Responses in Ozone and Its Production Efficiency Attributable to Recent and Future Emissions Changes in the Eastern United States

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ABSTRACT: Ozone production efficiency (OPE), a measure of the number of ozone (O₃) molecules produced per emitted NOX (NO + NO₂) molecule, helps establish the relationship between NOX emissions and O₃ formation. We estimate long-term OPE variability across the eastern United States using two novel approaches: an observation-based empirical method and a chemical transport model (CTM) method. The CTM approach explicitly controls for differing O₃ and NOX reaction product (NO Z) deposition rates and separately estimates OPEs from on-road mobile and electricity generating unit sources across a broad spatial scale. We find lower OPEs in urban areas and that average July OPE increased over the eastern United States domain between 2001 and 2011 from 11 to 14. CTM and empirical approaches agree at low NOZ concentrations, but CTM OPEs are greater than empirical OPEs at high NOZ. Our results support that NOX emissions reductions become more effective at reducing O₃ at lower NOZ concentrations. Electricity generating unit OPEs are higher than mobile OPEs except near emissions locations, meaning further utility NOX emissions reductions will have greater per unit impacts on O₃ regionally.

INTRODUCTION

Atmospheric scientists have understood the underlying mechanisms of ozone (O₃) production for decades; however, air quality managers continue to have trouble meeting ozone standards, particularly as they have been tightened in response to health studies identifying impacts at lower concentrations.¹,² The availability of detailed ambient monitoring data and much expanded modeling capabilities presents an opportunity for a detailed assessment of the effectiveness of past and future air quality improvement efforts. An assessment of this type—investigating changing factors attributable to air quality controls—serves to link accountability assessments (i.e., efforts to quantify the impacts of existing regulatory programs) to proposed air quality programs.

Largely as a result of air quality management policies, anthropogenic emissions of two contributors to ozone concentrations—nitrogen oxides (NOX = NO + NO₂) and volatile organic compounds (VOCs)—have decreased throughout the eastern United States over the past two decades, particularly in urban areas.³,⁴ Emissions reductions, particularly in electrical generating unit (EGU) and mobile source sectors, have led to reduced levels of ambient NOX, NOX reaction products (NO Z = total atmospheric oxidized reactive nitrogen (NOY) minus NOX), and VOCs.⁵,⁶ These reductions have been...
linked to changing \( \text{O}_3 \) concentrations—both reductions (primarily in the summer) and increases (primarily in the winter and in VOC-limited urban areas).\(^1\) Multiple studies have found that meteorology has a major impact on daily \( \text{O}_3 \) concentrations,\(^2,3\) and climate variability and synoptic patterns impact longer-term trends.\(^4,5\)

Ozone production efficiency (OPE) has historically been a popular method for reporting the relationship between \( \text{O}_3 \) and \( \text{NO}_x \). OPE is defined as “the number of molecules of \( \text{O}_3 \) formed per each \( \text{NO}_x \) molecule removed from the system.\(^6\) \( \text{NO}_x \) generates \( \text{O}_3 \) as it cycles between NO and \( \text{NO}_2 \), and since each \( \text{NO}_x \) molecule that enters the system must leave, the emissions rate approximates the loss rate across a large scale. The reaction of \( \text{NO}_2 \) with \( \text{OH} \)—which forms nitric acid (HNO\(_3\))—is typically the dominant pathway for \( \text{NO}_x \) loss, though it can combine with organics or form HNO\(_3\) via N\(_2\)O\(_5\) hydrolysis (which occurs primarily at night).\(^7\) OPE has important policy implications, since it provides an estimate for how much less ozone would be formed for a specified reduction in \( \text{NO}_x \) emissions.\(^8,9\)

Previous studies using both observation-based and chemical transport model (CTM)-based approaches have found increasing OPEs as \( \text{NO}_x \) or \( \text{NO}_2 \) decreases.\(^10,11\) This increase carries the implication that \( \text{NO}_x \) emission reductions become increasingly effective. There has, however, been little investigation of OPE at very low \( \text{NO}_2 \) concentrations. We set out to fulfill two objectives: (1) assess multiple observation and CTM-based approaches for estimating total and source-specific OPEs in the eastern United States and (2) project impacts of continuing \( \text{NO}_x \) emissions reductions on future OPEs and \( \text{O}_3 \) concentrations.

## METHODS

**Observation-based OPE.** We use observations from the SouthEastern Aerosol Characterization (SEARCH) network sampling sites,\(^12,13\) which provide meteorological data and \( \text{O}_3 \), \( \text{NO}_x \), and \( \text{NO}_y \) species observations at eight locations from 1996 to 2015 (not all sites were online for the entire period). The eight locations comprise four pairs: three urban—rural and one urban—suburban. Throughout this manuscript, we refer to the sites by their three-letter acronym and a superscript that denotes if the site is in an urban (U), rural (R), or suburban (S) location. The southeastern United States is characterized by hot, humid summers with periods of stagnation interrupted by large thunderstorms. Winters are typically mild and drier, though extended periods of wet weather accompany frontal activity. Isolated city centers and power plants, situated throughout mixed coniferous and deciduous forests and agricultural land, serve as major air pollution sources.\(^14\)

Previous studies have used the relationship between \( \text{O}_3 \) and \( \text{NO}_2 \) as an empirical estimate of OPE; in a single plume, the loss of \( \text{NO}_x \) equals the production of \( \text{NO}_2 \) when the deposition rate of \( \text{NO}_x \) is negligible.\(^15\) Kleinman et al. noted that a major limitation to using a fixed-site monitor to estimate OPE is that air masses crossing a monitor have potentially very different histories.\(^15\) Take, for instance, the case of a monitor near a city: at times, it would be downwind of the city; \( \text{O}_3 \) (and \( \text{NO}_2 \)) levels would be high as the city contributes fresh emissions that lead to high ozone levels, but the \( \text{NO}_2 \) would have had little time to deposit. At other times, the monitor would be upwind, the air masses impacting the monitor would have lower ozone, and much of the \( \text{NO}_2 \) will have been lost to deposition. Relating measured \( \text{O}_3 \) to \( \text{NO}_2 \) in this case is not indicative of the OPE.

We controlled for air parcel history by stratifying days based on their photochemical activity using an ensemble of observations across years. Days with high photochemical activity have similar meteorological characteristics, meaning changes in \( \text{O}_3 \) levels should relate to changes in \( \text{NO}_2 \), though other emissions changes can also play a role. We used long-term meteorological detrending of ozone observations at SEARCH sites to identify the 20% of days with all the relevant data available at each site that were most photochemically active. Photochemical state (PS\(^5\), described in detail in Henneman et al.\(^16\)) was estimated using the meteorological detrending method presented in Henneman et al.\(^16\) In brief, observed maximum daily average 8-h (MDA8h) \( \text{O}_3 \) was split into five trends with different periods: long-term (period >365...
days), seasonal (365 days), week-holiday (7−365 days), short-term meteorological (<365 days), and white-noise (1 day). The long-term and seasonal components were separated using the low-pass moving average KZ filter. We regressed the remaining fluctuations against similarly filtered daily fluctuations in various metrics: weekday and holiday factors along with 0-, 1-, and 2-day lags each of solar radiation (total and daily max), temperature (mean and daily maximum), wind speed (morning and daily means), relative humidity, and rainfall. We calculate the short-term meteorological trend as the fitted meteorological covariates in this regression. PS* is the sum of the seasonal and short-term meteorological trends (Figure S1) and represents an emissions-independent estimate of daily atmospheric photochemical activity. This metric is positively correlated with temperature and wind speed and negatively correlated with relative humidity.

For comparison, we calculated an alternative to the PS* metric (HNO₃/NOY), which was found to be likely impacted by long-term emissions changes (SI text and Figures S2 and S3); therefore, PS* was used as the final metric for photochemical plume age. Since PS* was calculated using MDA8h O₃ it is indicative of 8-h averaged photochemical states. We restrict the observation-based OPE analysis to days in the upper 20th percentile for PS* and use 2−3 pm averages (local time) for daily metrics of all observed species. We investigated the distribution of PS* days and found little evidence that decreasing emissions across the study period impacted PS* levels or their likelihood of meeting the top 20% criteria (Figures S4 and S5). We used only data from the middle afternoon in the primary analysis to approximate the time of maximum photochemical activity. NOZ was calculated as the difference between NOY and NOX.

We tested multiple models for the O₃−NOZ relationship, including linear and log models. Models of these types, however, are limited in their application to very low NOZ values, where the slope (d[O₃]/d[NOZ])—estimated with a spline-based regression model—increases and data are sparse. Spline models separate the domain of the independent variable into sections and fitted curves in each of the sections are required to be continuous at the knots. We applied cubic splines, which extend the constraints to include equal first and second derivatives at each knot (Figure 1). We take the marginal OPE—i.e., the additional amount of ozone formed due to an additional amount of NOZ—as the derivative of fitted O₃ vs NOZ models at each site. The spline model captures slope changes at multiple points and does not result in nonphysically high slopes at low NOZ (which were found using...
a log-based regression model). Slopes (i.e., OPEs) are constant outside the outermost knots. We employed the rcs and ols commands from the rms package in R version 3.3.3 for the spline modeling.24

Chemical Transport Model-based OPE. We used the Community Multiscale Air Quality (CMAQ) model with the direct decoupled method (DDM)25 to simulate air quality and first-order sensitivities to emissions over a 12 km domain covering the eastern United States (Figure 2). The model setup and application was first described in Henneman et al. and evaluated in detail in Henneman et al.19,26 We used results from the 2001 and 2011 simulations described in our previous work along with two additional month-long cases with July 2011 meteorology and domain-wide NOX emissions reduced by 50% and 90%. The latter simulations serve to control for meteorology and all other emissions sources completely while reducing NOX emissions. We preserve consistency with observations by using 2–3 p.m. averages, and focus on July because it is a summer month with typical conditions suitable for O3 formation.

For a first estimate of CTM-simulated OPE, we used a brute force (BF) method that assumes linear OPEs across changing NOX concentrations similar to previous approaches:21,27

$$\text{OPE}^{\text{BF}} = \frac{\Delta O_3}{\Delta \text{NO}_X}$$

(1)

where NOX is the sum of NOX reaction products—peroxynitric acid (denoted PAN and PANX in the default CMAQ CB05 chemical mechanism setup26), peroxynitric acid (PNA), organic nitrate (NTR), nitric acid (HNO3), nitrous acid (HONO), nitrate radical (NO3), aerosol nitrate in three modes (AN03I, AN03J, AN03K), and dinitrogen pentoxide (N2O5)—as N (e.g., N2O5 contains two N molecules). The changes in O3 and NOX (Δ) are matched by site and date across CMAQ simulations. We produced two OPEBF estimates per day at each grid cell in the domain: one each for the 2001 and 2011 simulations described in our previous work fi rst described in Henneman et al. and application was first described in Henneman et al. and evaluated in detail in Henneman et al.19,26 We used results from the 2001 and 2011 simulations described in our previous work along with two additional month-long cases with July 2011 meteorology and domain-wide NOX emissions reduced by 50% and 90%. The latter simulations serve to control for meteorology and all other emissions sources completely while reducing NOX emissions. We preserve consistency with observations by using 2–3 p.m. averages, and focus on July because it is a summer month with typical conditions suitable for O3 formation.

We compare OPEBF with a second estimate using the ratio of O3 to NOX sensitivities to on-road mobile (MOB) and electricity generating unit (EGU) source emissions:

$$\text{OPE}^{\text{nodep}} = \frac{S_{O_3,\text{MOB}} + S_{O_3,\text{EGU}}}{S_{\text{NO}_X,\text{MOB}} + S_{\text{NO}_X,\text{EGU}}}$$

(2)

where each sensitivity term (S) is in parts per million. This equation estimates the ratio of the number of O3 molecules produced per NOX molecule attributable to emissions from two sources. We focus on EGU and mobile sources because they make up the majority of anthropogenic NOX emissions. Equation 2, however, has one important omission; it does not account for O3 and NOX produced that deposits out (indeed, none of the empirical or chemical transport model methods described to this point explicitly account for deposition). We rectify this by adding source-specific deposition terms:

$$\text{OPE} = \frac{(S_{O_3,\text{MOB}} + S_{\text{DEP}^j,\text{MOB}}) + (S_{O_3,\text{EGU}} + S_{\text{DEP}^j,\text{EGU}})}{(S_{\text{NO}_X,\text{MOB}} + S_{\text{DEP}^j,\text{MOB}}) + (S_{\text{NO}_X,\text{EGU}} + S_{\text{DEP}^j,\text{EGU}})}$$

(3)

where $$S_{\text{DEP}^j}$$ is the sensitivity of species i deposition to emissions from source j (again, all sensitivity terms are in ppm). CMAQ-DDM calculates the total (wet and dry) O3 deposition (e.g., DEP03 for O3) and the sensitivities to total deposition from mobile ($$S_{\text{DEP}^j,\text{MOB}}$$) and EGU ($$S_{\text{DEP}^j,\text{EGU}}$$) sources. Deposition sensitivities, however, are in units of mass deposited per area; therefore, they require a conversion to concentration units. We achieve this for each source and species by dividing the source-specific deposition sensitivity (e.g., $$S_{O_3,\text{MOB}}$$) by the total deposition (e.g., DEP03) and multiplying by the concentration. For example:

$$S_{O_3,\text{MOB}}^{\text{DEP}} \times O_3$$

(4)

The CMAQ deposition-corrected sensitivities method presents a further opportunity—estimating source-specific OPEs—achieved by calculating ratios of mobile and EGU sensitivities, respectively:

$$\text{OPE}_{\text{MOB}} = \frac{(S_{O_3,\text{MOB}} + S_{\text{DEP}^j,\text{MOB}})}{(S_{\text{NO}_X,\text{MOB}} + S_{\text{DEP}^j,\text{MOB}})}$$

(5)

$$\text{OPE}_{\text{EGU}} = \frac{(S_{O_3,\text{EGU}} + S_{\text{DEP}^j,\text{EGU}})}{(S_{\text{NO}_X,\text{EGU}} + S_{\text{DEP}^j,\text{EGU}})}$$

(6)

where eqs 2, 3, 5, and 6 produce daily OPE estimates at each grid cell for each CMAQ simulation.

Approach Limitations. Various assumptions are inherent in the methods discussed in this study. The empirical method effectively uses an Eulerian framework, i.e., stationary measurements of plumes with different histories and degrees of photochemical activity. The approach is subject to varying background pollutant levels, night-time nitrate chemistry, air parcel transport, varying NOX and O3 deposition rates, and clouds.14 A Lagrangian approach, i.e., when observations are made while traveling with a specific air mass, does not suffer from effects from air parcels with varying histories and has been undertaken using aircraft.14,15,20–23 The Lagrangian approach typically has led to lower OPEs than those found using Eulerian approaches, although this may be due to higher NOX concentrations in plumes, a more limited time to react, or because the typical approach is to correlate O3 with NOX instead of taking the nonlinearity of the system into account.18,30,32,33

The empirical approach is further limited because it does not control for changing emissions of other species involved in ozone formation (e.g., VOCs and CO) or long-term changes in the meteorology leading to high ozone days (e.g., due to climate change). Sensitivity studies find that O3 is primarily sensitive to NOX in the southeast on high ozone days,34,35 though results in downtown areas suggest negative sensitivity to local NOX emissions and VOC sensitivity even on high ozone days.35,36 Urban NO emissions inhibit O3 production, albeit primarily on days with low photochemical activity.11

Recent work has shown that a portion of NOX in the southeast may react with organics and hydrolyze to form organic nitrogen aerosol. Fisher et al. found that 21% of NOX was lost to RONO2 and that this fraction increases with decreasing NOX emissions.37 A total of 59% of RONO2 was made while traveling with a specific air mass, does not suffer from effects from air parcels with varying histories and has been undertaken using aircraft.14,15,20–23 The Lagrangian approach typically has led to lower OPEs than those found using Eulerian approaches, although this may be due to higher NOX concentrations in plumes, a more limited time to react, or because the typical approach is to correlate O3 with NOX instead of taking the nonlinearity of the system into account.18,30,32,33

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September 2013. This portion of NOZ is not present in NOX measurements and would lead to increasing bias in the empirical OPE model at low NOZ concentrations.

A limitation of the CMAQ approach is the use of concentrations, deposition, and sensitivities to anthropogenic emissions that are found at the same location/cell (an Eulerian frame), whereas each of these would be impacted by transport and deposition between the NOZ source location and the location of interest. Total O3 and NOZ deposition fields are spatially similar to, but smoother than, their respective concentration fields—with the exception of localized NOZ deposition hot-spots associated with wet deposition of aerosol NOX—suggesting this issue is of limited importance when using sensitivity-based approaches, particularly if deposition is accounted for in the OPE calculations (Figures S6 and S7 show modeled O3 concentrations and deposition).

RESULTS AND DISCUSSION

Observation-based OPE. We compared mean 2–3 p.m. O3 against mean 2–3 p.m. NOZ for days with PS* greater than the 80th percentile. The resulting relationships have positive slopes and negative second derivatives, corroborating results from previous studies. (Figure 1 and Figure S8 for results obtained selecting a wider PS* range). NOX and NOZ levels decreased across the study period, driven by reductions in NOX emissions (Figure S9). OPE results from linear and log models are presented in the Supporting Information (Figure S10; further, Blanchard et al. investigate OPE at SEARCH sites using linear models and other methods). Here we focus on the cubic spline model results.

Empirical model intercepts at each of the sites represent an estimate of local background concentrations, i.e., expected concentrations when NOZ levels are quite small due to low local NOX emissions and/or nearly complete NOZ deposition. Local background ozone results from global and regional emission sources—not local sources—although it can be generated nearby. For example, urban sources may affect surrounding background ozone, resulting in elevated background ozone nearby and increased titration in cities further downwind. These intercepts likely represent an upper bound of the background for two reasons. First, the spline model’s restriction to linearity outside the outermost knots is rather stringent and may miss small slope increases at the lowest NOZ concentrations. Second, differences between O3 and NOZ deposition are magnified at low concentrations; accounting for this would shift the points plotted in Figure S1 rightward, thus creating a lower intercept.

The estimated level that O3 levels would reach in the absence of local NOX emissions varies for each site with meteorological conditions and long-term climate and emissions changes. Using a Monte Carlo sampling technique, we fit multiple spline models at each site using intercepts selected from the normal distribution around the mean estimated in the original model fit and calculated an uncertainty distribution of the slopes at each NOZ concentration (Figure 3 and S11). This method was chosen because of the high uncertainty in background O3 and OPE at low NOZ concentrations and the difficulty in assessing individual model parameter error in spline models. Uncertainty in OPE is larger at sites closer to the Gulf of Mexico.

All O3–NOZ spline model intercepts fall between 30.2 (GFPU) and 47.2 ppb (OAKR; Figure 2). Urban sites tend to have lower intercepts than rural sites, and the two sites closest to the Gulf of Mexico (GFPU and PNSU) have the lowest intercepts (i.e., local background O3) with the greatest uncertainty. CTRR, in Alabama, stands out as the rural site with the lowest intercept. Background estimates align with the upper end of previous estimates of the levels that ozone would reach in the absence of NOX emissions in the Southeast. Emery et al. found very few days on which policy-relevant background—i.e., absent North American emissions—MDA8h O3 exceeded 40 ppb in 2006, and Lefohn et al. found estimates of background levels to be less than about 30 ppb in Atlanta. These previous estimates used air quality models to estimate background O3; the present approach uses observed data to estimate regional background levels, which are expected to be somewhat more variable. Elevated intercepts at rural sites (e.g., YRK and OAK) suggest impacts from nearby urban centers, which corroborates previous findings by Blanchard et
though the lack of urban—rural diﬀerence between BHMU and CTRR again suggests some level of uncertainty.

Empirical OPEs at JSTU and YRKR, two sites in Georgia, have similar shapes (Figure 3), and OPEs at the rural site are slightly higher than OPEs at the urban site. This trend repeats at BHMU and CTRR, with the rural site (CTRR) exhibiting greater OPEs across all NOZ levels. The remaining sites (GFPU, OAKR, PNSU, OLFS) have OPEs that diﬀer from the urban—rural relationships at the four inland sites. Limited data availability for these sites contribute to larger uncertainty bounds. GFPU, OLFS, and PNSU are near the Gulf of Mexico; the air from the Gulf causes OPEs at these sites to increase dramatically at low NOZ because ozone is eﬃciently transported over the water with relatively little deposition, while nitric acid is very soluble and reacts with sea salt, leading to larger particles that readily deposit. Neuman et al. suggest high variability in regional background depending on wind direction in Houston; these results reﬂect large uncertainties in coastal sites compared to inland found in the present study.31 OLFS, a suburban site somewhat inland from PNSU, has a higher OPE at elevated NOZ levels and lower OPE at low NOZ levels than PNSU. The two sites nearest the Gulf of Mexico (GFPU and PNSU) have the lowest intercepts and the highest OPEs at low NO2.

Chemical Transport Model-based OPE. For two July 2011 comparisons—i.e., between the change from base emissions to 50% NOX emissions and from 50% NOX emissions to 10% NOX emissions—correlation analysis of OPEnodep versus OPEBF finds a slope near 1 and $R^2$ of 0.39 and 0.27, respectively (Figure S12). The comparison controls for meteorology, but neither controls for deposition. A potential source of bias in OPEnodep is the exclusion of higher order sensitivities; Cohan et al. showed that second order eﬀects could contribute $\sim 30\%$ bias. Still, the slopes near 1 support the sensitivity-based approach.

Without correcting for deposition, overland average July 2001 and 2011 OPEs were 10.9 and 13.8, similar to the with-deposition values (Table 1). Remaining discussions focus on deposition-corrected OPEs (eqs 3, 5, and 6); all summary statistics are reported for the portion of the domain encompassed by the superimposed polygon in Figure 4 to exclude boundary eﬀects and impacts of high OPEs over water.

### Table 1. Information on the Modeling Runs

<table>
<thead>
<tr>
<th>July NOX emissions, $10^3$ tons</th>
<th>mean July concentrations, ppb (std. dev.)</th>
<th>mean July OPE (std. dev.)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>all</td>
<td>MOB</td>
</tr>
<tr>
<td>2001</td>
<td>1364</td>
<td>773</td>
</tr>
<tr>
<td>2011</td>
<td>679</td>
<td>364</td>
</tr>
<tr>
<td>2011 50% NOx</td>
<td>339</td>
<td>182</td>
</tr>
<tr>
<td>2011 10% NOx</td>
<td>68</td>
<td>36</td>
</tr>
</tbody>
</table>

*Emissions are summed over the entire domain, while concentrations and OPEs are averaged over the polygon superimposed on the inland region of each of the plots in Figure 4 to exclude boundary eﬀects and high OPEs over water.*

Figure 4. CMAQ-modeled mean daily July deposition-corrected OPE (2–3 p.m.) values for 2001 (A–C) and 2011 (D–F), including total OPE (A,D), mobile OPE (B,E), and EGU OPE (C,F).
increasing overland OPEs increased from 11.2 to 14.0 (Table 1), while OPEs at SEARCH locations increased from 9.6 to 12.7 (Figure S13, Table S1). Between 2001 and 2011, estimated domain-wide NOX emissions decreased 50% and mean overland OPE increased 25%. A hypothetical 50% decrease in NOX emissions would lead to only an additional 15% increase in OPE, and a further 80% emissions cut (90% total reduction from base 2011) would increase OPE just 4% more (Figure S14). Average July overland OPEs do not exceed 25, even at the most extreme (90%) NOX emission reduction (Figure S15). Even on July days with the second-highest simulated O3 concentrations in each location, OPE does not exceed 27. These results show that OPE is expected to increase at a decreasing rate with further emission reductions and corroborate the empirical results that show that OPE increases to location-specific upper limits at lower NOX.

Mobile and EGU OPEs differ spatially. Mobile OPEs are slightly lower than the total OPEs in 2001 and 2011 (Table 1). Their spatial pattern generally mirrors that of total OPE, with lower values near concentrated mobile emissions in urban centers and along interstates (Figure 4). EGU OPEs are generally greater than the total OPEs, with low spots centered near individual plants.

CMAQ OPE results agree with empirical OPEs at low NO2 concentrations for most sites, although CMAQ OPE estimates at rural sites are slightly higher (Figure 3). Note that in this comparison, empirical results use days across the entire period with PS* > 80th percentile, and CMAQ values use only July days in 2001 and 2011. Further, the three coastal sites (GFP, OLP, and PNS) are not located within the overland domain used for analysis (Table 1), and direct comparisons between the methods are inherently problematic because both are models with uncertainties and bias.

CMAQ-modeled domain-wide average O3 concentration in the 10% NOX scenario, at 28.6 ppb, is lower than the background O3 concentrations estimated by the empirical approach. While the comparison here is not direct, it does again suggest that the empirical methods estimate a regional (instead of a global) background that is still influenced by nonlocal emissions.

Implications. The empirical and CMAQ-based methods applied here were designed to reduce biases associated with the limitations discussed above. In the empirical method, the use of meteorologically similar days with high photochemical activity (PS*) across multiyear data sets limits (but likely does not remove) effects of plumes with markedly different origins. We assessed OPE uncertainty based on a distribution of statistically modeled background O3 levels and found the largest impacts at coastal sites. Using CMAQ-DDM, we controlled for air parcel transport and differing O3 and NO2 deposition rates by applying source-specific concentration and deposition sensitivity ratios instead of just concentrations.

Rising OPEs with decreasing NO2 concentrations suggests a NO2-limited regime, with increasing effectiveness for reducing O3 concentrations for each subsequent avoided NOX molecule emitted. We show this for the empirical models by integrating under the OPE curves in Figure 3. For a 0.5 ppb NO2 concentration decrease, the expected change in O3 concentrations (ΔO3) increases with decreasing starting NO2 concentrations for all sites (Figure 5). That ΔO3 reaches a maximum at the lowest NO2 concentrations is somewhat a function of the choice of spline model; however, CMAQ results provide evidence for a maximum OPE (and subsequently a maximum ΔO3 in response to emissions decreases). The 2011 OPEs across the domain and at all SEARCH sites increased at a decreasing rate with NOX emissions reductions (Table S1, Figure S13); at CTR, GFP, and OAK, the reduction from 50% to 10% NOX emissions led to slight decreases in OPE, suggesting a plateauing OPE.

We tested the agreement between the empirical spline model and CMAQ-modeled changes in O3 for a 50% NOX emissions reduction at the SEARCH sites (Figure S16). For relative reductions (as opposed to absolute reductions addressed above), both models find decreasing effectiveness at lower starting NO2 concentrations (since relative reductions at lower total emissions refer to increasingly small mass-based emissions). The models generally agree for all sites. The comparison assumes that NOX emissions reductions directly correlate with NO2 concentration reductions, which is a close (though not perfect) approximation; NO2 concentrations are linear with reductions using consistent meteorology but are nonlinear between 2001 and 2011 due to changing meteorological conditions (Table 1, Figure S14). CMAQ results yield strong OPE differences between rural and urban areas and a lesser—though still significant—trend with decreasing latitude (Figures S17 and S18). We found negative relationships between OPE and both NO2 and formaldehyde (HCHO—a reaction product of volatile organics). We found a positive relationship between OPE and the organic fraction of NO2 (fNO2), which explains variability consistent with change across latitude (see discussion in the Supporting Information).

Empirical and CMAQ results provide evidence that maximum OPEs are site-specific, reflecting site-specific meteorologies and emissions of species other than NOX. At the lowest NO2 concentrations, the potential for reducing O3 concentrations through NOX emissions reductions levels off; however, O3 concentrations have a positive relationship with NO2 at all NO2 concentrations. This suggests that continuing emissions controls will reduce O3 concentrations at increasing rates, but the effect will level off at location-specific NO2 concentrations.

EGU OPEs are on average greater than mobile OPEs across the domain. This suggests greater expected O3 reductions per absolute NOX emissions reduction from EGUs than mobile. However, this comparison does not consider the amount of emissions left to reduce—mobile sources emitted more than 2 times the NOX than EGU sources in 2011. Since modeled 2011 EGU OPE is 10% larger than mobile OPE (15.3 vs 13.8), more
O₃ reduction is available through proportional mobile emission reductions than EGU. This study shows that future NOₓ emissions reductions remain a viable option for reducing the highest O₃ concentrations. OPE increases with decreasing NOₓ concentrations but appears to level out or reach a maximum, which implies that incremental NOₓ emissions reductions will become more effective at reducing O₃ up to a point, after which the incremental benefit will level off. Empirical results based on ambient observations suggest that maximum OPE has already been attained in rural areas, and results obtained using the chemical transport modeling approach corroborate this finding.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b04109.

Supplemental analyses, 18 figures, and two tables (DOCX)

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Notes
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