

Investigating Changes in Ozone Formation Chemistry during Summertime Pollution Events over the Northeastern United States

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ABSTRACT: Understanding the local-scale spatial and temporal variability of ozone formation is crucial for effective mitigation. We combine tropospheric vertical column densities (VCD_{Trop}) of formaldehyde (HCHO) and nitrogen dioxide (NO_2), referred to as $HCHO-VCD_{Trop}$ and NO_2-VCD_{Trop} , retrieved from airborne remote sensing and the TROPOspheric Monitoring Instrument (TROPOMI) with ground-based measurements to investigate changes in ozone precursors and the inferred chemical production regime on high-ozone days in May–August 2018 over two Northeast urban domains. Over New York City (NYC) and Baltimore/Washington D.C. (BAL/DC), $HCHO-VCD_{Trop}$ increases across the domain, but higher NO_2-VCD_{Trop} occurs mainly in urban centers on ozone exceedance days (when maximum daily 8 h average (MDA8) ozone exceeds 70 ppb at any monitor in the region). The ratio of $HCHO-VCD_{Trop}$ to NO_2-VCD_{Trop} , proposed as an indicator of the sensitivity of local surface ozone production rates to its precursors, generally increases on ozone exceedance days, implying a transition toward a more NO_x -sensitive ozone production regime that should lead to higher efficacy of NO_x controls on the highest ozone days in NYC and BAL/DC. Warmer temperatures and enhanced influence from emissions in the local boundary layer on the high-ozone days are accompanied by slower wind speeds in BAL/DC but stronger, southwesterly winds in NYC.



KEYWORDS: ozone, formaldehyde, nitrogen dioxide, remote sensing, Northeastern United States

1. INTRODUCTION

Surface ozone (O_3), a major constituent of ground-level smog, can damage the human respiratory system^{1–3} and negatively affect ecosystems.^{4,5} In 2015, the United States (U.S.) Environmental Protection Agency (EPA) revised the primary and secondary National Ambient Air Quality Standards (NAAQS) to a maximum daily 8 h average (MDA8) ground-level ozone concentrations of 70 parts per billion (ppb).⁶ Motivated by regulations and public health, much effort has been expended to reduce ground-level ozone, but the complexity of ozone production makes mitigation a persistent challenge. We aim to improve our understanding of tropospheric ozone formation chemistry on days when MDA8 ozone exceeds 70 ppb (hereafter referred to as “exceedance days”). We focus on the northeast U.S. during the summer of 2018 (May–August) when two air quality field campaigns, the Long Island Sound Tropospheric Ozone Study (LISTOS)⁷ and the Ozone Water-Land Environmental Transition Study (OWLETS-2),⁸ provide a rich set of airborne and ground-based measurements of ozone and its precursors. These regional field campaigns provide an opportunity to test the capability of satellite-derived products to discerning different ozone production regimes.

New York City (NYC) and Baltimore/Washington D.C. (hereafter denoted as BAL/DC) are two densely populated regions along the Northeast Corridor that frequently exceed

the ozone NAAQS.⁹ Local anthropogenic^{10,11} and biogenic emissions,^{12,13} long-distance pollutant transport,^{14–16} high temperature,^{17,18} and land-water breezes over Long Island Sound^{19,20} and Chesapeake Bay^{21–23} have all been implicated in contributing to ozone nonattainment in our study region. Understanding ozone production and trends in NYC and BAL/DC are vital due to the large populations inhabiting the Northeast U.S. (57.6 million based on the 2020 U.S. Census Bureau estimate)²⁴ and may provide insights into other urban settings.

Tropospheric ozone forms when volatile organic compounds (VOCs) and nitrogen oxides (NO_x = nitric oxide (NO) + nitrogen dioxide (NO_2)) react in the presence of sunlight.²⁵ Sources of VOCs are diverse, including anthropogenic (e.g., from fuel combustion, solvents, and other volatile chemical products)²⁶ and biogenic emissions (e.g., isoprene, the dominant source in the eastern U.S. in summer).^{27,28} Primary sources of NO_x include fossil fuel combustion, biomass

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burning, microbial activity in soils, and lightning, where the majority in the eastern U.S. in summer comes from anthropogenic sources such as road traffic and electricity-generating units (EGUs).²⁹ Because the ozone production rate depends nonlinearly on its precursors, ozone sensitivity to its precursor emissions is often classified into three photochemical regimes based on the primary loss pathway of odd hydrogen (HO_x) radicals.^{30–33} In the NO_x -saturated regime, ozone production rates increase with declining NO_x or increasing VOCs. In contrast, ozone production increases with NO_x , while VOC changes have little impact on ozone in the NO_x -sensitive/ NO_x -limited regime. Ozone production is similarly sensitive to NO_x and VOC changes in the transitional regime.^{34–36}

This study uses vertical column densities (VCD_{Trop}) of formaldehyde (HCHO) and NO_2 , hereafter referred to as $\text{HCHO-VCD}_{\text{Trop}}$ and $\text{NO}_2\text{-VCD}_{\text{Trop}}$, as well as their ratio, which has been used to indicate the relative sensitivity of surface ozone production to emissions of VOC and NO_x .^{37–40} HCHO is a commonly produced intermediate of VOC oxidation with a relatively short lifetime (~ 2 h at mid-day in summer) whose spatial variability closely follows isoprene emissions over the eastern U.S. in summer and anthropogenic emissions in some urban areas.^{27,41–45} Produced alongside ozone during VOC oxidation, HCHO correlates with surface ozone and even more strongly with odd oxygen ($\text{O}_x = \text{O}_3 + \text{NO}_2$).^{46,47} Previous work suggests that the ratio of $\text{HCHO-VCD}_{\text{Trop}}$ to $\text{NO}_2\text{-VCD}_{\text{Trop}}$ (hereafter referred to as $\text{HCHO/NO}_2\text{-VCD}_{\text{Trop}}$) retrieved from satellite instruments can detect spatial and temporal variation trends in near-surface ozone photochemistry.^{48–51} While these studies examine the long-term trends in $\text{HCHO/NO}_2\text{-VCD}_{\text{Trop}}$, we focus on the day-to-day variations in the ratio. We have more confidence in using the ratio to detect trends in ozone photochemistry than in determining the exact photochemical regime due to spatiotemporal variations in the threshold values that demarcate ozone production regimes and limitations in inferring surface concentrations using column densities.^{49,52–54} Ozone concentrations reflect the combined impact of local photochemistry, transport (horizontal and vertical), and deposition, prompting us to examine changes in VCD_{Trop} of HCHO and NO_2 concentrations in parallel with their ratios for insights into local photochemistry conditions. We also consider the role of meteorological conditions on high-ozone versus other days.

Past climatological analyses aggregate high-ozone episodes to identify the meteorological conditions and transport patterns dominating high-ozone events.^{55–58} We evaluate ozone production conditions in NYC and BAL/DC during summer 2018 from a parallel perspective by compositing measurements of ozone precursors, meteorological fields, and simulations from a Lagrangian atmospheric transport model on exceedance versus nonexceedance days. We investigate the differences in ozone precursor concentrations on ozone exceedance versus nonexceedance days and infer changes in local photochemistry. This study provides a unique perspective by aggregating different observational data products over pollution events versus other days, allowing us to detect variability not evident from simple temporal averaging, laying the groundwork for interpreting atmospheric composition retrievals from future geostationary satellites.

2. DATA AND METHODS

Data sources used in this study are listed in Table S1. We use trace gas names to refer to concentrations and explicitly state when we discuss emissions. Ozone exceedance days are defined as days on which any U.S. Environmental Protection Agency (EPA) Air Quality System (AQS) State and Local Monitoring Stations (SLAMS) (locations shown in Figure S1) in the study domain records an MDA8 ozone concentration exceeding 70 ppb (≥ 71 ppb). During May–August 2018, we identify a total of 22 ozone exceedance days in NYC (region defined in Figure S1b) and 17 ozone exceedance days in BAL/DC (region defined in Figure S1c) based on this criterion.

We adopt the previously derived threshold values for NYC and Washington D.C. from Jin et al.⁵⁰ to demarcate the three ozone formation regimes. Jin et al.⁵⁰ used observed ozone exceedance probabilities to identify $\text{HCHO/NO}_2\text{-VCD}_{\text{Trop}}$ threshold values associated with the boundaries between the NO_x -saturated, transitional, and NO_x -sensitive ozone formation regimes for seven major U.S. cities. The transitional regime is identified as the top 10% of a fitted third-order polynomial curve associating the ground-level ozone exceedance probability with the Ozone Monitoring Instrument (OMI; the precursor of TROPOMI) retrieved $\text{HCHO/NO}_2\text{-VCD}_{\text{Trop}}$, where the exceedance probability is defined as the number of surface ozone observations exceeding 70 ppb divided by the total number of observations on all days coinciding with available VCD_{Trop} of HCHO and NO_2 .⁵⁰ Given uncertainties in the exact value corresponding to a specific regime, we are most interested in the differences between exceedance versus nonexceedance days to discern relative changes in local ozone production on the most polluted days.

We use the nonparametric Wilcoxon signed-rank test,^{59,60} appropriate for the non-normal distributions of $\text{HCHO-VCD}_{\text{Trop}}$ and $\text{NO}_2\text{-VCD}_{\text{Trop}}$, to determine the significance of differences calculated between pairs of exceedance and nonexceedance days. Specifically, our null hypothesis assumes a distribution of these differences centered on zero. The null hypothesis is rejected if the one-sided p -value < 0.01 for a median value of zero is estimated from the distribution of all differences calculated from our pairs of exceedance/nonexceedance days.

2.1. Airborne and Satellite Retrievals. We use column HCHO and NO_2 concentrations retrieved from the GEOCAPE Airborne Simulator (GCAS) flown on the NASA LaRC B200 and Geostationary Trace gas and Aerosol Sensor Optimization (GeoTASO) flown on the NASA LaRC HU-25 Falcon aircraft during the LISTOS (June 18–October 19, 2018) and OWLETS-2 field campaigns (June 18–June 30, 2018).^{7,8} GCAS and GeoTASO operate in a push-broom mode to measure backscattered ultraviolet, visible, and near-infrared (only by GCAS) light from a typical altitude of 8.5 km. These two airborne mapping spectrometers are similar, with differences in size (GCAS weighs 36 kg; GeoTASO weighs 90 kg) and spectral range (290–390 and 415–695 nm for GCAS; 300–490 and 480–900 nm for GeoTASO).⁶¹ Further details about GCAS and GeoTASO can be found in Kowalewski and Janz,⁶² Nowlan et al.,⁶³ Leitch et al.,⁶⁴ and Nowlan et al.⁶⁵ Judd et al.⁶⁶ provide details of these measurements during LISTOS. We use version R1 vertical column densities of HCHO and NO_2 below the aircraft (approximately the VCD_{Trop}) converted from the slant column

retrievals at a spatial resolution of $0.01^\circ \times 0.01^\circ$ (Table S1). The region is sampled two to four times per flight day. The air mass factor (AMF) for column conversion is calculated using the Smithsonian Astrophysical Observatory AMF tool^{65,67} following the methodology described in Palmer et al.⁴¹ as the integrated product of the scattering weights and shape factor.^{61,66–68}

During the LISTOS campaign, HCHO-VCD_{Trop} and NO₂-VCD_{Trop} retrieved from GCAS or GeoTASO are available for 12 days from June to August 2018. Seven are on NYC ozone exceedance days, and five are on nonexceedance days. We select the maximum number of available GCAS/GeoTASO flight days with sampling times closest to the TROPOMI overpass time of 1:30 PM. Our analysis uses five ozone exceedance days (2018-06-30, 2018-07-02, 2018-08-06, 2018-08-28, and 2018-08-29) and five nonexceedance days (2018-06-25, 2018-07-20, 2018-08-15, 2018-08-16, and 2018-08-24) (slashed days in Figure S2a) with the flight sampling times listed in Table S2. We do not include a parallel analysis using GCAS/GeoTASO for BAL/DC since aircraft measurements during OWLETS-2 are only available for NO₂ and only on 2 days.

We use retrievals from TROPOMI aboard Sentinel 5 Precursor (S5P) in operation since 2018 to extend our study to the entire summer (May–August). TROPOMI is a nadir-viewing shortwave spectrometer with a spatial resolution of $7 \times 3.5 \text{ km}^2$ at nadir and daily global coverage at 1:30 PM local time.⁶⁹ Note that the improved along-track spatial resolution of $5.5 \times 3.5 \text{ km}^2$ retrieved at nadir is only available after August 6th, 2019. We use the reprocessing stream (RPRO) version 01.01.05 L2 HCHO-VCD_{Trop} product (doi: 10.5270/S5P-tjlxfd2; access date: 8/5/2022)⁷⁰ and RPRO version 01.02.02 L2 NO₂-VCD_{Trop} product (doi: 10.5270/S5P-s4ljg54; access date: 8/5/2022)⁷¹ re-gridded to a resolution of $0.05^\circ \times 0.05^\circ$, after selecting only pixels with quality assurance (QA) values >0.75 . The QA value ranges from 0 (error) to 1 (all is well) and documents the quality of individual observations by considering cloud cover, surface albedo, geometry, and other factors. The recommended pixel filter for NO₂-VCD_{Trop} is QA > 0.75 ,⁷² which removes errors, problematic retrievals, and cloud-covered scenes. While QA > 0.5 is recommended for HCHO-VCD_{Trop},⁷³ we use a stricter filter of QA > 0.75 for consistency with NO₂. Limiting the TROPOMI data to days with QA > 0.75 for both VCD_{Trop} of HCHO and NO₂ for $>90\%$ pixels in NYC or BAL/DC further restricts our analysis to 19 out of the total 22 ozone exceedance days in NYC and 10 out of 17 total days in BAL/DC.

To create as consistent a comparison as possible when comparing changes on ozone exceedance relative to non-exceedance days, we apply the same QA criterion to select a parallel set of ozone nonexceedance days, with careful attention to include similar days of the week to minimize the impact of the ozone weekday/weekend effect. In NYC, the 19 exceedance or nonexceedance days are partitioned by day of the week as: four Mondays, two Tuesdays, three Wednesdays, three Fridays, four Saturdays, and two Sundays. To minimize sampling bias, we select nonexceedance days with a similar day-of-week distribution that fall closest in time to the recorded exceedance dates. We replicate this process to identify 10 nonexceedance days in BAL/DC compared with the exceedance days: four Mondays, two Tuesdays, two Fridays, one Saturday, and one Sunday. Darker shading in Figure S2 indicates the dates used for TROPOMI analysis.

We compare the TROPOMI-retrieved HCHO-VCD_{Trop} and NO₂-VCD_{Trop} averaged separately for exceedance versus nonexceedance days. Average HCHO/NO₂-VCD_{Trop} ratios are calculated from the mean HCHO-VCD_{Trop} and mean NO₂-VCD_{Trop} on exceedance or nonexceedance days. We also conduct the same analysis using the more coarsely resolved OMI products over the NYC region (Text S1). For comparison with the LISTOS aircraft measurements, we also average the TROPOMI-retrieved HCHO-VCD_{Trop}, NO₂-VCD_{Trop}, and HCHO/NO₂ ratio only on the five exceedance versus nonexceedance days (slashed days in Figure S2a) when airborne retrievals are available.

To analyze the ozone weekend effect, we compare TROPOMI-retrieved HCHO-VCD_{Trop} and NO₂-VCD_{Trop} averaged separately for 24 Tuesdays/Thursdays and 24 Saturdays/Sundays with TROPOMI QA greater than 0.75 during May–August 2018 (Figure S3 and Text S2). We use TROPOMI retrievals to confirm that the ozone weekday/weekend effect in NYC, BAL, and DC urban centers (small regions defined in Figure S1) are distinct from the changes we find on exceedance days relative to nonexceedance days (Text S2).

We note that higher GCAS/GeoTASO HCHO-VCD_{Trop} over water is likely an artifact of the moderate resolution imaging spectroradiometer (MODIS)/bidirectional reflectance distribution function (BRDF) parametrization used for surface reflectance characterization. To avoid the impact of these errors, we remove pixels over water from the GCAS/GeoTASO retrievals. For consistency, we also remove over-water pixels from TROPOMI retrievals. We classify a pixel as over land or water using its latitude and longitude based on the version 1.0 Global Land One-kilometer Base Elevation (GLOBE) dataset (Table S1). This dataset samples the elevation of the entire earth at 1 km resolution, masking out ocean areas with a “no data” fill value of -500 .⁷⁴ We define a pixel as over water if this location has a value of -500 . The pixels over water are masked and removed based on the latitude and longitude grids of GCAS/GeoTASO and TROPOMI before all calculations and analysis. We only include pixels that have valid measurements (QA > 0.75 for TROPOMI and covered by aircraft flights with GCAS/GeoTASO measurements) on both exceedance and non-exceedance days.

2.2. Ground-Based Monitoring Networks. We examine surface HCHO measurements collected every five minutes during LISTOS from the EPA Office of Research and Development (ORD) Aerodyne Quantum Cascade Laser mini instrument⁷⁵ at Westport, a site along the Connecticut shoreline where ozone exceedances occur frequently. We also use hourly surface NO₂ concentrations from the SLAMS (Figure S1). The estimated measurement uncertainty is about 0.03 ppb for surface HCHO. NO₂ measurement methods and QA requirements are in compliance with EPA guidance.⁷⁶ We select measurements for the hour nearest to the TROPOMI or airborne sensors overpass time. For example, we average measurements between 1 and 2 PM as an approximation for a 1:30 PM TROPOMI overpass, and between 1 and 4 PM for a flight during 1:12–3:55 PM.

We supplement aircraft measurements with retrievals from Pandora instruments from the Pandonia Global Network (PGN) sponsored by the National Aeronautics and Space Administration (NASA) and the European Space Agency (ESA), additional Pandora instruments deployed in support of

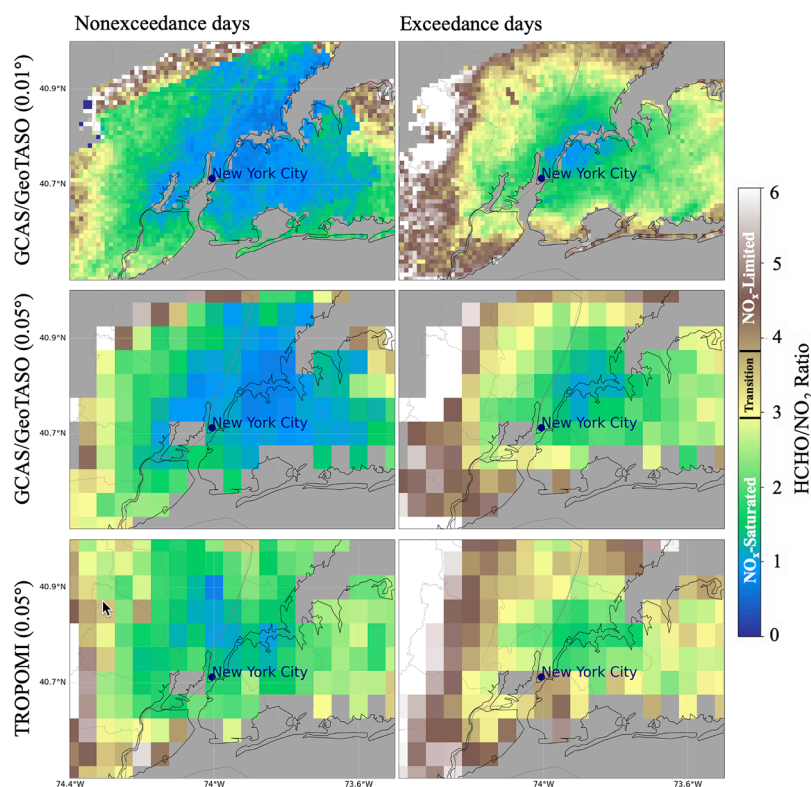


Figure 1. Areal extension of NO_x -sensitive and transitional regimes on ozone exceedance days in the New York City region. The chemical regime is diagnosed from $\text{HCHO}/\text{NO}_2\text{-VCD}_{\text{Trop}}$ ratios, following Jin et al.,⁵⁰ as retrieved from GCAS and GeoTASO in $0.01^\circ \times 0.01^\circ$ (top), re-gridded to $0.05^\circ \times 0.05^\circ$ (middle), and TROPOMI in $0.05^\circ \times 0.05^\circ$ (bottom) on 5 nonexceedance days (2018-06-25, 2018-07-20, 2018-08-15, 2018-08-16, and 2018-08-24; left column) and 5 exceedance days (2018-06-30, 2018-07-02, 2018-08-06, 2018-08-28, and 2018-08-29; right column) over the NYC metropolitan area during the LISTOS campaign. We only include pixels over land with measurements on both ozone exceedance and nonexceedance days; all other pixels are colored in gray.

the field campaigns, and through the Enhanced Monitoring Plans of Connecticut and New Jersey state air agencies (Table S1).^{77–79} Pandora spectrometers were deployed at 10 sites during LISTOS: Rutgers (NJ), Bayonne (NJ), Manhattan (NY), Queens College (NY), Bronx Pfizer (NY), Flax Pond (NY), Westport (CT), New Haven (CT), Hammonasset (CT), Outer Island (CT) (Figure S1a); and at three sites during the OWLETS-2 campaign: Earth System Science Interdisciplinary Center (ESSIC), the University of Maryland Baltimore County (UMBC), and Hart-Miller Island (HMI), all in Maryland (Figure S1c).^{80,81} The Pandora instruments are ground-based ultraviolet–visible spectrometers that can operate in direct-sun and sky-scan mode to retrieve O_3 , NO_2 , sulfur dioxide (SO_2), HCHO total columns, tropospheric columns, and vertical profiles.^{82–85} We do not use HCHO columns from the Pandora spectrometers due to sensor off-gassing-induced errors in the current 2018 products.⁸⁶ Trace gas abundances along the light path are determined using differential optical absorption spectroscopy (DOAS). The estimated error in the Pandora retrievals of total VCDs of NO_2 ($\text{NO}_2\text{-VCD}_{\text{Total}}$) is approximately 1.35×10^{15} molecules/ cm^2 .⁸⁷ We filter $\text{NO}_2\text{-VCD}_{\text{Total}}$ following Tzortziou et al.⁸⁴ and estimate $\text{NO}_2\text{-VCD}_{\text{Trop}}$ by subtracting the TROPOMI NO_2 stratospheric VCDs ($\text{NO}_2\text{-VCD}_{\text{Strat}}$) from the Pandora $\text{NO}_2\text{-VCD}_{\text{Total}}$ (Text S3). We examine $\text{NO}_2\text{-VCD}_{\text{Trop}}$ measured by the Pandora spectrometers for the hour surrounding the TROPOMI overpass time (around 1:30 PM local time) for the entire summer (19 exceedance days versus 19 nonexceedance days) to allow sufficient data for comparison.

2.3. Continuous Emission Monitoring Systems (CEMS) NO_x Emissions, Meteorology, and Transport.

We use hourly NO_x emissions recorded by continuous emission monitoring systems (CEMS) that estimate NO_x emissions based on reported operations from a large subset of power generation and industrial sources.⁸⁸ We calculate average NO_x emissions for 24 h and mid-day (10 AM to 2 PM) time spans summed for all monitored power plant units in NYC (42 total) and BAL/DC (22 total) on ozone exceedance and nonexceedance days as well as on Tuesdays/Thursdays and Saturdays/Sundays for our weekday/weekend analysis. The locations of power plants within and near NYC and within BAL/DC are shown in Figure S1.

We contrast meteorological conditions using 2 m above ground temperatures and 10 m above ground winds from Phase 2 of the North American Land Data Assimilation System (NLDAS-2) derived from the North American Regional Reanalysis (NARR).⁸⁹ We use the version 002 hourly level-4 primary forcing data product with a spatial resolution of $0.125^\circ \times 0.125^\circ$ (Table S1). We calculate the average of the 1 and 2 PM local time to coincide with the TROPOMI overpass (around 1:30 PM). We also examine day-by-day wind maps to show that the average wind patterns are not dominated by a small number of days. We use the Stochastic Time-Inverted Lagrangian Transport (STILT) model driven by NOAA High-Resolution Rapid Refresh (HRRR) meteorology at 3 km horizontal resolution (together referred to as HRRR-STILT), as a relative indicator of the influence of surface emissions on

Table 1. Change on Exceedance Days Relative to Nonexceedance Days^a

Change on exceedance days relative to nonexceedance days				
Nonexceedance → Exceedance				
	$\Delta HCHO$	ΔNO_2	$\Delta(HCHO/NO_2)$	Percentage of Pixels in (NO _x -Saturated, Transitional, NO _x -Sensitive)
NYC (5 days; 0.01° × 0.01°; 2983 pixels)	+ 96%	+ 4%	+ 144%	(81, 8, 11) → (52, 18, 30)
NYC (5 days; 0.05° × 0.05°; 125 pixels)	+ 96%	+ 4%	+ 62%	(81, 10, 9) → (53, 18, 29)
NYC (5 days; 137 pixels)	+ 66%	+ 4%	+ 63%	(80, 13, 7) → (28, 33, 39)
NYC (19 days; 137 pixels)	+ 79%	+ 36%	+ 35%	(81, 16, 3) → (52, 28, 20)
BAL/DC (10 days; 840 pixels)	+ 13%	+ 5%	+ 5%	(2, 4, 94) → (0, 0, 100)

^aWe only include pixels with QA > 0.75 for TROPOMI or covered by aircraft flights with GCAS/GeoTASO measurements on both exceedance and nonexceedance days. Relative changes in HCHO-VCD_{Trop}, NO₂-VCD_{Trop}, and HCHO/NO₂ on exceedance days (left three columns; see Figure S2 for date classifications, Figure S1b for NYC, and Figure S1c for BAL/DC), and the percentage of pixels in each region where the HCHO/NO₂-VCD_{Trop} falls into each chemical regime for ozone formation using the values derived from Jin et al.⁵⁰ for the New York City (NYC), Baltimore (BAL), and Washington D.C. (DC) regions, respectively (right column). Retrievals are from TROPOMI except in bold for airborne sensors (GCAS or GeoTASO). Shaded values indicate Wilcoxon signed-rank tests with a *p*-value <0.01, suggesting that the difference between exceedance and nonexceedance days are significant (distribution of the differences is not centered at zero).

ozone concentrations at selected locations on exceedance versus nonexceedance days (Text S4).

3. OZONE EXCEEDANCE VERSUS NONEXCEEDANCE DAYS

3.1. New York City. Our analysis excludes pixels that are over waterbodies or have retrievals only on exceedance or nonexceedance days (gray pixels in Figure 1). Table 1 shows changes in regional averaged HCHO-VCD_{Trop}, NO₂-VCD_{Trop}, and HCHO/NO₂ ratios on ozone exceedance days relative to nonexceedance days and the percentage of pixels classified as NO_x-saturated, transitional, and NO_x-sensitive based on Jin et al.⁵⁰ Differences with a *p*-value <0.01 for a one-sided Wilcoxon signed-rank test are shaded (Table 1). We find increases in HCHO-VCD_{Trop} and NO₂-VCD_{Trop} in NYC from both airborne GCAS/GeoTASO (+96 and +4%, respectively) and TROPOMI satellite retrievals (+66 and +4%, respectively) on high-ozone days during the LISTOS campaign (Table 1 and Figures S4 and S5). TROPOMI satellite retrievals for May–August 2018 in NYC also show enhanced VCD_{Trop} of both

species (+79 and +36%, respectively; Figure S6). The TROPOMI enhancement in NO₂-VCD_{Trop} on ozone exceedance days is more significant during the summer (*p*-value <0.01) versus during the LISTOS campaign (*p*-value = 0.1 for GCAS/GeoTASO and TROPOMI). To test the significance of the differences detected on the flight days, we randomly select and compare TROPOMI HCHO-VCD_{Trop} and NO₂-VCD_{Trop} on five exceedance versus five nonexceedance days from the 19-day exceedance/nonexceedance pairs over the entire summer. This comparison suggests that these 10 flight days are representative of the differences from nonexceedance to exceedance days during summer 2018 (Text S5 and Figure S7). We do not find a distinct rural–urban gradient in HCHO-VCD_{Trop}, whereas NO₂-VCD_{Trop} is consistently higher in the NYC urban core.

Figure 1 shows HCHO/NO₂-VCD_{Trop} ratios averaged over 5 nonexceedance days (left) and averaged over 5 exceedance days (right), from GCAS and GeoTASO at 0.01° × 0.01° (top), at 0.05° × 0.05° (middle), and TROPOMI in 0.05° × 0.05° (bottom) for the dates and flight times specified in Figure S2 and Table S2. For NYC, Jin et al.⁵⁰ diagnosed the

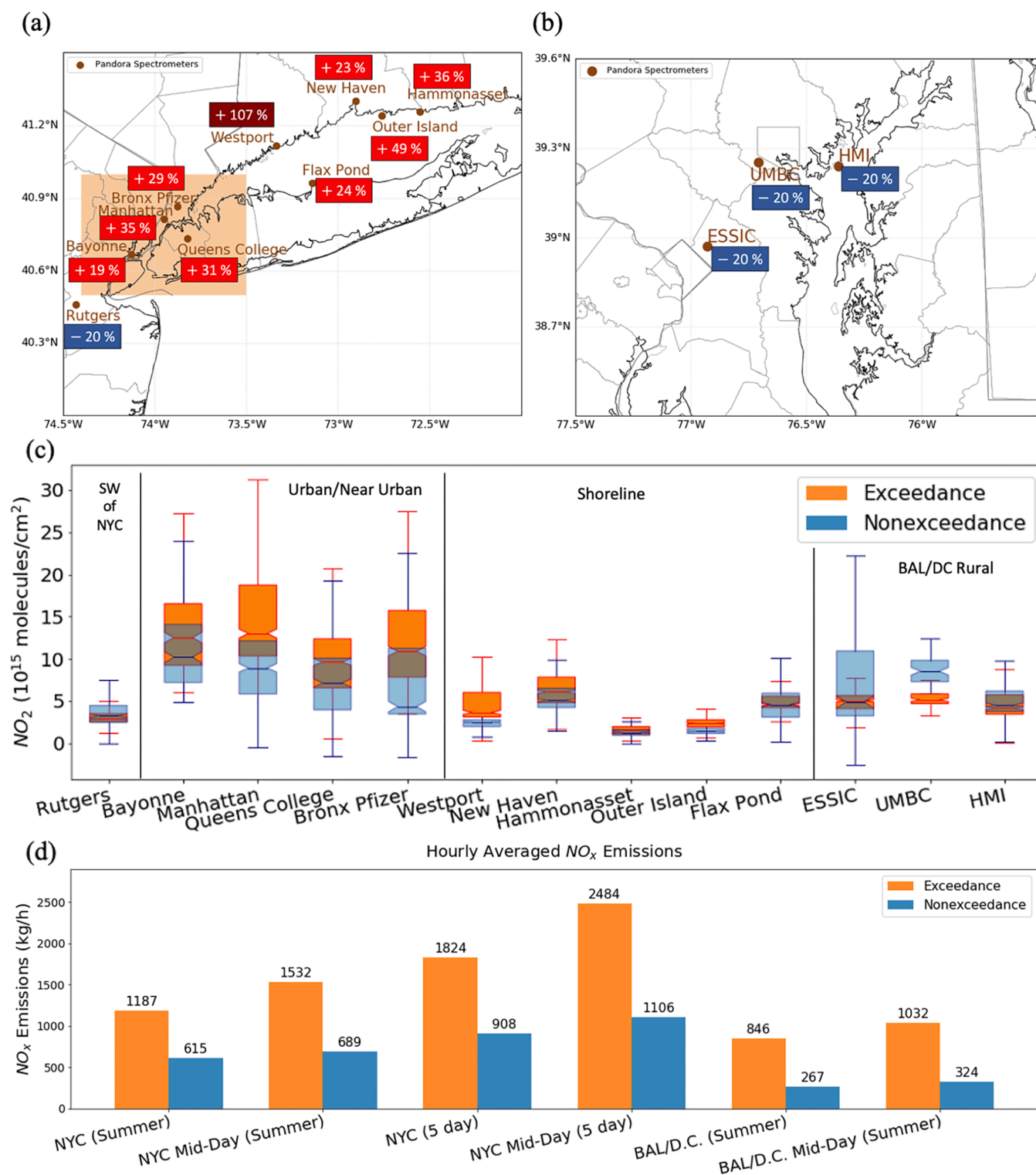


Figure 2. Higher $\text{NO}_2\text{-VCD}_{\text{Trop}}$ at four urban sites near NYC and along the shoreline but lower $\text{NO}_2\text{-VCD}_{\text{Trop}}$ at Westport and three suburban BAL/DC sites on high-ozone days during summer 2018, along with higher power plant NO_x emissions in NYC and BAL/DC. Changes in averaged Pandora $\text{NO}_2\text{-VCD}_{\text{Trop}}$ estimated at 1:30 PM for the entire summer on exceedance days relative to nonexceedance days site in (a) NYC and (b) BAL/DC. (c) Box plots for $\text{NO}_2\text{-VCD}_{\text{Trop}}$ measured by the Pandora spectrometers extending from the 25th to the 75th percentile, with a line at the median and a whisker showing the range of the data. (d) NO_x emissions from EGUs monitored by continuous emission monitoring systems (CEMS) are higher on ozone exceedance days in both NYC and BAL/DC. We calculate hourly averaged NO_x emissions for 24 h and mid-day (10 AM to 2 PM) periods, summed for 42 power plant units in NYC and 22 units in BAL/DC on exceedance (orange), and nonexceedance days (blue).

transitional regime as occurring when $\text{HCHO}/\text{NO}_2\text{-VCD}_{\text{Trop}}$ ratios range from 2.9 to 3.8, with ratios below this range

indicating NO_x -saturated ozone formation and above indicating a NO_x -sensitive regime. We apply these values to infer

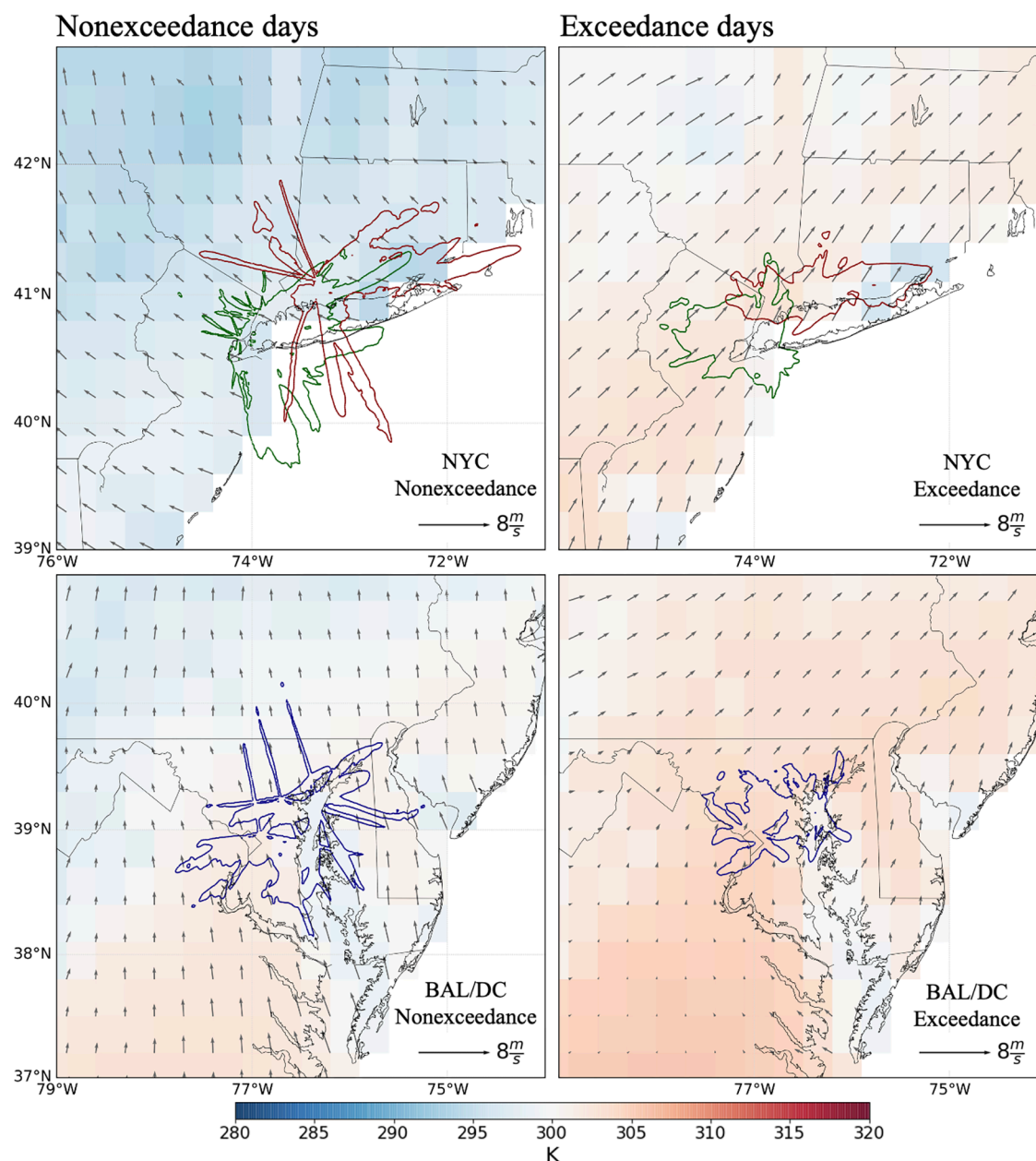


Figure 3. Higher temperatures and stronger winds occur on ozone exceedance days in NYC, but weaker winds co-occur with ozone exceedance and warmer temperature days in BAL/DC, with a greater impact from local ozone sources on exceedance days in both regions. Shown are 0.01 ppb ($\mu\text{mol m}^{-2} \text{s}^{-1}$)⁻¹ contour lines from the mean HRRR-STILT footprint that represents the summed 6 h surface influence on concentrations at 50 m above ground level for the Pandora site at Westport (Figure S1a; red), four sites near NYC (Figure S1b; green), and three sites in BAL/DC (Figure S1c, blue). The 2 m above ground temperature and 10 m above ground wind from NLDAS-2 estimated at 1:30 PM averaged for 19 nonexceedance (upper left) and 19 exceedance (upper right) days in NYC and 10 nonexceedance (bottom left) and 10 exceedance (bottom right) days in BAL/DC are re-gridded to 0.3° by 0.3° resolution to improve wind arrow legibility.

shifts in the ozone production regime from the ratios. On exceedance days, changes in $\text{HCHO-VCD}_{\text{Trop}}$ dominate and higher $\text{HCHO/NO}_2\text{-VCD}_{\text{Trop}}$ ratios occur over a larger area in NYC. The rural–urban $\text{HCHO/NO}_2\text{-VCD}_{\text{Trop}}$ gradient in Figure 1 agrees with previous findings of less NO_x -sensitive regimes in urban areas relative to the surrounding suburbs.^{38,90} The regional mean $\text{HCHO/NO}_2\text{-VCD}_{\text{Trop}}$ ratios on the 5 exceedance- versus nonexceedance days increase by 62% for the re-gridded aircraft and 63% for TROPOMI retrievals (Table 1 and Figure 1). On the 19 exceedance versus nonexceedance days, the regional mean TROPOMI $\text{HCHO/NO}_2\text{-VCD}_{\text{Trop}}$ ratio increases by 35% (Table 1 and Figure S6).

For the 19-day comparison, OMI suggests similar qualitative changes in $\text{HCHO-VCD}_{\text{Trop}}$ and $\text{NO}_2\text{-VCD}_{\text{Trop}}$ as TROPOMI, although the ratio only increases for the pixels closest to NYC urban center (Text S1 and Figure S8). The more coarsely resolved OMI products ($0.25^\circ \times 0.25^\circ$ versus $0.05^\circ \times 0.05^\circ$ for TROPOMI) miss the fine-scale spatial changes and indicate a greater enhancement in $\text{HCHO-VCD}_{\text{Trop}}$ and $\text{NO}_2\text{-VCD}_{\text{Trop}}$ than either the TROPOMI or GCAS/GeoTASO retrievals.

The tropospheric column increases in Figures 1, S4, and S5 over NYC from nonexceedance to exceedance days are consistent in sign with the changes in the surface measurements of HCHO at Westport and surface NO_2 at SLAMS. On

ozone exceedance days, mean surface HCHO at Westport increased by about 3 ppb (more than 80%) averaged for the hour surrounding 1:30 PM (TROPOMI overpass) and for the aircraft sampling times during the campaign (Figure S9a). This enhancement is greater when we consider all 19 exceedance days for which TROPOMI data is available, with a 4 ppb increase in the mean (about 176%). In NYC, the regional mean surface NO₂ concentrations reported by the SLAMS during the 5-day comparison at around 1:30 PM increased from 8.4 to 10.3 ppb (+22%) and from 11.9 to 13.1 ppb (+10%) during times when airborne observations are available (Figure S9b). Regional mean concentrations of surface NO₂ around 1:30 PM increased from 9.3 to 10.8 ppb (+16%) for the 19-day comparison (Figure S9b), with enhancements observed at all individual sites in NYC (not shown).

Next, we examine changes observed by the ground-based Pandora spectrometers operating during LISTOS. The changes in NO₂-VCD_{Trop} on exceedance relative to nonexceedance days at each Pandora spectrometer site are denoted as percentages on maps to show the differences in the means (Figure 2a,b) and as box plots extending from the 25th to the 75th percentile with a horizontal line at the median and a whisker showing the range (Figure 2c). As in prior work,⁸⁵ we find that summer-averaged NO₂-VCD_{Trop} is highest at sites within or near the urban core, including Manhattan (>1 × 10¹⁶ molecules/cm²), Bayonne, Queens College, and Bronx Pfizer (all ~10¹⁶ molecules/cm²), with lower summer mean NO₂-VCD_{Trop} at the shoreline sites (Westport, New Haven, Hammonasset, Outer Island, and Flax Pond; ~10¹⁵ molecules/cm²) (Figure 2c). Focusing on the TROPOMI overpass time, the average across all Pandora sites increases by 28% from the 19 nonexceedance to exceedance days. Only the upwind site to the southwest of NYC (Rutgers), shows a drop (−20%; *p*-value >0.01) in NO₂-VCD_{Trop} on exceedance days (Figure 2a), which agrees with surface NO₂ measurements from the co-located SLAMS monitor (−14% drop on exceedance days). The most substantial relative increase on high-ozone days occurs at Westport, CT (+107%; *p*-value <0.01), while a 19–49% (*p*-value <0.01) increase occurs at other NYC sites (Figure 2a). The larger relative enhancement in NO₂-VCD_{Trop} retrieved from the Pandora instruments versus from TROPOMI on exceedance days may reflect the more localized scale sampled by the individual spectrometers and spatial representation errors⁵⁴ in TROPOMI retrievals.

High-ozone days in NYC are accompanied by higher power plant NO_x emissions, warmer temperatures, and stronger winds (all with *p*-values <0.01). Figure 2d shows NO_x emissions (kg/h) from CEMS for selected exceedance days (orange) and nonexceedance days (blue) following the date classifications in Figure S2. In NYC, power plant NO_x emissions on the 5 exceedance days when the aircraft flew are 50% higher than on the five nonexceedance flight days (Figure 2d). The summed NO_x emissions for the 19 exceedance days when TROPOMI retrievals are available are 48% higher than on our selected 19 nonexceedance days. Increases in NO₂-VCD_{Trop} near NYC urban areas are possibly associated with increased energy demand on hotter high-ozone days.^{91,92} High HCHO across the domain on ozone exceedance days may reflect increasing biogenic emissions from vegetation and evaporative sources^{42,93–95} as regional mean temperature rises by about 5 K on exceedance days.

The top row of Figure 3 shows 10 m wind vectors, the 2 m temperatures, and the contours encompassing ~90% of the

cumulative surface influence (estimated by summing 6 h HRRR-STILT footprints outlined by trajectories initiated from 50 m above the ground) at the Westport (red) site and combined over the four NYC urban and near-urban Pandora sites (Bayonne, Manhattan, Queens College, and Bronx Pfizer in Figure S1b) (green) for the 19 exceedance versus 19 nonexceedance days. Faster winds (about +1 m/s) with a broad-scale shift in the average wind direction from southeasterly to southwesterly occur on exceedance days in NYC, suggesting a role for ozone transport from upwind regions. The HRRR-STILT footprints, however, indicate a coincident increase in local surface influence (and thus local emission sources) within NYC on exceedance days. This surface influence diagnosed with HRRR-STILT includes more transport from upwind (New Jersey) to the four NYC urban and near-urban Pandora sites (Figure S1b), as well as from Long Island Sound to Westport, CT. In contrast, on nonexceedance days, winds blow from multiple directions with a larger footprint over the ocean and to the north (top row in Figure 3). Southwesterly winds dominate in NYC during high-ozone episodes (4 of 5 days during the LISTOS campaign and 13 of 19 for the entire summer; Figure S10a), whereas wind speeds and directions are more diverse on nonexceedance days (Figure S10b).

Southwesterly winds on ozone exceedance days in NYC have been documented in previous studies focused on individual episodes as well as climatological analyses.^{57,96–98} The prevailing wind patterns during high-ozone episodes in summer 2018 are similar to the dominant wind direction associated with the average summer day ozone transport along the Atlantic coast for 1991–1995, when the climatological transport to New York was from the west-southwest.⁵⁵ Consistent with the more localized influence suggested by HRRR-STILT, we find shallower planetary boundary layers on exceedance days (Text S4 and Figure S11), as noted in past studies.^{22,99–102} Though stronger winds suggest additional transport of ozone and its precursors into the NYC domain from upwind sources on ozone exceedance days, we also find more local boundary layer influence, and thus presumably local sources on local ozone production, including from the higher NO_x emissions recorded in the CEMS data.

3.2. Baltimore/Washington D.C. Using only pixels over land, we find smaller increases in TROPOMI-retrieved HCHO-VCD_{Trop} (+13%; *p*-value <0.01) on 10 exceedance days relative to 10 nonexceedance days occurring over BAL/DC, with little rural–urban gradient (Figure S12). Regional mean NO₂-VCD_{Trop} on polluted days are higher by 5% (*p*-value <0.01). In contrast, NO₂-VCD_{Trop} retrieved from three suburban Pandora spectrometers is lower on ozone exceedance days by 6–22% (*p*-values <0.01; Figure 2b,c). There is no change (difference of around 0%) in the regional mean surface NO₂ concentrations at the SLAMS around 1:30 PM in BAL/DC (Figure S9b), but individual monitors within DC and near BAL urban centers show an increase in surface NO₂ on high-ozone days, whereas one suburban site observes a decrease (not shown).

Jin et al.⁵⁰ previously found that HCHO/NO₂-VCD_{Trop} ratios below 3.2 indicate a NO_x-saturated regime over Washington D.C., while ratios above 4.1 indicate NO_x-sensitive ozone formation, with the transitional regime falling between these values. Based on these threshold values, more than 90% pixels in BAL/DC are NO_x-sensitive as inferred from HCHO/NO₂-VCD_{Trop} ratios >4.1 on both ozone exceedance

and nonexceedance days. TROPOMI shows higher HCHO/NO₂-VCD_{Trop} ratios on ozone exceedance days (+5% on average; *p*-values <0.01). According to this classification, 6% more pixels (from 94 to 100%) in the domain (Figure S1c) shift into NO_x-sensitive regimes on ozone exceedance days (Table 1 and Figure S12).

High-ozone days in BAL/DC coincide with higher CEMS NO_x emissions (+68%; Figure 2d), warmer temperatures (+3 K; Figure 3), and slower surface wind speeds (about -1 m/s; Figure 3), all with *p*-values <0.01. Wind directions are diverse on both ozone exceedance (Figure S10c) and nonexceedance days (Figure S10d). As in NYC (Section 3.1), we find a more localized footprint of surface emission influence on ozone exceedance days in BAL/DC (bottom row of Figure 3). The meteorological situation matches the classic conceptual model of air stagnation accompanying higher temperature,^{17,103–105} indicating a dominant role for local ozone production. Our findings resonate with previous studies emphasizing the impact of local industrial and traffic emissions and mesoscale meteorology (for example, boundary layer depth, humidity, air circulation) on surface ozone pollution over BAL/DC and the Chesapeake Bay.^{22,106–108}

3.3. Ozone Weekend Effect. Comparing 24 Saturdays/Sundays versus 24 Tuesdays/Thursdays (Figure S3), the spatial average surface MDA8 ozone concentrations increase about +2 ppb (+4%) in NYC, with no change (~0%) in BAL/DC. We examine TROPOMI-retrieved VCD_{Trop} of HCHO, NO₂, and HCHO/NO₂ ratios averaged over the same period over NYC (Figure S13) and BAL/DC (Figure S14), as well as in the urban cores (Table S3). The spatial average of TROPOMI-retrieved NO₂-VCD_{Trop} decreases on the weekends, with higher HCHO-VCD_{Trop} and HCHO/NO₂-VCD_{Trop} in all three urban regions of NYC, BAL, and DC (Text S2). We only find reduced NO_x emissions from power plants recorded by CEMS on weekends in the NYC and BAL urban regions (Figure S15), with cooler spatial average temperatures and weaker winds (Figure S16).

As inferred from the ratio, the ozone production regime does not change on the weekends in the urban cores of NYC and DC (Table S3). In the NYC urban center, all pixels remain NO_x-saturated as indicated by the TROPOMI-retrieved HCHO/NO₂-VCD_{Trop} ratio <2.9 (Table S3).⁵⁰ While previous analyses found a diminishing ozone weekend effect in the northeast U.S. with NO_x controls,^{109,110} we still detect higher ozone and lower NO₂ concentrations and NO_x from power plant emissions on weekends. The continued existence of a weekday/weekend effect where ozone increases with lower weekend NO_x emissions implies that deeper cuts in NO_x emissions are needed to shift the ozone formation chemistry to NO_x-sensitive in the NYC urban core. By contrast, all pixels in DC urban center are always in the NO_x-sensitive regime with ratios >4.1,⁵⁰ indicating that further NO_x controls should reduce ozone, regardless of the day of week.

3.4. Uncertainties and Limitations. Earlier evaluations of version 1 TROPOMI HCHO-VCD_{Trop} and NO₂-VCD_{Trop} products showed improved performance relative to OMI, the TROPOMI predecessor instrument, with better precision (HCHO column retrieval precision improved by 25% for individual pixels¹¹¹) and finer native spatial resolution.^{112,113} However, TROPOMI-retrieved HCHO-VCD_{Trop} and NO₂-VCD_{Trop} products showed a low bias in urban regions compared with independent observations, such as GeoTASO,⁶¹ Multiaxis differential optical absorption spectroscopy

(MAX-DOAS),^{111,114} and Fourier transform infrared (FTIR) measurements.¹¹⁵ We assess here how these biases may influence our conclusions by applying generalized corrections based on the median biases in HCHO-VCD_{Trop} and NO₂-VCD_{Trop} identified in previous evaluations of the same product versions. We apply these corrections at the pixel level for all days in summer 2018 (May 14–August 31) when data is available (Text S6; corrections are based on Vigouroux et al.¹¹⁵ for HCHO-VCD_{Trop} and Verhoelst et al.¹¹⁴ for NO₂-VCD_{Trop}). We find that the tendency toward higher HCHO-VCD_{Trop}, NO₂-VCD_{Trop}, and HCHO/NO₂ ratios on ozone exceedance days in NYC and BAL/DC does not change following this bias correction (Text S6, Table S4, and Figures S17 and S18). We emphasize, however, that the biases identified in earlier work are not universal in time and space^{111,114–117} and different corrections may be more appropriate in NYC and BAL/DC.

While HCHO-VCD_{Trop}, NO₂-VCD_{Trop} and HCHO/NO₂ changes from nonexceedance to exceedance days retrieved from airborne remote sensing are consistent in sign with the TROPOMI products during the LISTOS campaign in NYC, the magnitudes differ. Compared with the GCAS/GeoTASO observations (version R1), TROPOMI retrievals (RPRO version 1) show higher absolute concentrations of HCHO-VCD_{Trop} but lower NO₂-VCD_{Trop} over NYC (Figures S4 and S5), most likely due to different sampling times and potentially reflecting differences in the retrieval products and uncertainties.^{61,67,115} TROPOMI also show a smaller increase in HCHO-VCD_{Trop} on high-ozone days. The relative increase in the HCHO/NO₂-VCD_{Trop} ratio on ozone exceedance days is smaller, but TROPOMI indicates that a larger percentage of pixels within NYC shifts into transitional and NO_x-sensitive regimes (Table 1). The increase in HCHO/NO₂-VCD_{Trop} ratio on high-ozone days is smaller (from 144 to 62%) and closer to that indicated by TROPOMI (63%) when we re-grid GCAS/GeoTASO observations to the same resolution as TROPOMI, possibly because taking the spatial average across pixels (2983 to 125 pixels) reducing the variations. Findings are similar even when we apply bias corrections based on previous work to TROPOMI HCHO-VCD_{Trop} and NO₂-VCD_{Trop} (Text S6).

An inherent challenge in using the HCHO/NO₂-VCD_{Trop} ratio to study local ozone production is that the ratio may not fully describe the chemical regime because HCHO production rates can vary with NO₂.^{53,54,118} Souri et al.⁵⁴ systematically evaluate and separately weight the errors associated with the retrievals, vertical column to planetary boundary layer translation, and spatial representation for daily TROPOMI (HCHO product version 2.02.01 and NO₂ version 2.2.0) in summer 2021 over the U.S. They conclude that uncertainty in the retrievals is the largest contributor to total error in HCHO/NO₂-VCD_{Trop}, with HCHO-VCD_{Trop} retrievals generally contributing larger errors than NO₂ as a result of narrower molecular absorption in the ultraviolet–visible range.¹¹⁹ TROPOMI HCHO-VCD_{Trop} retrievals contain larger uncertainties than NO₂-VCD_{Trop}, which enlarge the uncertainties in using HCHO/NO₂-VCD_{Trop} ratio (Text S6 and Figures S17 and S18). Nonuniform vertical mixing in the lower troposphere also impairs the relevance of column densities for indicating surface ozone chemistry.^{49,52} In addition, the relationship between column HCHO to the surface total organic reactivity, determined by the local mix of VOCs, is uncertain.^{50,120}

4. DISCUSSION

The various datasets we analyzed all point toward increased HCHO and NO₂ concentrations on ozone exceedance days. We infer that these increases may reflect common drivers, such as warmer temperatures that could enhance HCHO concentrations from biogenic VOC emissions^{121,122} and higher NO_x emissions from EGUs to meet rising energy demand.^{91,92} Higher NO_x levels on ozone exceedance days may also enhance HCHO concentrations by facilitating VOC oxidation in a warmer environment. A source appointment study is needed to quantify the dominant emissions contributing to the observed enhancements more precisely. The increase in HCHO-VCD_{Trop} is larger than NO₂-VCD_{Trop}, leading to an overall increase in the HCHO/NO₂-VCD_{Trop} on ozone exceedance days, regardless of the city-specific initial ratio values, even in the NYC, BAL, and DC urban core areas. These findings imply a transition toward a more NO_x-sensitive photochemical environment on high-ozone days even as more NO_x is available for ozone production in NYC and BAL/DC, suggesting that additional NO_x emission reductions may effectively reduce ozone levels, especially on the most polluted days. Improvement in the products retrieved from satellite instruments and better uncertainty quantification would increase the confidence in using the VCD_{Trop} of HCHO and NO₂ as well as the HCHO/NO₂ ratio in a more quantitative manner for decision making.

Based on HCHO/NO₂-VCD_{Trop} retrieved from GCAS/GeoTASO and TROPOMI and threshold values calculated in Jin et al.,⁵⁰ the NYC urban region falls in the NO_x-saturated regime, whereas the BAL/DC region with lower summertime mean NO₂ VCD_{Trop} is more sensitive to NO_x. Earlier work also concludes that the NYC urban core remains NO_x-saturated despite a general trend across the United States, including areas in the broader NYC metropolitan region, shifting urban chemistry toward NO_x-sensitive in the past two decades.^{50,51,123–125} The BAL/DC region has also been identified as becoming dominated by the NO_x-sensitive regime since the early 2000s.¹⁰⁸ In any urban region that remains NO_x-saturated, even though VOC emission reductions may help abate ozone locally, it would first be critical to determine whether local anthropogenic (for example, VOC from volatile chemical products^{126–129}) versus biogenic emissions dominate the VOC reactivity contributing to ozone formation, especially as biogenic VOC emissions are generally not controllable. In all cases, however, reducing NO_x emissions will reduce the overall regional ozone production, and shift the urban core to NO_x-sensitive with sufficient reductions.

This study focused on the local chemistry on high versus low-ozone days in the afternoons with TROPOMI retrievals and airborne flights two to four times on a limited number of days during field campaigns in summer 2018. Ozone precursor emissions, concentrations, and photochemistry also vary diurnally. Observing diurnal variations could improve our understanding of the interactions and feedback between emissions and meteorology that shape ozone pollution distributions, including on the highest ozone days. Continuous surface HCHO concentrations measurements from more locations, such as New York Botanical Garden and Flax Pond with continuously running Picarro instruments starting fall 2021¹³⁰ may provide new insights into the diurnal variations in HCHO at the surface versus the remotely sensed column and their links to specific VOC sources. Future field

campaigns, such as the Greater New York Oxidant Trace gas Halogen and Aerosol Airborne Mission (GOTHAAM; planned for summer 2023), and new anticipated satellites, such as the Tropospheric Emissions Monitoring of Pollution (TEMPO; scheduled to launch in 2023), will provide new opportunities to test the utility of applying the VCD_{Trop} of HCHO and NO₂ to infer local photochemical conditions for ozone formation.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.2c02972>.

Observations using OMI retrievals (Section S1); ozone weekend effect in NYC, BAL, and DC urban centers (Section S2); calculations of NO₂-VCD_{Trop} from the Pandora spectrometers (Section S3); supplementary analysis in meteorology and transport on ozone exceedance/nonexceedance days (Section S4); sensitivity test of observed exceedance/nonexceedance differences to the selection of days (Section S5); evaluate bias and uncertainties in TROPOMI products (Section S6); data information summary (Table S1); flight sampling times (Table S2); change on weekends relative to weekdays for smaller urban core regions (Table S3); change on ozone exceedance days relative to nonexceedance days based on TROPOMI data with bias correction (Table S4); locations of surface AQS SLAMS, Pandora spectrometers, and CEMS power plants (Figure S1); days selected for high-ozone events analysis during May–August 2018 (Figure S2); days selected for ozone weekday/weekend effect analysis during May–August 2018 (Figure S3); **Figure 1** for HCHO-VCD_{Trop} (Figure S4); **Figure 1** for NO₂-VCD_{Trop} (Figure S5); VCD_{Trop} of HCHO, NO₂, and HCHO/NO₂ ratio from TROPOMI on ozone exceedance versus nonexceedance days during summer in NYC (Figure S6); distribution of changes in the differences in VCD_{Trop} of HCHO, NO₂, and HCHO/NO₂ ratio from randomly sampled 5-day pairs of ozone exceedance versus nonexceedance days (Figure S7); **Figure S6** from OMI retrievals in NYC (Figure S8); distribution of surface HCHO at Westport and surface NO₂ at AQS SLAMS on ozone exceedance and nonexceedance days (Figure S9); daily wind patterns on days selected for high-ozone episode analysis (Figure S10); differences in the planetary boundary layer height between ozone exceedance and nonexceedance days (Figure S11); **Figure S6** from TROPOMI retrievals in BAL/DC (Figure S12); VCD_{Trop} of HCHO, NO₂, and HCHO/NO₂ ratio from TROPOMI on weekends versus weekdays during summer in NYC (Figure S13); **Figure S13** in BAL/DC (Figure S14); **Figure 2d** for weekends versus weekdays (Figure S15); temperature and wind conditions on weekends versus weekdays (Figure S16); uncertainties in TROPOMI-retrieved VCD_{Trop} of HCHO and NO₂, and HCHO/NO₂ ratio (Figure S17); and uncertainties in concentrations and ratio in percentage as divided by their absolute values (Figure S18) (PDF)

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All authors have given approval to the final version of the manuscript.

Notes

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