

Ozone Production Efficiencies in the Three Largest United States Cities from Airborne Measurements

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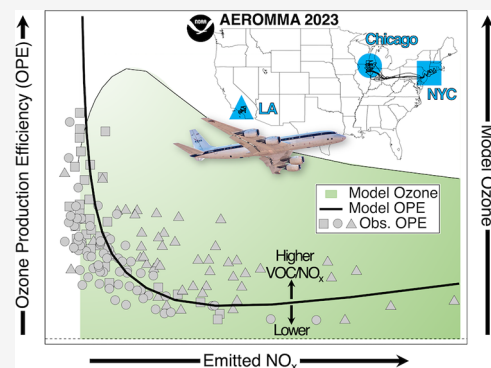
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ABSTRACT: Despite ongoing reductions in emissions of ozone (O_3) precursors, nitrogen oxides ($NO_x = NO + NO_2$) and volatile organic compounds (VOCs), the three largest urban areas in the United States — New York City (NYC), Chicago, and Los Angeles (LA) — continue to exceed national air quality standards for O_3 . Airborne measurements during the 2023 Atmospheric Emissions and Reactions Observed from Megacities to Marine Areas (AEROMMA) campaign investigated nonlinear O_3 photochemistry in these cities. We report mean ozone production efficiency (OPE), the enhancement ratio of $O_x (= O_3 + NO_2)$ to NO_x oxidation products, of 9 ± 4 (1σ), 6 ± 3 , and 6 ± 3 ppbv ppbv $^{-1}$ in NYC, Chicago, and LA, respectively. Compared to historical values, OPE has increased in NYC but remains constant in LA. We find that OPE during AEROMMA has a nonlinear, inverse relationship with total reactive nitrogen (NO_y , a proxy for initial NO_x) and a positive correlation with the nonmethane VOC to NO_y enhancement ratio. A zero-dimensional photochemical model supports these observed OPE dependences on NO_x and VOCs and shows that OPE is a distinct metric from total O_3 production that is informative to the development of O_3 pollution control strategies. We find that OPE values have higher variability, and a larger increase with NO_x emissions reductions, in areas that experience NO_x -sensitive rather than NO_x -saturated O_3 photochemistry; nonetheless, NO_x reductions under NO_x -sensitive conditions still reduce total O_3 production despite the corresponding increase in OPE.

KEYWORDS: tropospheric ozone, ozone production efficiency, urban air quality, air pollution, megacities



1. INTRODUCTION

The majority of the global population resides in urban areas, with 13% of urban dwellers living in megacities (population > 10 million) as of 2018.¹ Poor urban air quality is a leading threat to human health that causes millions of annual premature deaths worldwide;^{2,3} with projections for continued urbanization and population growth, an increasing number of people will experience the impacts of urban air pollution in the coming decades. One major pollutant that degrades air quality is tropospheric ozone (O_3), which forms photochemically from primary emissions of nitrogen oxides ($NO_x = NO + NO_2$) and volatile organic compounds (VOCs). In the United States (US) and Europe, substantial decreases in urban O_3 pollution have been achieved over the past decades through the mitigation of NO_x emissions.^{4,5} For the largest urban areas in the US, however, reductions in O_3 pollution have stagnated in recent years despite continually decreasing national NO_x emissions.^{6,7} Recent work has shown that as motor vehicle VOC emissions

continue to decline,⁸ biogenic VOCs,^{9–11} the class of VOCs known as volatile chemical products (VCPs),^{12,13} cooking VOCs,¹⁴ and asphalt VOCs¹⁵ have an increasingly important contribution to O_3 photochemistry.¹⁶ Other emission sources, such as increasing oil and gas development^{17–20} and wildfire activity,^{21–24} have also affected recent trends in urban O_3 . This changing emissions landscape may impact the photochemical regime in which urban O_3 production occurs. It is well-known that O_3 production and abundances depend nonlinearly on NO_x and VOCs.^{25–27} Reactions R1–R6 are a partial list of the

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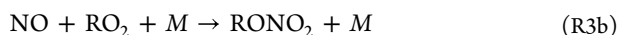
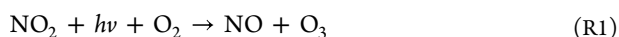
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reactions discussed in this work, where R represents an organic constituent and M is an inert third body.



In a NO_x -sensitive regime, radical propagation reactions (e.g., Reactions R3a and R4) dominate O_3 photochemistry and therefore NO_x emissions reductions decrease O_3 production while VOC emissions reductions have little to no effect on O_3 . In contrast, NO_x radical termination reactions (e.g., Reactions R3b and R6) govern O_3 photochemistry in a NO_x -saturated regime, resulting in increased O_3 production with decreasing NO_x emissions or increasing VOC emissions.

A common metric in the O_3 photochemistry literature is the ozone production efficiency (OPE), a concept introduced by Liu et al. (1987) that quantifies the number of O_3 molecules produced per emitted and subsequently oxidized NO_x molecule.²⁸ These NO_x termination products, such as nitric acid (HNO_3), acyl peroxy nitrate (PAN), or organic nitrates, are collectively termed NO_z (total reactive nitrogen, NO_y , minus NO_x). The conventional definition of OPE from observations is the slope of the linear regression of measured O_3 against NO_z .^{29,30} To account for the rapid daytime interconversion between NO_2 and O_3 as represented by Reactions R1 and R2, it is useful to replace O_3 with odd oxygen, or O_x ($= \text{NO}_2 + \text{O}_3$), in OPE calculation.^{31,32} We calculate OPE in this work as the slope of O_x versus NO_z (eq 1), where Δ indicates the enhancement above background.

$$\text{OPE} = \frac{\Delta \text{O}_x}{\Delta \text{NO}_z} = \frac{\Delta(\text{O}_3 + \text{NO}_2)}{\Delta(\text{NO}_y - \text{NO}_x)} \quad (1)$$

An observation-derived OPE is an integrated metric that represents the cumulative O_3 photochemistry in an air parcel; physical processes such as mixing, deposition, dilution, and fresh emissions can complicate its interpretation.³³ Photochemical modeling, when paired with observations, can parse the impacts of chemical and physical processes on OPE. Model OPE calculated from the ratio of the O_3 production rate to the NO_x loss rate, $\text{P}(\text{O}_3)/\text{L}(\text{NO}_x)$, gives an instantaneous measure of OPE,³⁴ while other methods such as temporal averaging of instantaneous OPE³⁵ or calculation of modeled plume enhancements above background^{33,36} provide a cumulative modeled OPE that is comparable to empirical values. As indicated by the definitions above, OPE is a distinct metric from total O_3 mixing ratio or O_3 production rate; the latter are the focus of many urban O_3 sensitivity analyses.^{37,38} An OPE modeled as $\text{P}(\text{O}_3)/\text{L}(\text{NO}_x)$ can be considered against $\text{P}(\text{O}_3)$, as both represent instantaneous quantities, whereas an observation-based or cumulative modeled OPE is an integrated measure and thus comparable to total O_3 mixing ratio.

Numerous studies have determined OPE from observations to understand the efficacy of O_3 production and, with the support of models, probe the chemistry underlying changes in

O_3 production with emissions reductions. Reported observation-based OPE ($\Delta \text{O}_3/\Delta \text{NO}_z$ or $\Delta \text{O}_x/\Delta \text{NO}_z$) values vary widely, from as low as 1 ppbv ppbv⁻¹ in urban areas to >100 ppbv ppbv⁻¹ in remote marine environments.³⁹ The general trend of increasing OPE with cleaner locations (i.e., urban to rural to remote marine) points to the nonlinear dependence of OPE on NO_x and VOCs. It is well established that air masses with lower NO_x mixing ratios or emissions tend to have higher observed OPE, such as in analyses of OPE in power plant plumes,⁴⁰ urban plumes,^{32,41} and remote or rural areas.^{42,43} Modeling studies support the trend of increasing OPE with decreasing NO_x for both instantaneous and cumulative definitions of OPE.^{17,33,44} Some models demonstrate this trend only above a certain NO_x threshold, below which OPE has a positive correlation with NO_x (e.g., NO_x threshold of ~0.2 ppbv in Lin et al., ~0.3 ppbv in Sillman and He, and ~1 ppbv in Mazzuca et al.),^{34,36,45} but this OPE turnover has not been observed experimentally.⁴⁶ Observation-based comparisons of OPE in low- versus high-VOC environments are rare in the literature.³⁰ However, modeling studies consistently demonstrate an increase in OPE with increasing VOCs or VOC reactivity (VOCR, the sum of VOC abundances multiplied by their OH reaction rate coefficients) over a broad range in NO_x ,^{33,34,44,47} and this understanding has been used to interpret the response of observation-based OPE to the counteracting impacts of NO_x and VOC emission reductions.^{48–50} Some studies have looked at the combined effect of emissions changes as the VOC/ NO_x ratio, finding an increase in OPE with increasing VOC/ NO_x in both observations and models.^{41,51,52} Although OPE tends to be higher in NO_x -sensitive environments and lower in NO_x -saturated environments, an observation-based OPE alone does not allow definitive assignment of O_3 sensitivity regime (Section S1). Nonetheless, OPE provides valuable insight on how effectively NO_x catalytically produces O_3 , with implications for changes in total O_3 production under different emission reduction scenarios.

The Atmospheric Emissions and Reactions Observed from Megacities to Marine Areas (AEROMMA) field campaign of June–August 2023 provided an unprecedented opportunity to determine OPE in the three largest US urban areas within a single O_3 season. The campaign utilized the NASA DC-8 aircraft, with a suite of in situ and remote sensing instruments, to address major science goals that included urban emissions and chemistry, remote marine emissions and chemistry, and validation of new geostationary satellite remote sensing capability.⁵³ The majority of the 148 total science flight hours during AEROMMA were spent on urban sampling patterns in New York City (NYC), Chicago, and Los Angeles (LA) during peak O_3 photochemistry months. In this work, we calculate OPE for these three cities from in situ observations of O_3 and reactive nitrogen species, and we examine the relationship between OPE and other measurements from the DC-8 platform. The results of this analysis help to define the current state of O_3 photochemistry in the three largest urban areas in the US, home to a combined 42 million people,⁵⁴ all of which are in nonattainment status for the current US National Ambient Air Quality Standard for O_3 .⁵⁵

2. METHODS

2.1. In Situ Measurements for OPE Analysis. This analysis focuses on 11 of the 14 urban flights during AEROMMA. These include three of the four NYC flights (July 28, Aug. 9, Aug. 16; July 26 omitted due to lack of NO_y data

for that flight), all of the Chicago flights (Aug. 1, 2, 8, 12, 15), and all of the LA flights (Aug. 23, 25, 26). The research flights in this analysis each included approximately 6 h of urban measurements, during which time the DC-8 made two to three “passes” (repeated raster patterns, *e.g.*, Figure S1) within the boundary layer. Each pass began upwind of the metropolitan area and consisted of sequential downwind transects, ideally perpendicular to the prevailing wind direction. Typical transects were 20–50 km apart and flown at approximately level altitude (~ 550 magl). Table S1 summarizes the meteorological conditions for each of the analyzed flights. Transported smoke from the historic Canadian wildfires of 2023 influenced some of the NYC and Chicago flights but did not impact the results of this study, as addressed in Section 3.4.

The DC-8 payload included two measurements of in situ O_x — the NOAA cavity ring-down spectrometer (CRDS)^{56,57} measured O_x directly, while the sum of the NOAA fast-response chemiluminescence (CL)⁵⁸ O_3 and the NOAA laser-induced fluorescence (LIF)^{59,60} NO_2 provided an additional O_x measurement (CL + LIF O_x) — and the difference of LIF NO_y , NO_2 , and NO enabled calculation of in situ NO_z (instrument details in Section S2). Together, these measurements enabled determination of observed OPE. Many other measurements from the DC-8 payload, listed in Table S2, also contributed to the analysis.

2.2. OPE Calculation Method. An accurate OPE calculation requires that the slope of the regression ($\Delta O_x / \Delta NO_z$) represents the urban plume enhancement above constant background mixing ratios, rather than the effects of mixing between air masses with different emissions, meteorology, and photochemistry. The DC-8 was often unable to traverse the entirety of the plume during AEROMMA due to flight pattern restrictions, so we were unable to compare plume-edge mixing ratios of urban tracers (*e.g.*, CO) as a method for transect filtering, as done in previous analyses.⁶¹ Instead, we first employed several methods to refine the bounds of each transect, and then we tested the sensitivity of the city mean OPEs to the application of different transect-elimination filters.

Across a level transect, where pressure and temperature are expected to remain constant, abrupt changes in potential temperature may indicate a difference in vertical mixing. Steps in relative humidity, especially for transects near the shore of a lake or ocean, may similarly indicate a mixing boundary between two airmasses. We used changes in potential temperature, relative humidity and/or altitude to trim or split transects. The regression of NO_y versus CO across the transect (slope = $\Delta NO_y / \Delta CO$) provided an additional refinement technique, where NO_y serves as a proxy for emitted NO_x .²⁹ A strong positive $\Delta NO_y / \Delta CO$ correlation indicates a constant emission ratio, typically dominated by motor vehicle emissions, in the sampled air mass. Transect $\Delta NO_y / \Delta CO$ regressions showing two discrete populations or distinct curvature, indicative of the mixing of air masses with different emission sources, were either trimmed or split into separate transects before calculating OPE (*e.g.*, Figure S1); no transects were eliminated based on $\Delta NO_y / \Delta CO$ correlation. There were 196 total transects in the analysis after applying these refinement methods.

The OPE was calculated from a linear regression of the O_x and NO_z measurements for each individual transect across the urban plume, where the slope is the OPE ($\Delta O_x / \Delta NO_z$) and the y -intercept is the theoretical background O_x mixing ratio when NO_z equals zero (Figure S2). The results presented in the main text, and in the SI unless explicitly noted, use directly measured

CRDS O_x for OPE calculation and subsequent analysis. A second version of the analysis was conducted in parallel using summed CL + LIF O_x , resulting in OPEs on average 25% higher than those calculated with CRDS O_x (within the city-wide mean OPE uncertainty) and demonstrating the same trends (Tables S3 and S4 and Figure S3). For each transect, an ordinary least-squares (OLS) linear regression was first used to assess the correlation strength via the coefficient of determination (R^2), and then the transect data were evaluated with a weighted orthogonal distance regression (ODR) linear fit^{51,62,63} to obtain the final transect OPE values. Two filters were applied to eliminate transects that may not represent the chemistry in the plume, resulting in a final total of 153 transects in the analysis (additional details in Sections S3 and S4 and Tables S3 and S4). All OPEs reported in this analysis are upper limits due to the potential for dry deposition of HNO_3 that may systematically reduce observed NO_z and thus enhance the apparent OPE.^{29,33,61} We found that correcting the observed transect NO_z for HNO_3 dry deposition lowered the city mean OPE by 3–30%, depending on the literature dry deposition velocity, estimated boundary layer height, and estimated transport time used in the calculation, and the corrections had no impact on the reported trends (Figure S4 and Section S5).

2.3. Zero-Dimensional Photochemical Box Modeling of OPE. We probed the chemistry driving observed OPE values with a simple photochemical box model using the Framework for 0-Dimensional Atmospheric Modeling (F0AM)⁶⁴ with the full Master Chemical Mechanism (MCMv3.3.1) as the near-explicit gas-phase mechanism.⁶⁵ The intent of the model was not to comprehensively model an urban plume, but rather to understand the dependence of OPE on NO_x and VOCs. First, we modeled the observations from a single transect from the Aug. 2 Chicago flight, which we will henceforth call the “target transect.” We chose to model this transect for several reasons: its location over Lake Michigan on a day with south–southwesterly winds allows for the assumption that emissions predominantly come from land-based urban sources at time zero (Figure S5); the target transect observed OPE ($8 \pm 2 / -3$ ppbv ppbv⁻¹) falls within the uncertainty of the mean OPE for each of the three cities, and the high mean ($\pm 2\sigma$) O_3 measured across the transect (81 ± 2 ppbv) is representative of a high O_3 day in the Chicago metropolitan area. We define a section of the flight path west of the target transect, outside of the urban plume, as the “background transect.” The model setup and inputs, described extensively in Section S6, are summarized here.

The model is a Lagrangian framework and is initialized with mixing ratios of VOCs and NO_x that are representative of emissions from biogenic and anthropogenic sources. The model assumes that the evolution of a chemical species is determined by reaction and dilution with background air (eq 2),

$$\frac{dC_i}{dt} = \sum r_i(t) - k_{dil}(C_i - C_{b,i}) \quad (2)$$

where C_i is the concentration of species i , $r_i(t)$ represents the time-dependent reaction rate for species i (sum of gas-phase chemical production and loss terms), and dilution is parametrized by a first-order rate coefficient (k_{dil}) and the background (*i.e.*, out-of-plume) species concentration ($C_{b,i}$). For HNO_3 , we also include a first-order dry deposition loss term. The model run length of 5 h represents the approximate transport time between the urban center and the target transect as determined from a HYSPLIT back-trajectory analysis.⁶⁶ Background concentrations for all species were set as the mean

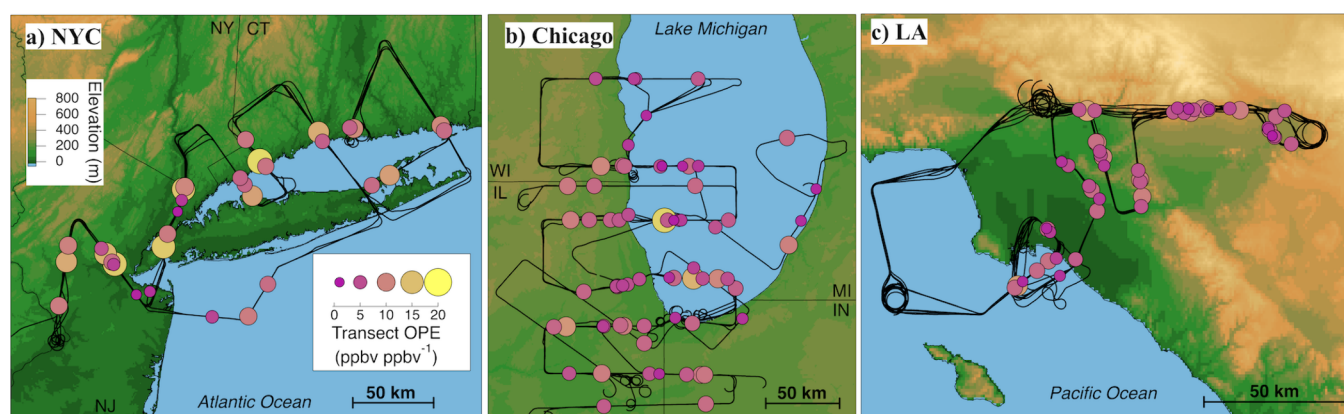


Figure 1. Boundary layer flight tracks (black traces) for all flights included in the analysis. The size and color of the circular markers, plotted at the center of each transect, indicate the magnitude of the observed OPE at that transect. The legends in panel (a) apply to all three panels.

observed mixing ratios across the background transect. The initial concentrations ($C_{i,t=0}$) of primary species in the model, such as NO_x and isoprene, were estimated using an iterative scheme (see below), while the initial concentrations of secondary species in the model, such as O_3 and PAN, were set equivalent to the background concentration for that species. The model was constrained with measured temperature, pressure, water vapor, and NO_2 photolysis rate ($j\text{NO}_2$) across the target transect.

The “base model” was determined by iterating initial concentrations of primary species and tuning k_{dil} until model output O_3 , NO_z , NO_x , and VOCR agreed within $\pm 2\sigma$ of the observed target transect mean, and observed and modeled OPE agreed within the observed OPE uncertainty (Section S6). We subsequently used the base model for OPE sensitivity tests (see Section S7 for details). Briefly, a range of initial NO_x values (0.1 to 100 ppbv) and initial primary VOC scaling factors (0.1 to 15) were applied to the model. Each sensitivity test consisted of a single model run in which the base model was perturbed with a unique combination of initial NO_x and primary VOC scaling, and the final model OPE, time-averaged VOCR, and final species mixing ratios were recorded. The modeled OPE was calculated as the enhancement ratio of O_x to NO_z (eq 1), where the enhancement as represented in the model is the difference between the final modeled mixing ratio and background mixing ratio of O_x and NO_z , respectively.

3. RESULTS AND DISCUSSION

The arithmetic mean ($\pm 1\sigma$) OPE during AEROMMA in NYC was 9 ± 4 ppbv ppbv⁻¹, while the mean OPE for both Chicago and LA was 6 ± 3 ppbv ppbv⁻¹. Table S7 provides the mean OPE for each individual flight along with other city-wide statistics. Ozone production efficiency depends on a variety of factors within urban areas. In the following, we investigate the dependence of OPE on: the spatial distribution of emissions and their interaction with local meteorology, the chemical plume age and local time of day, concentrations of NO_x , concentrations of VOCs and VOCR, and the ratio of VOC to NO_x .

3.1. Spatial Dependence of OPE. Since OPE is an integrated measure of photochemistry in an air parcel that has a different dependence on NO_x and VOCs than total O_3 mixing ratio or production rate, its spatial distribution may differ from that of maximum O_3 mixing ratios. We examine this relationship in each of the three cities in Figure 1, where transect OPEs are overlain on the boundary layer flight tracks in that city.

Coastal meteorology, and its association with O_3 exceedances, is a long-standing area of research.^{67–69} In addition to elevated O_3 in NYC itself, the downwind, densely populated regions of Long Island and southern Connecticut regularly experience high surface O_3 due to coastal circulation patterns.⁷⁰ The NYC urban plume frequently transports from the southwest with the prevailing morning winds over Long Island Sound, where pollutants may be concentrated within the shallow marine boundary layer before experiencing onshore transport from sea breeze meteorology in the afternoons or evenings.^{69,71} The spatial distribution of transect OPEs in this work does not align strongly with the usual location of high O_3 mixing ratios in the NYC metro area (Figure 1a and Figure S7a). Because meteorology (Table S1) and maximum O_3 concentrations were variable during the NYC flights, the AEROMMA observation-based OPEs may not represent a typical NYC metro area O_3 exceedance day.

In Chicago, the highest O_3 values in the region consistently occur on the shore of Lake Michigan.⁷² Several modeling studies point to lake-land breeze circulation as a driver for this spatial pattern in O_3 exceedances. High O_3 production rates tend to occur over the surface of Lake Michigan,^{73,74} and the mixed layer above the lake — which frequently remains shallow and stable throughout the day and demonstrates suppressed vertical mixing — enables persistent high O_3 over the water despite a lack of fresh emissions.⁷⁵ The lake breeze, predominately from the southeast, then transports high O_3 onto the western shore of Lake Michigan.^{67,76} The distribution of Chicago transect OPEs in the present analysis do not show strong spatial trends, regardless of wind direction or maximum observed O_3 on the flight day (Figure 1b and Figure S7b,d). The AEROMMA data thus suggest that high lakeshore O_3 results from the unique meteorology of Lake Michigan rather than a shift in chemistry at the shoreline.

The topography and meteorology of the LA Basin has a well-understood influence on the location of maximum O_3 mixing ratio.⁷⁷ With a strong westerly sea breeze that transports polluted air inland, monitoring sites in the eastern part of the LA Basin have historically experienced the highest and most persistent O_3 .⁷⁸ The shift in the LA Basin O_3 sensitivity regime over the past decade, from more to less NO_x -saturated, impacts the location of the highest O_3 mixing ratios.^{7,79–82} In the present study, however, transect OPEs show no spatial dependence across the region (Figure 1c and Figure S7c), consistent with OPE as a measure that is independent of O_3 mixing ratio itself.

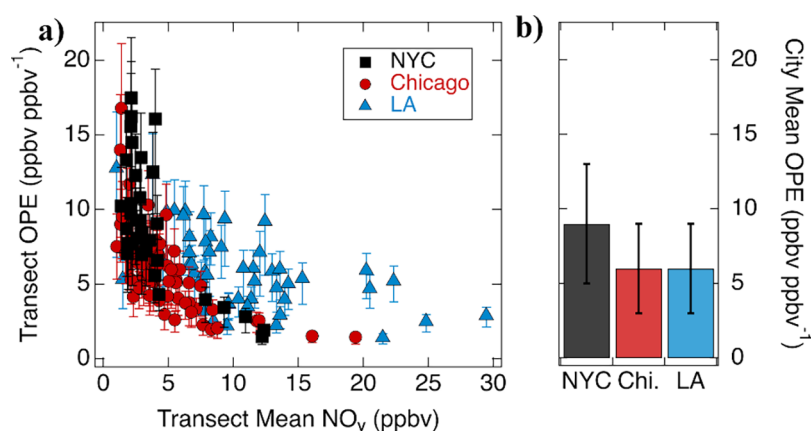


Figure 2. (a) Ozone production efficiency at each transect plotted against mean NO_y . The asymmetric OPE error bars incorporate weighted ODR fit error, systematic measurement uncertainty, and uncertainty due to NO_z loss (see Section S3 and S5 for details). (b) Mean OPE for each city, where error bars represent $\pm 1\sigma$.

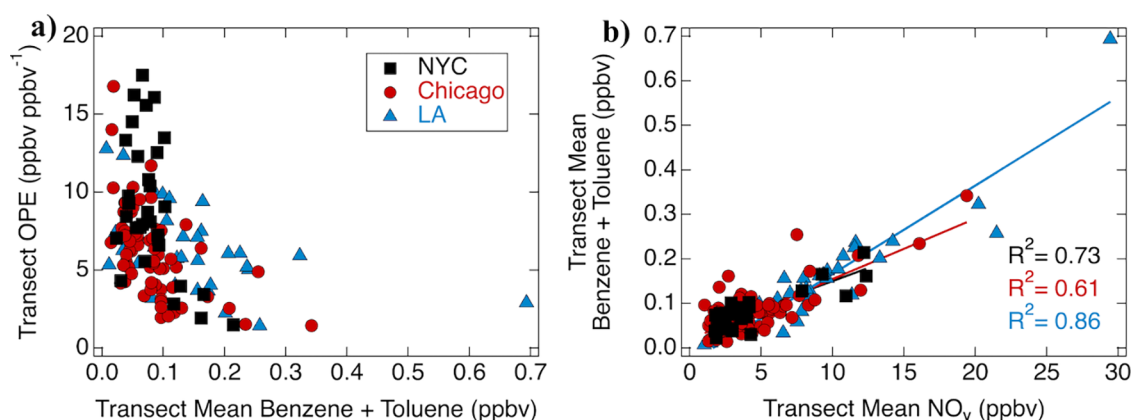


Figure 3. (a) Ozone production efficiency at each transect plotted against mean benzene + toluene as a tracer for fossil fuel VOCs. (b) Transect mean benzene + toluene plotted against mean NO_y , with OLS linear fit (solid lines) R^2 values appearing in each city's corresponding color. The legends in panel (a) apply to both panels. See Figure S11 for equivalent plots with VCPs, biogenic VOCs, and VOCR.

3.2. Temporal Dependence of OPE. We assessed two temporal variables for their potential impacts on OPE: chemical plume age and the time of day. Observations of NO_x and NO_y across each transect enable an estimation of the chemical age of the plume at the time of measurement (t), where $\tau (= 1/k')$ is the effective NO_x lifetime (eq 3). Although τ is unknown for these transects, if τ is approximately constant then the natural log of the $\Delta\text{NO}_x/\Delta\text{NO}_y$ enhancement ratio yields a value that is proportional to chemical plume age (eq 4); if NO_x emissions are continuous rather than from a discrete source, this equation provides an average measure of chemical plume age.

$$\frac{[\text{NO}_x]}{[\text{NO}_y]} \approx \frac{[\text{NO}_x]_t}{[\text{NO}_x]_0} = \exp\left(-\frac{t}{\tau}\right) \quad (3)$$

$$t \propto \ln \frac{[\text{NO}_x]}{[\text{NO}_y]} \quad (4)$$

Within a single air parcel, modeled instantaneous OPE is expected to increase with plume age due to the reduction in NO_x over time.³² Studies of observation-based OPEs in a single plume (*i.e.*, the integrated sum of instantaneous OPEs) have also found an increase in OPE with plume age.^{33,40,83} In our analysis, however, the value of the calculated OPEs do not have a strong dependence on this measure of chemical plume age (Figure S8).

There is no positive correlation between OPE and the locally observed $j\text{NO}_2$ (Figure S9), although there is a weak positive correlation ($R^2 = 0.43$) between OPE and local time in LA only (Figure S10). Increased photolysis rates, for which $j\text{NO}_2$ is a proxy, increase the total primary radical source and thus the rate of instantaneous O_3 production for a given amount of NO_x . The lack of dependence of OPE on photolysis rates demonstrates that OPE is an integrated rather than instantaneous quantity.

3.3. OPE Dependence on NO_x . The transect OPEs determined from aircraft observations during AEROMMA display a strong inverse, nonlinear dependence on the mean transect NO_y in all three cities (Figure 2a). The use of NO_y on the x -axis serves as a proxy for NO_x in the plume at the time of emission.²⁹ The OPEs for NYC and Chicago fall on a similar curve, while the OPEs for LA have a somewhat different dependence, as we explore further in Sections 3.4–3.6. This demonstrates that cities with a similar mean OPE (Figure 2b) may not necessarily have a similar OPE dependence on emitted NO_x (*i.e.*, NO_y). The inverse relationship between observation-based OPE and NO_x during AEROMMA is similar to that in the literature where both OPE and NO_x observations are reported, such as the dependence of aircraft-based OPEs on NO_x in Phoenix, Arizona (May 1998)³² and the dependence of ground-based summer OPE on NO_z in the southeastern US (1996–2014).⁸⁴ We compare the AEROMMA observation-based OPEs

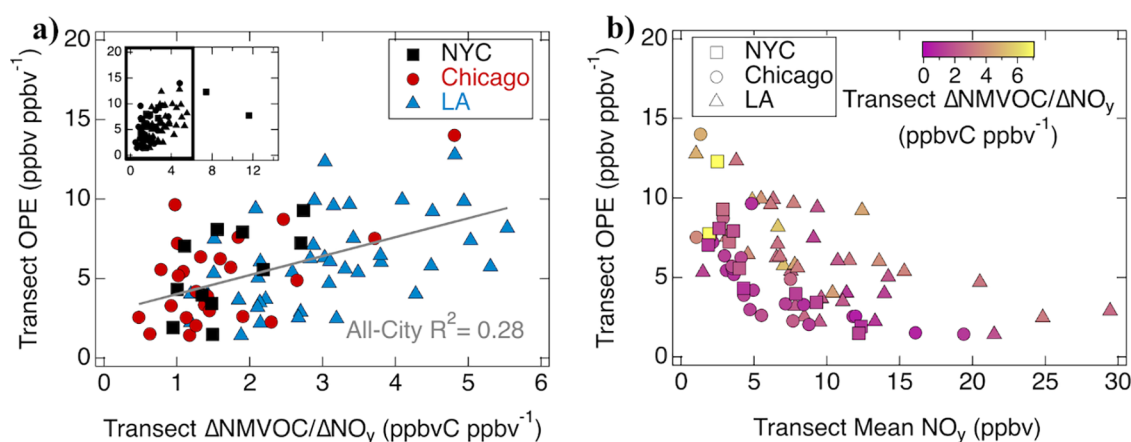


Figure 4. (a) Ozone production efficiency at each transect plotted against the $\Delta\text{NMVOC}/\Delta\text{NO}_y$ enhancement ratio. Transects with $\Delta\text{NMVOC}/\Delta\text{NO}_y$ OLS fit $R^2 < 0.5$ are excluded. The inset figure shows the full x -axis, while the main figure excludes the two NYC outlier points. Ordinary least-squares fit (solid line) R^2 value for all cities together, excluding the two outlier points, is 0.28. (b) Transect OPE plotted against mean NO_y and colored by $\Delta\text{NMVOC}/\Delta\text{NO}_y$.

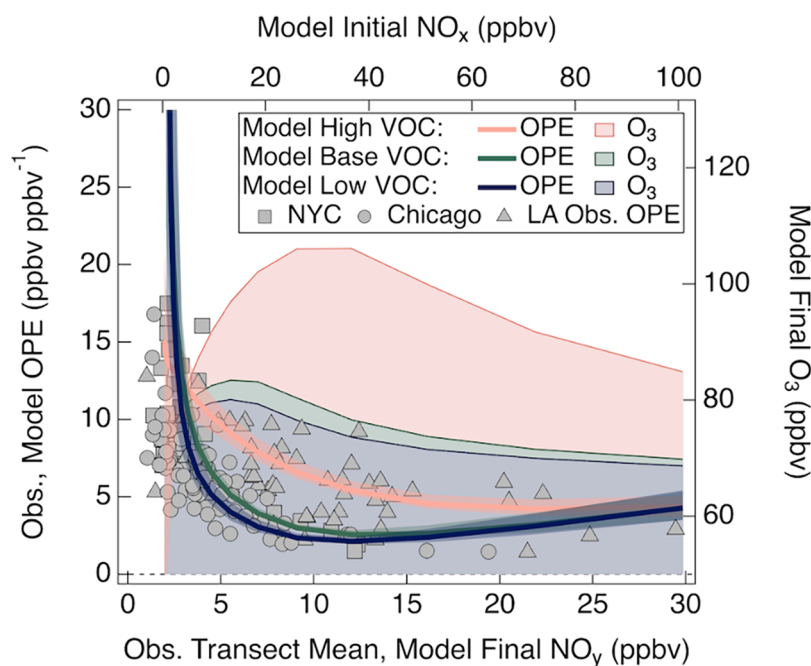


Figure 5. Comparison of observed OPE to model output to provide context for model results; the box model does not necessarily represent the true position of the observed transects on an OPE or total O_3 curve. Observed OPE at each transect is plotted against mean observed NO_y (gray markers). Solid lines represent model OPE (translucent error shading represents model sensitivity to transport time, photolysis rate scaling, and background mixing ratios) and solid shading represents model final O_3 for low ($0.1\times$), base ($1\times$), and high ($10\times$) initial primary VOC scaling. Corresponding mean time-averaged model VOCR for low, base, and high VOC scaling is 1.8 , 2.7 , and 13 s^{-1} , respectively.

to historical OPE values and emissions trends in NYC and LA in Section 3.6.

3.4. OPE Dependence on VOCs. To investigate possible OPE correlations with VOCs from different emissions sources, we identified three tracer VOCs (or groups of VOCs) that are relatively long-lived and come predominantly from a single emission sector: the sum of benzene and toluene as a tracer for fossil fuel emissions;^{85,86} decamethylcycllopentasiloxane (DS siloxane) as a tracer for VCP emissions;⁸⁷ and the sum of isoprene and two of its major oxidation products, methyl vinyl ketone (MVK) and methacrolein (MACR), as a tracer for biogenic emissions (Table S8). Measurements of total OH reactivity and speciated VOCs during AEROMMA indicate that these three sources of VOCs make up the majority of identifiable

urban VOCR during the campaign.⁸⁸ We also calculated VOCR from observed OH reactivity (Table S2 and Section S8), however VOCR provides limited insights because it is an instantaneous rather than integrated metric. In Figure 3a, transect OPEs demonstrate a nonlinear, inverse correlation with fossil fuel tracer VOCs in all three cities that mirrors the nonlinear correlation between OPE and NO_y (Figure 2a). There is a strong positive correlation between fossil fuel VOCs and transect mean NO_y (Figure 3b; NYC $R^2 = 0.73$, Chicago $R^2 = 0.61$; LA $R^2 = 0.86$). If the dependence of OPE on NO_x is stronger than the relationship between OPE and VOCs, then the apparent dependence of OPE on fossil fuel VOCs in Figure 3a is a result of colocated NO_x and VOC sources. We test this hypothesis using a photochemical box model in Section 3.5.

Figure S11a–f present equivalent figures for VCPs, biogenic VOCs, and VOCR. The correlation of OPE with VCPs (Figure S11a) is similar to Figure 3a, and there is also a strong positive correlation between VCPs and NO_y (Figure S11b; NYC $R^2 = 0.90$; Chicago $R^2 = 0.86$; LA $R^2 = 0.73$). In contrast, there is little to no correlation between biogenic VOCs and OPE or NO_y (Figure S11c,d; $R^2 < 0.30$ for all cities). The correlation between OPE and VOCR is very weak for all cities ($R^2 < 0.20$; Figure S11e), while the correlation between VOCR and NO_y (Figure S11f) is strong in LA ($R^2 = 0.68$) and weak in Chicago ($R^2 = 0.36$). The lack of correlation between VOCR and NO_y in NYC may be due to the influence of biogenic VOCs, which do not correlate with NO_y in NYC (Figure S11d). Additionally, there is no strong dependence of OPE on acetonitrile (ACN), a biomass burning tracer VOC, allowing us to conclude that transported wildfire smoke during summer 2023 did not significantly impact our results (Section S9 and Figure S12).

From the OPE modeling literature discussed in Section 1, we expect an increase in OPE with increasing VOCs or VOCR,^{33,34,44,47} but this dependence is difficult to distinguish in the simple correlations shown thus far. We next assess the dependence of OPE on the nonmethane VOC (NMVOC) to NO_y enhancement ratio as an estimate of the VOC/ NO_x ratio. We calculate $\Delta\text{NMVOC}/\Delta\text{NO}_y$ as the weighted ODR slope of the carbon-weighted sum of calibrated, in situ VOCs (Table S8) against NO_y across the transect, omitting transects with OLS fit $R^2 < 0.5$ from the subsequent analysis. Because this $\Delta\text{NMVOC}/\Delta\text{NO}_y$ calculation does not include integrated whole-air sampler VOC canister samples, the magnitude is an underestimate due to the omission of alkanes and small alkenes, but the trend with OPE is informative. There is a positive correlation between transect OPE and $\Delta\text{NMVOC}/\Delta\text{NO}_y$ in all three cities (Figure 4a; NYC $R^2 = 0.38$ with two outlier points excluded; Chicago $R^2 = 0.37$; LA $R^2 = 0.25$), as has been observed in the literature.^{41,51,52} However, since both increasing VOCs and decreasing emitted NO_x lead to increased $\Delta\text{NMVOC}/\Delta\text{NO}_y$ and are also expected to increase OPE, this correlation alone does not provide further information about the dependence of OPE on VOCs compared to NO_x . Figure 4b effectively demonstrates that increased VOCs correlate with increased OPE, where $\Delta\text{NMVOC}/\Delta\text{NO}_y$ helps to explain the variation in OPE for similar values of transect mean NO_y .

3.5. Modeled OPE Dependence on NO_x and VOCs. The zero-dimensional photochemical box model for the Aug. 2 Chicago target transect was iterated to achieve agreement (within $\pm 2\sigma$ of the target transect mean, or within OPE uncertainty) between modeled and observed OPE (modeled = 8.2 ± 0.6 ppbv ppbv⁻¹; observed = $8 \pm 2/-3$ ppbv ppbv⁻¹), O_3 , NO_z , NO_x , and VOC reactivity (Figure S13). The model also agreed with observations of the top four contributors to model VOC reactivity (Figure S14): formaldehyde (modeled as a secondary species), acetaldehyde, methanol, isoprene (modeled as primary species, *i.e.*, constrained). This representation of the target transect was then used as the base model upon which to test the response of OPE to perturbations in initial NO_x and primary VOCs.

Figure 5 presents a comparison of the OPE observations at each transect to the model OPE and model final O_3 . The model curves represent a subset of the six initial primary VOC scaling factors tested: 0.1 $\times$ scaling as “low VOC” (mean of time-averaged model VOCRs for each model run at this VOC scaling is 1.8 s^{-1}), 1 $\times$ scaling as “base VOC” (mean VOCR is 2.7 s^{-1}), and 10 $\times$ scaling as “high VOC” (mean VOCR is 13 s^{-1}). To

facilitate comparison between the observations and the model, the model OPE and O_3 curves are plotted against final model NO_y on the bottom axis, with the corresponding model initial NO_x on the top axis. The intent of the comparison in Figure 5 is to provide an observational context for the modeled dependence of OPE on NO_x and VOCs; perturbations of a single base model cannot accurately represent all of the observed transects with respect to their position on an OPE or total O_3 versus NO_x curve. The model-observation comparisons are therefore qualitative rather than quantitative. For the majority of the observed NO_y values, both modeled and observed OPE increase with decreasing initial NO_x (final NO_y). Trends in model final O_3 , O_x , NO_z , OH , and HO_2 as a function of initial NO_x and primary VOC scaling factors (Figure S15) help to explain the chemistry driving the model OPE, as discussed further in Section S10. The agreement of the high VOC model OPE curve with many of the LA observations suggests that high VOCs (high VOCR) in LA could explain the elevated values of observed OPE despite corresponding high values of measured NO_y , as Figure 4b also supports. Robust comparisons between observed and modeled OPE break down below the value of the observed background NO_y mixing ratio, 2.3 ppbv (~ 1.5 ppbv model initial NO_x), because the background mixing ratios in the model remain fixed regardless of the initial model NO_x perturbation. The model OPE error shading captures some of uncertainty induced by this effect (Section S7).

3.6. Observed and Modeled OPE in the Context of Historical Measurements. The results of the observations and model help us to understand historical trends in OPE with changing emissions in NYC and LA. To our knowledge, there are no historical, observation-based OPEs reported in Chicago. From 1996 to 2023, inventory NO_x emissions (expressed as mass of NO_2) in New York state decreased from ~ 8 to 2 Mtons yr^{-1} .⁸⁹ Over the same period, the mean OPE in NYC increased from 2–4 ppbv ppbv⁻¹ in 1996 (OPE defined as $\Delta\text{O}_3/\Delta\text{NO}_z$; the equivalent $\Delta\text{O}_x/\Delta\text{NO}_z$ value may be slightly higher),⁹⁰ to 6–8 ppbv ppbv⁻¹ in 2016,⁴⁶ to 9 ± 4 ppbv ppbv⁻¹ in 2023 during AEROMMA (Figure S16). In contrast, over the period 1973 to 2010 in LA, Pollack et al. (2013) found no discernible trend in OPEs determined from field campaign data despite statistically significant decreases in both NO_x and VOCs, likely due in part to the counteracting effects of these decreases on OPE.⁵¹ The two most recent airborne field campaigns (ARCTAS-CARB in 2008, CalNex in 2010) in the analysis both measured OPEs of ~ 6 ppbv ppbv⁻¹, and the mean observed LA OPE in 2023 during AEROMMA was also $6 (\pm 3)$ ppbv ppbv⁻¹, although NO_x emissions decreased over the intervening period.^{7,91} In the observation-based component of our analysis, the dependence of individual transect OPEs on emitted NO_x during AEROMMA align with these historical trends; the individual transect OPEs in NYC have a stronger dependence on (change more steeply with) transect NO_y than those in LA.

Our model results suggest an explanation for these different trends in OPE despite similar reductions in NO_x and VOCs across the US. In Figure S17, we consider the lower and upper quartiles of the mean NO_y values for all OPE transects to roughly represent NO_x -sensitive and NO_x -saturated conditions, respectively. The position of the NO_y quartiles with respect to the base model total O_3 curve supports this approximation. Observed OPEs for all three cities have larger variability ($\sigma = 3$ ppbv ppbv⁻¹) under NO_x -sensitive conditions compared to NO_x -saturated conditions ($\sigma = 2$ ppbv ppbv⁻¹). This variability is

consistent with model OPE predictions, which vary strongly with NO_x in the NO_x -sensitive regime but vary little with NO_x in the NO_x -saturated regime. Therefore, we expect OPE under more NO_x -sensitive conditions to have a stronger response to decreases in NO_x emissions. We also compare the distribution of OPE for individual cities under different O_3 sensitivity regimes (Table S9). Across all three cities, NO_x -sensitive conditions correspond to larger and more variable OPEs when compared to NO_x -saturated conditions. The OPE distribution in LA presents an interesting example of the nuance within a city-wide mean OPE. LA has a higher NO_x -saturated mean OPE than NYC and Chicago, likely due to higher VOCR (Figure 5), yet the overall mean OPE in LA is lower than that in NYC because of overall higher NO_x in LA.

4. IMPLICATIONS FOR NO_x -VOC O_3 MITIGATION STRATEGIES

We analyzed the efficiency of summertime urban O_3 production across the largest US urban areas during July–August 2023. Mean aircraft-based OPEs were 9 ± 4 , 6 ± 3 , and 6 ± 3 ppbv ppbv^{-1} in NYC, Chicago, and LA, respectively, marking an increase in OPE in NYC but not in LA when compared to available historical data. The observations show a distinct increase in OPE with decreasing NO_y , and an increase in OPE with increasing $\Delta\text{NMVOC}/\Delta\text{NO}_y$, in all three cities. The observations exhibit no strong spatial or temporal relationship with OPE. A zero-dimensional photochemical box model describes the observed OPE, providing qualitative insight into the chemistry driving the nonlinear dependence of OPE on NO_x and VOCs and the distinction between OPE and total O_3 production. This analysis emphasizes several important attributes of urban OPE:

1. NO_x produces O_3 most efficiently at the lowest NO_x values. Therefore, at low NO_x , OPE continues to increase even as total O_3 production decreases with decreasing NO_x . For example, at ~ 5 ppbv initial NO_x and model base VOC scaling (Figure 5), a 20% reduction in emitted NO_x increases OPE by 9% but nonetheless reduces O_3 by 1%. Although an increasing OPE means that each individual emitted NO_x molecule produces more O_3 , reducing NO_x emissions (when NO_x is low) still effectively reduces total O_3 production.
2. At most urban levels of NO_x , decreases in VOCs or VOCR will decrease OPE. Concomitant reductions in NO_x and VOCs may have a counteracting impact on OPE, especially when the range in possible OPE values is relatively small (when NO_x is high). The opposing dependencies of OPE on NO_x and VOCs both drive the increase in OPE with an increasing VOC/ NO_x ratio.
3. Ozone production efficiency increases most steeply with decreasing NO_x at low NO_x values, whereas OPE changes relatively slowly with decreasing NO_x at high NO_x values. This means that observed OPEs in NO_x -sensitive photochemical regimes likely have higher variability, and a larger response to NO_x emissions reductions, compared to more NO_x -saturated regimes.
4. Without comprehensive and location-specific modeling, a single OPE does not indicate the photochemical regime that dictates O_3 production; similar OPE spatially or temporally does not necessarily mean that the O_3 production regime is the same. Instead, an observation-based OPE analysis, such as that presented here,

elucidates the efficiency of NO_x as an O_3 formation catalyst and how this efficiency may change with emissions reductions. This analysis illustrates the value of combined measurements of O_x and NO_z component species (O_3 , NO_2 , NO_x , and NO_y) to facilitate the calculation of OPE. Consideration of observation-based OPE alongside total O_3 production or O_3 production rates will enhance the understanding of urban O_3 photochemistry in the context of changing NO_x and VOC emissions.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are publicly available on the AEROMMA data archive: <https://csl.noaa.gov/projects/aeromma/data.html>.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.5c02073>.

Text, figures, and tables containing additional descriptions of instrumentation, analysis methods, box model setup, and results (PDF)

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Notes

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