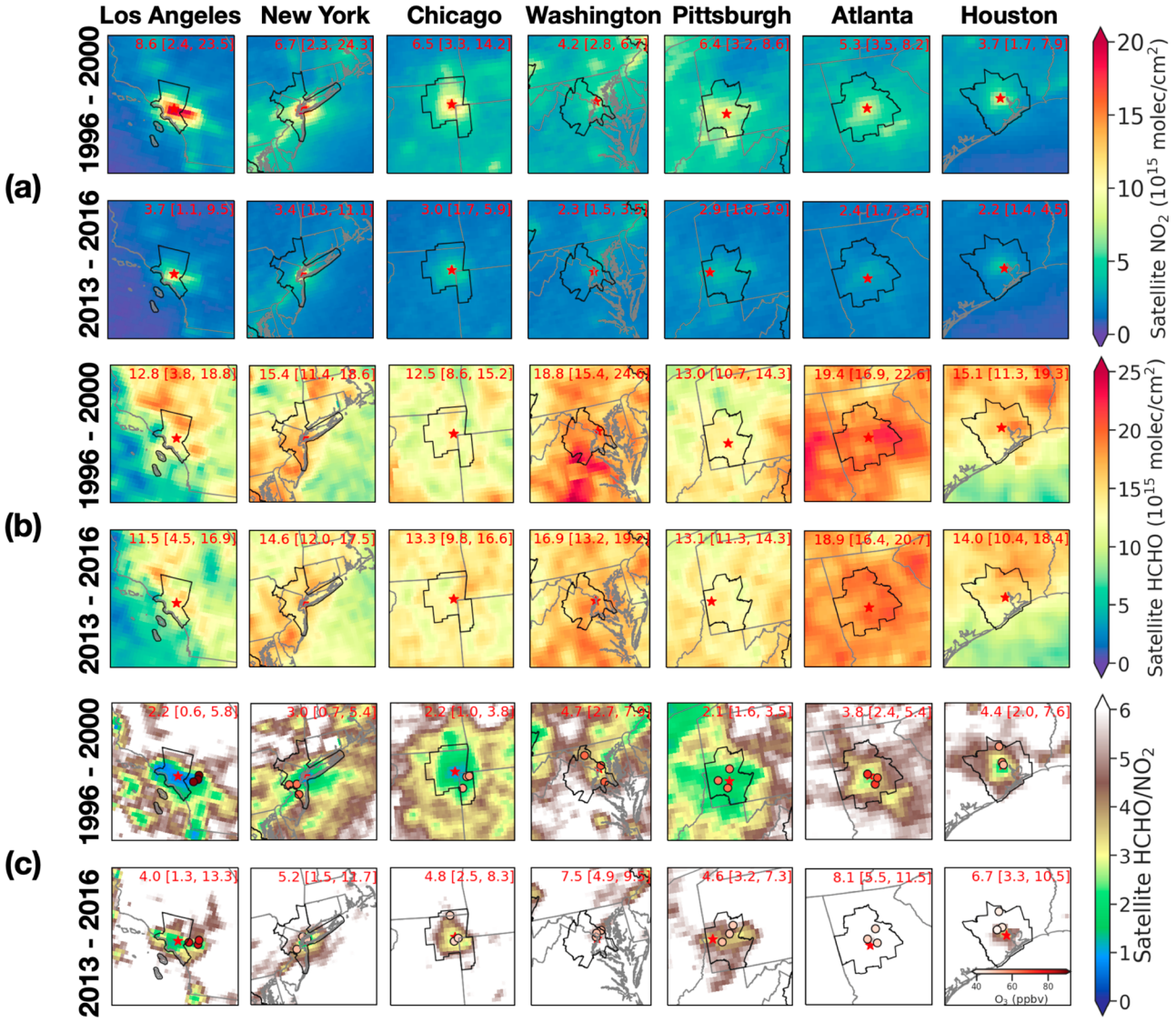

Figure 2. Maps of satellite-based summertime average: (a) ΩNO_2, (b)$\Omega HCHO$, and (c) $HCHO/NO_2$ for seven cities (New York, Los Angeles, Chicago, Washington, DC, Pittsburgh, Atlanta, and Houston) in 1996−2000 and 2013−2016. The white area in (c) indicates $HCHO/NO_2$ above 6. The numbers show the mean and the range of Ω_{NO2}, Ω_{HCHO}, and $HCHO/NO_2$ for each core-based statistical area (CBSA, outlined in black). The red star shows the location with highest Ω_{NO2} in the CBSA. The red circles in the bottom two rows label the locations of three AQS sites where the highest O_3 occurred in the region, and the color represents the summertime mean O_3 (color bar inset in bottom right panel). Maps for 2001−2004, 2005−2008, and 2009−2012 are shown in Figure S11.

decreases in Ω_{NO2} over the past two decades, consistent with previous studies (Figure 2a).[7,52,58] The mean Ω_{NO2} in each CBSA has decreased by 40% (Atlanta) to 56% (LA) in 2013−2016 relative to 1996−2000. We use ground-based measurements of NO_x to evaluate the long-term changes of satellite-based Ω_{NO2}, since our approach assumes Ω_{NO2} is a good indicator of ground-level NO_x. Satellite-based Ω_{NO2} captures the decrease of ground-level NO_x over LA, Chicago, and Washington to within 5%, but underestimates the decrease over NYC, Pittsburgh, and Houston, while overestimating the decreases in Atlanta (Figure S9). Both satellite-based Ω_{NO2} and ground-level NO_x show the largest decline before 2004 over Pittsburgh, associated with emission controls on coal-fired power plants.[59,60] Satellite-based Ω_{NO2} does not show decreases over NYC and Houston before 2000, but ground-based NO_x suggests large decreases (Figure S10). This discrepancy is likely due to the coarse resolution of GOME; while we have corrected the spatial patterns of GOME Ω_{NO2}, the total Ω_{NO2} may still be biased low, due to the contributions from the nearby ocean where NO_2 is low. Satellite-based Ω_{NO2} does capture the large decreases between 2005 and 2012 in NYC and Houston (Figure S10). Over LA, Chicago, Washington, and Atlanta, both satellite and ground-based observations suggest the largest reductions occurred between 2005 to 2012 (Figure S10), when emission controls on power plants and stricter vehicle emission standards were implemented.[26,61] The substantial decrease in 2008−2010 may also reflect the economic recession.[7,61] In the most recent period (2013−2016), satellite data show flattening trends in Ω_{NO2} in all seven cities (Figure S10), possibly related to a slowdown of NO_x emission reductions,[29] changes in NO_x lifetime,[28] and the relatively larger influence of upper tropospheric NO_2 as anthropogenic contributions decline.[22]

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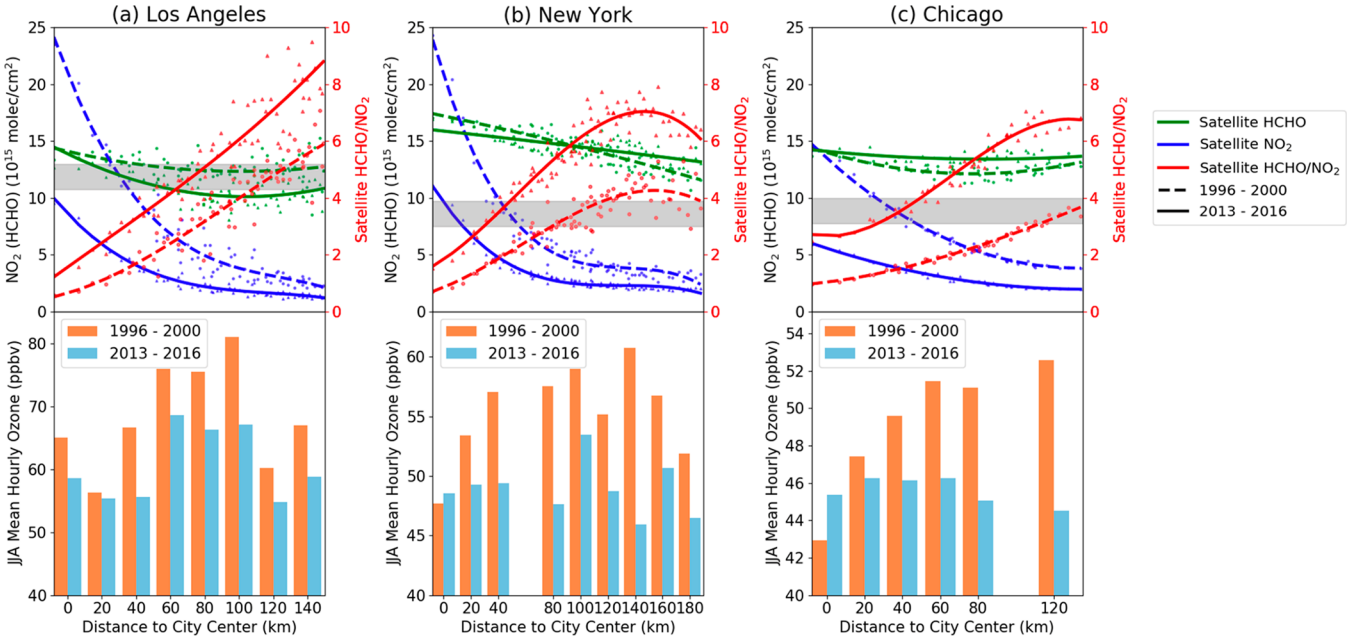

Figure 3. Satellite-based summertime Ω_{NO2} (blue dots), Ω_{HCHO} (green dots), $HCHO/NO_2$ (red dots), and summertime average O_3 (bars) as a function of distance to the city center during 1996−2000 and 2013−2016 for three cities: (a) Los Angeles, (b) New York, and (c) Chicago. City center is defined as the grid cell with highest summertime Ω_{NO2} within this region (labeled as red stars in Figure 2), which we find does not change over time in these cities (Figures 2 and S11). The curves shown in the top row are a polynomial fit (third order for Ω_{NO2} and $HCHO/NO_2$, second order for Ω_{HCHO}) curves. The gray area indicates the regime transitions for $HCHO/NO_2$, which is derived for each city individually as shown in Figure 1b. Summertime average O_3 is calculated from hourly AQS observations at OMI overpass time (averaged at 1 PM and 2 PM local time). AQS O_3 sites are grouped by distance to the city center at 20 km intervals.

Heterogeneous Trends of HCHO. Figure 2b compares summertime multisatellite Ω_{HCHO} in 1996−2000 versus 2013−2016. The spatial patterns of HCHO over the U.S. are largely driven by variations in biogenic VOCs, especially isoprene, which is mainly emitted from broadleaf trees, and is most abundant in the southeastern U.S.A.[53] As expected, the mean Ω_{HCHO} is highest over the southeastern city of Atlanta, followed by Washington and NYC. Ω_{HCHO} shows strong interannual variability (Figure S12), driven by interannual variability of meteorology, temperature in particular.[55,62] Over urban areas, satellite-based Ω_{HCHO} decreased by 7% in LA, 4% in NYC, 3% in Pittsburgh, 4% in Atlanta, and 3% in Houston in 2013−2016 relative to 1996−2000 (Figure S9), consistent with the widespread reduction of anthropogenic VOC emissions.[25] Over surrounding rural areas, satellite-based Ω_{HCHO} decreased near LA, Washington, Atlanta, and Houston, but increased near New York, Chicago, and Pittsburgh. These changes in Ω_{HCHO} correspond to estimated long-term changes in isoprene emissions (Figure S13), which have previously been shown to be related to changes in vegetation coverage.[63] In addition, NO_x reductions could lead to lower the HCHO yield from isoprene oxidation,[64,65] but the available observations are insufficient to conclusively determine the changes in HCHO yield. Overall, long-term changes in HCHO are driven by several factors,[66] such as anthropogenic and biogenic emissions, OH abundance, and HCHO yield dependence on NO_x, which warrant further investigation as more measurements become more available.[67] Most relevant to our study is that the overall changes in HCHO are much smaller than the NO_2 changes over the last two decades (Figure 2).

Spatial Expansion of NO_x-limited Regime Over Time. As Ω_{NO2} decreased over time, while changes in Ω_{HCHO} were relatively small, satellite-based $HCHO/NO_2$ increased from 1996−2000 to 2013−2016, indicating a shrinking extent of NO_x-saturated O_3 formation in urban areas (Figure 2c). Using the thresholds derived from Figure 1b to identify the O_3 production regimes, NO_x-saturated chemistry existed during summer in all cities during 1996−2000, with the largest areal extent in Pittsburgh. By 2013−2016, NO_x-saturated chemistry only occurred in the center of LA, Chicago, and NYC. The spatial expansion of the NO_x-limited regime suggests that NO_x emission reductions are more effective today at reducing O_3 pollution, as confirmed from prior modeling[35,36,68] and ground-based observational studies.[34,56] In recent years, as Ω_{NO2} remains at low levels, Ω_{HCHO} plays a more important role in determining the spatial and temporal variability in $HCHO/NO_2$. For example, the mean Ω_{HCHO} over LA is 8.2×10^{15} molecules/cm^2 in 2010, but increases to 15.2×10^{15} molecules/cm^2 in 2011, leading the mean O_3 formation regime to shift from NO_x-saturated to NO_x-limited (Figure S14). Also, Atlanta and Pittsburgh show similar Ω_{NO2} in 2013−2016, but Ω_{HCHO} is 50% higher in Atlanta, leading to 76% higher $HCHO/NO_2$ and thus more NO_x-limited chemistry in Atlanta, consistent with the well-understood regional differences in summertime O_3 sensitivity.[69,70]

LA, NYC, and Chicago are the three cities where we find strong urban−rural gradients in $HCHO/NO_2$, where O_3 production transitions from NO_x-saturated at city centers toward a NO_x-limited regime over rural areas in both periods. Figure 3 shows summertime average satellite-based NO_2, HCHO, and $HCHO/NO_2$ as a function of the distance to the city center during 1996−2000 and 2013−2016 over these three cities. Satellite observations detect large urban−rural gradients of NO_2 in LA and NYC with 20×10^{13} molecules/cm^2/km in 1996−2000, which decrease to 8×10^{13} molecules/cm^2/km in 2013 to 2016. The urban−rural gradient has

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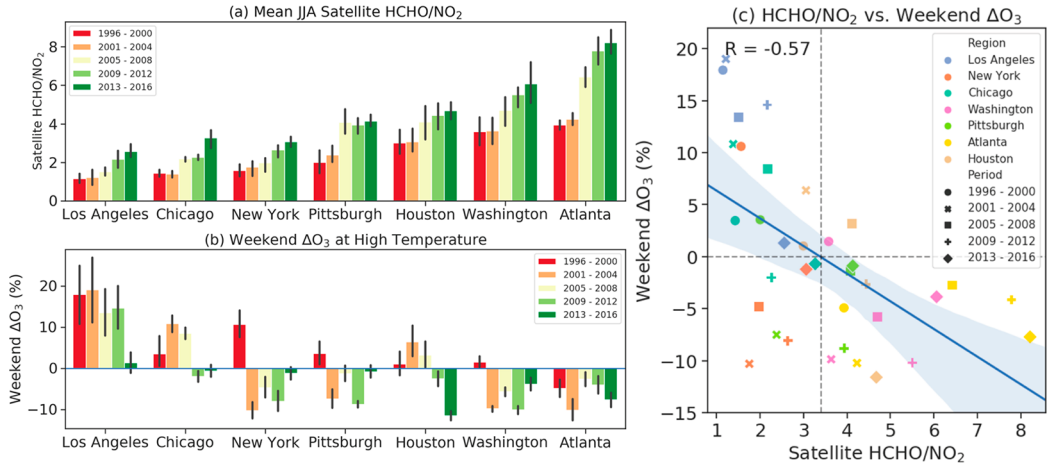

Figure 4. (a) Satellite-based summertime average $HCHO/NO_2$ in seven cities during five periods. (b) Weekday-to-weekend difference in average 1−2 pm summertime O_3 (weekend ΔO_3, mean O_3 Saturday−Sunday minus mean O_3 Tuesday−Friday) within each city on high temperature days (>median summer average temperature 1−2 pm) observed at AQS sites during five periods. Satellite-based $HCHO/NO_2$ is sampled over ground-based AQS O_3 sites. The error bars represent year-to-year variability in a given period. (c) Scatter plot between summertime average satellite-based $HCHO/NO_2$ and the weekend ΔO_3 with colors representing different cities and symbols representing different periods. The blue line is the fitted linear regression line with the 95% confidence interval shaded.

decreased from 11 × 10^{13} molecules/cm^2/km to 3 × 10^{13} molecules/cm^2/km in Chicago. We find a small enhancement of Ω_{HCHO} in urban areas over NYC and LA of 2 to 3 × 10^{13} molecules/cm^2/km, and negligible urban−rural difference of Ω_{HCHO} in Chicago. The urban−rural gradient of OMI $HCHO/NO_2$ is therefore mainly driven by the variations in NO_2. Using the regime thresholds we estimated, we infer the regime transition occurred at 110 to 130 km away from the city center in LA, 80 to 120 km in NYC, and 120 to 130 km in Chicago in 1996−2000. By 2013−2016, the locations of regime transition have moved closer to the city centers: 50 to 70 km for LA, 40 to 60 km for NYC and 30 to 60 km for Chicago (Figure 3).

Observed Response of Ground-Level O_3 to Regime Transitions. Theoretically, O_3 production regime transitions should correspond to the conditions at which O_3 formation is most efficient.[57] As the regime transition moves closer to populated city centers, peak O_3 production efficiency is expected to move toward the city center. We hypothesize that we should observe the highest O_3 concentration where the transitional regime occurs, assuming that local changes in meteorology, chemical and depositional loss do not contribute strongly to the observed summertime mean urban-to-rural O_3 gradients. We find that the ground-based sites measuring the highest summertime mean O_3 in each region move toward the city centers over time, except for Atlanta and Houston, where the highest O_3 is found near the city center in both periods (Figure 2c). We aggregate ground-based O_3 sites based on their distance to the city center for LA, NYC, and Chicago (Figure 3), where the VOC-limited regime still existed in 2013−2016. As expected, peak O_3 has moved toward the city center from 1996−2000 to 2013−2016 in LA and Chicago: from ∼100 km to ∼60 km in LA, from 120 km to 20 km in Chicago. The locations of peak O_3 are largely consistent with the locations of the regime transition identified by the satellite-based $HCHO/NO_2$. In NYC, we find that O_3 peaks ∼140 km away in 1996−2000, which is consistent with the regime transition inferred from satellite-based $HCHO/NO_2$. In 2013−2016, O_3 shows peaks at 100 and 160 km, however, which may be due to the noncircular nature of city shape and possibly confounding role of nearby ocean. If we only consider the small region within 100 km, then O_3 peaks at 40 km away from the city center, more consistent with the regime transition inferred from satellite-based $HCHO/NO_2$.

Regionally, surface O_3 in summer has decreased over the past two decades over the U.S.A., especially over the eastern U.S.A.[30,33,71,72] As expected, summertime mean O_3 is smaller in 2013−2016 than 1996−2000 over the three megacities, but the reduction is larger over rural areas where O_3 formation falls in the NO_x-limited regime (Figure 3). The faster decline in O_3 over rural areas than urban areas has previously been demonstrated.[33] In NYC and Chicago, we find an increase in O_3 at the city center where O_3 formation is NO_x-saturated. In the NO_x-saturated regime, NO_x emission reductions decrease NO_x titration, which increases O_3 directly, and also increases OH available for VOC oxidation and subsequent O_3 production. The spatial difference between maximum and minimum O_3 narrows from 13 ppbv in 1996−2000 to 7 ppbv in 2013−2016 in NYC, and 10 ppbv to 2 ppbv in Chicago. In LA, O_3 decreases in urban areas, which we attribute to decreases in anthropogenic VOC emissions.[73] The largest O_3 decreases occur in the transitional regimes in LA, where reductions in both anthropogenic VOCs and NO_x lower O_3.

Reversal of the O_3 Weekend Effect. The decrease of urban NO_x emissions associated with road traffic on weekends provides an observation-based natural test for investigating O_3 sensitivity to NO_x emissions;[74,75] over urban areas where O_3 formation is NO_x-saturated, reduction of NO_x emissions on weekends increases in O_3 (referred to as the O_3 weekend effect). Figure 4 shows the mean satellite-based $HCHO/NO_2$ sampled over long-term O_3 sites for the seven selected cities in five periods, and the corresponding in situ observed weekday-to-weekend difference in average summertime O_3 (weekend ΔO_3) within each metropolitan area. Here we only select days with high temperature (>median summertime average), as they are generally associated with high pressure, clearer skies, and slower winds, conditions suitable for efficient O_3 production.[37,57] As O_3 production becomes more sensitive to NO_x, the weekend ΔO_3 lessens and even reverses in some cities. The extent of the NO_x-saturated regime is largest in LA, as

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suggested by the lowest average satellite $HCHO/NO_2$ (Figure 4a). The O_3 weekend effect in LA persists from 1996 to 2016, but is smallest in the most recent period. During 1996−2000, we find a positive weekend ΔO_3 in 18 (11 with $p < 0.1$) out of 20 sites along southern California (Figure S15), but only 11 out of 18 sites (5 with $p < 0.1$) during 2013−2016. The shrinking O_3 weekend effect after 2000 in LA is reported in previous studies.[76,77] Chicago has the second lowest $HCHO/NO_2$, and the weekend ΔO_3 changes from positive to negative in 2009−2012. Over Chicago, the O_3 weekend effect is strongest during 2001−2004, when 32 out of 34 sites show positive weekend ΔO_3, and diminishes to 10 out of 23 sites during 2013−2016 (Figure S15). The reversal of the O_3 weekend effect occurs earlier in 2001−2004 over NYC, Pittsburgh, and Washington, though satellite $HCHO/NO_2$ does not change much compared with 1996−2000. In Houston, we find the reversal of weekend ΔO_3 occurs around 2009−2012. In Houston, 17 out of 24 sites show positive weekend ΔO_3 during 2001−2004, but they all changed sign during 2013−2016 (Figure S15). In Atlanta, where O_3 formation is most NO_x-limited based on our metric, O_3 concentration remains lower on weekends than weekdays at high temperature, but a reversal of the O_3 weekend effect does occur at moderate temperature during 2005−2008 (Figure S16).

The observed long-term changes in the O_3 weekend effect are overall consistent with the increasing sensitivity to NO_x, as suggested by the increasing satellite-based $HCHO/NO_2$ (Figure 4a). We find that satellite-based $HCHO/NO_2$ and weekend ΔO_3 is moderately correlated ($R = -0.57$, $p < 0.001$, Figure 4c). The regression line intercepts 0 at $HCHO/NO_2 = 3.4$, which is close to the regime transition derived in Figure 1b. Using this satellite-based indicator to quantitatively predict the occurrence of O_3 weekend effect in any particular city for a given time period, however, is subject to uncertainties. The definition of the O_3 weekend effect we invoke here assumes that the only difference in O_3 is directly attributable to changes in NO_x emission. The observed O_3 differences, however, may also be influenced by variability in meteorology.[42,78] The early reversal of the O_3 weekend effect in 2001−2004 over northeastern cities (NYC, Washington and Pittsburgh) is better explained by the overall colder temperature on weekends than weekdays over these three cities (Figure S17). Pierce et al.[42] suggest the long-term trend in the O_3 weekend effect over the Northeast U.S.A. is strongly influenced by the interannual variability in meteorology. We find larger fluctuations of the weekend ΔO_3 at moderate temperatures in most cities except for LA (Figure S16), which may be related to meteorological conditions that act to weaken urban-to-rural gradients through regional-scale O_3 transport that dilutes the signal of local urban O_3 production.

Limitations and Future Directions. Our study is the first attempt to directly connect satellite-based $HCHO/NO_2$ with ground-based O_3 observations. We show that space-based $HCHO/NO_2$ captures the nonlinearities of O_3−NO_x−VOC chemistry and detects spatial expansion of the NO_x-limited regime as supported by ground-based observations. However, using satellite $HCHO/NO_2$ to quantitatively diagnose the effectiveness of emission controls is subject to the following uncertainties that warrant further investigation. First, theoretical studies that relate indicator ratio to O_3−NO_x−VOC sensitivity show variations among different locations, which are subject to uncertainties in deposition and interactions with aerosol.[14,79] Second, satellite instruments measure the vertically integrated column density, and inhomogeneities in vertical distributions degrade the ability of satellite-based column $HCHO/NO_2$ to identify the near-surface O_3 sensitivity.[19,21] Third, we use an empirical observation-based approach to derive the thresholds marking the transitions between chemical regimes, which are likely to be affected by not only biases in the satellite retrieval algorithms,[19] but also by sampling size and biases of both ground-based and space-based observations. Fourth, the extent to which satellite-based Ω_{HCHO} relates to local surface organic reactivity is unclear. Satellite-based Ω_{HCHO} shows small decreasing trends over urban areas, and are mostly insensitive to observed decreases in anthropogenic VOCs,[56,73] partially due to relatively small HCHO yields from some classes of anthropogenic VOCs (e.g., alkanes).[80] As HCHO is a weaker UV−visible absorber than NO_2, satellite retrieval of HCHO is more prone to errors,[46] which may limit its ability to detect HCHO from local sources of anthropogenic VOCs. We find small enhancements of satellite Ω_{HCHO} over urban areas, but the magnitudes of the enhancement are insensitive to resolution, suggesting satellite Ω_{HCHO} is more indicative of the regional VOC reactivity, which is mainly influenced by biogenic isoprene emissions across much of the U.S.A. in summer.[81] Finally, although the retrieval uncertainty associated with different instruments has largely been reduced in the QA4ECV products,[49] our applications of satellite-based $HCHO/NO_2$ are nonetheless limited to long-term averages or data aggregations of sufficiently large sample size to reduce retrieval noise. It is challenging to use current satellite retrievals to observe short-term variability and detailed spatial patterns within urban cores. The new generation of satellites, including the newly launched TROPOMI aboard Sentinel-5P, and the upcoming geostationary satellite instruments such as TEMPO will offer an unprecedented view to characterize the near-surface O_3 chemistry at finer spatial and temporal scales.[82,83]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b07785.

S1, Details on satellite retrieval of NO_2 and HCHO; S2, gridding of satellite products; S3, discussion on the choice of resolution; Figure S1, difference between OMI and SCIAMACHY Ω_{NO2}; Figure S2, resolution correction factor for Ω_{NO2}; Figure S3, year-to-year variability in RC_{NO2_OMI}; Figure S4, temporal correlation between RC_{NO2_OMI} and RC_{NO2_SCIA}; Figure S5, resolution correction of OMI Ω_{HCHO} and systematic difference between OMI and SCIAMACHY Ω_{HCHO}; Figure S6, Figure 1b for comparison of multiple models; Figure S7, Figure 1b for comparison of two periods; Figure S8, resolution corrected versus original GOME Ω_{NO2}; Figure S9, relative changes in summertime average satellite-based Ω_{NO2} and ground-based measurements of NO_x, Ω_{HCHO} over urban and rural areas; Figure S10, time series of satellite-based Ω_{NO2} and ground-based NO_x; Figure S11, Figure 2 for the other three periods; Figure S12, time series of satellite-based Ω_{HCHO}; Figure S13, long-term changes in biogenic isoprene emissions; Figure S14, time series of satellite-based $HCHO/NO_2$; Figure S15, maps of O_3 weekend

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effect; Figure S16, Figure 4b for moderate temperature; and Figure S17, weekday-to-weekend difference in temperature. (PDF)

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Notes

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