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The impact of nitrogen oxides concentration decreases on ozone trends in the USA

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Abstract

Ozone (O₃) has harmful effects on human health and ecosystems. In the USA, significant reductions of O₃ precursors—nitrogen oxides (NO_x) and volatile organic compounds (VOCs)—have not yielded proportionate decreases in O₃. NO_x is a major precursor of O₃ as well as a quencher of O₃ through NO_x titration, which is especially important during the night and wintertime. In this study, we investigated the potential dual impact of NO_x concentration decreases on recent O₃ trends by season and time of day. We analyzed hourly O₃ and NO_x measurement data between 1994 and 2010 in the continental USA. Nationally, hourly O₃ concentrations decreased by as much as −0.38 ppb/year with a standard error of 0.05 ppb/year during the warm season midday, but increased by as much as +0.30±0.04 ppb/year during the cold season. High O₃ concentrations (75th percentile) during the warm season decreased significantly, however, there were notable increases in the cold season as well as warm season nighttime; we found that these increases were largely attributable to NO_x decreases as less O₃ is quenched. These O₃ increases, or “penalties”, related to NO_x reductions remained robust at a wide range of O₃ concentrations (5th to 99th percentile), and even after accounting for VOC reductions and meteorological parameters, including temperature, wind speed, and water vapor pressure. In addition, we observed O₃ penalties across rural, suburban, and urban areas. Nonetheless, peak O₃ concentrations (99.9th percentile) were mitigated by NO_x reductions. In addition, there was some suggestive evidence that VOC reductions have been more effective in reducing O₃.

Keywords

Ozone; Nitrogen oxides; Air pollution; Trends

Introduction

Ground-level ozone (O_3) is an important atmospheric oxidant that is harmful to human health (US EPA 2010; WHO 2006) and ecosystems (UNEP and WMO 2011). The US Environmental Protection Agency (EPA) achieved significant decreases in major O_3 precursors, such as nitrogen oxides ($NO_x=NO_2+NO$) and volatile organic compounds (VOCs) (US EPA 2012). However, decreasing O_3 trends have leveled off in recent years and low O_3 concentrations have increased (Lefohn et al. 2010). Ozone has been challenging to control, and in 2010, over a third of the US population resided in areas exceeding the national O_3 standard (US EPA 2012). This warrants investigation on the efficacy of O_3 precursor reductions and the underlying chemical mechanisms that influence the responsiveness of O_3 .

Among NO_x species, NO_2 is a major precursor of O_3 in the presence of sunlight, while NO is an important scavenger of O_3 during the night and wintertime ($NO+O_3\rightarrow NO_2+O_2$) (Sillman 1999). During the winter, the removal of O_3 through NO_x titration is enhanced by less efficient NO_x transport from the boundary layer as well as a slower rate of photochemical O_3 production (Parrish et al. 1999). Currently, there are limited studies on the extent to which this dual role of NO_x as an O_3 precursor and quencher affects the efficacy of NO_x emission reductions for O_3 mitigation. One study noted that the increase in lower hourly O_3 concentrations is consistent with decreased NO scavenging, but did not explicitly analyze the relationship (Lefohn et al. 2010). A recent study conducted in Europe observed that NO_x emission reductions did not have a substantial impact on annual O_3 trends, but also did not directly quantify the NO_x impact (Wilson et al. 2012).

In this study, we presented a statistical framework to create an O_3 penalty term that quantifies the effect of NO_x reductions on O_3 trends. We estimated recent O_3 trends in the USA (1994–2010), with and without adjusting for NO_x concentrations, as the difference between these trends reflects the impact of NO_x decreases. By analyzing trends by time of day, we provided a more holistic view on O_3 trends compared to prior studies, which have primarily focused on trends based on daily or seasonal metrics. In particular, NO_x contributes to the diurnal variation of O_3 , which can be better characterized by analyzing trends at a higher temporal resolution. We also assessed the role of meteorology, VOC reductions, and urbanicity on the impact of NO_x decreases on O_3 trends.

Materials and methods

Data collection

We gathered hourly O_3 , hourly NO_x , and daily VOCs data from EPA's Air Quality System (AQS) and Photochemical Assessment Monitoring Stations (PAMS) monitoring networks as well as meteorological data (24-h temperature, wind speed, and water vapor pressure) from

the National Oceanic and Atmospheric Administration (NOAA)'s National Climatic Data Center between 1994 and 2010. Air pollution sites were matched to the nearest distance weather station. We chose 1994 as the starting year due to wider availability of NO_x concentration data thereafter, and selected 437 O_3 monitoring sites, which operated year-round (Jan–Dec) for at least 10 years; among these sites, 133 also measured NO_x . The co-located O_3 - NO_x sites included 35 rural, 55 suburban, and 42 urban sites (1 site unknown). Selected sites had at least 12 out of 24 hourly measurements for at least 14 days in each month. Sites were categorized into seven regions—Northwest (NW), Upper Midwest (UM), Industrial Midwest (IM), Northeast (NE), Southern California (SC), Southwest (SW), and Southeast (SE)—as defined by the National Morbidity Mortality Air Pollution Study (NMMAPS; Fig. 1) (Samet et al. 2000). Among these sites, daily VOCs were measured in addition to O_3 and NO_x in 21 sites (two NW, two NE, seven SC, one SW, and nine SE).

Daily metrics and national monthly time series

While our main results were derived from analyses of hourly data, we also created daily 24-h O_3 , 8-h max O_3 , and 24-h NO_x metrics to analyze their monthly time series. The 24-h O_3 and 24-h NO_x metrics were created on days with at least 12 out of 24 hourly valid measurements. The 8-h max O_3 metric was computed on days with at least 12 of 24 valid 8-h moving averages, which were calculated from at least 4 valid hourly values. In order to account for differences in the number of sites and heterogeneity between sites in each region, we employed a two-stage approach to estimate the national monthly time series of 24-h O_3 , 8-h max O_3 , and 24-h NO_x . In the first stage, the daily average and standard errors of each daily metric were estimated within each NMMAPS region. In the second stage, we obtained national daily averages from daily regional averages by applying the meta-analysis technique of Berkey et al. (1998).

National hourly O_3 trend analysis

To estimate national hourly O_3 trends, we first estimated regional O_3 trends by applying linear mixed effects (LME) models (Fitzmaurice et al. 2011). These models account for serial correlation among the time series data and allow modeling of random effects (i.e., site-to-site variation within each region) of annual trends (slope) as well as initial O_3 concentrations (intercept). The following model was applied iteratively by region, season, and hour with the statistical package, SAS (version 9.3):

$$(\text{O}_3)_{ij} = (\beta_0 + b_{0i}) + (\beta_1 + b_{1i})\text{year}_{ij} + \gamma \text{month}_{ij} + \delta \text{weekday}_{ij} + \varepsilon_{ij} \quad (1)$$

where, $(\text{O}_3)_{ij}$ is the O_3 concentration at site i and date j ; β_1 estimates the annual O_3 change (ppb/year) in 1994–2010 for a specific season, region, and hour of day; b_{0i} and b_{1i} are the random site-specific effects for the intercept (β_0) and slope (β_1), respectively; and γ and δ are vectors of coefficients that represent monthly and weekday variability of O_3 concentrations, respectively. We meta-analyzed the regional O_3 trends obtained from model (1) to estimate national trends.

Ozone penalty calculation

To assess the impact of NO_x emission reductions on O₃ trends, we estimated actual and NO_x-adjusted O₃ trends. Here, we applied generalized additive models (GAMs) (Hastie and Tibshirani 1990) to adjust for the nonlinear relationship between O₃ and NO_x. GAMs have been applied extensively for both meteorological and nonmeteorological adjustment in air pollution trend analyses (Barnpadimos et al. 2012; Zheng et al. 2007; Jhun et al. 2013). Trends of O₃, NO_x-adjusted O₃, and NO_x were calculated for each region, season, and time of day from the following GAMs, using the statistical package R (<http://www.r-project.org>):

$$(O_3)_{ij} = \beta_0 + \beta_{1,actual} year_{ij} + \gamma month_{ij} + \delta weekday_{ij} + \varepsilon_{ij} \quad (2)$$

$$(O_3)_{ij} = \beta_0 + \beta_{1,adjusted} year_{ij} + \gamma month_{ij} + \delta weekday_{ij} + s((NO_x)_{ij}) + \varepsilon_{ij} \quad (3)$$

$$(NO_x)_{ij} = \beta_0 + \beta_{1,NO_x} year_{ij} + \gamma month_{ij} + \delta weekday_{ij} + \varepsilon_{ij} \quad (4)$$

where, $(O_3)_{ij}$ and $(NO_x)_{ij}$ represent O₃ and NO_x concentrations, respectively, at site i and on date j and; $\beta_{1,actual}$, $\beta_{1,adjusted}$, and β_{1,NO_x} estimate regional trends of O₃, NO_x-adjusted O₃, and NO_x, respectively, for a given season and hour of the day. The smoothing spline function, denoted by $s()$, characterizes and adjusts for the nonlinear relationship between hourly O₃ and NO_x concentrations. To estimate the impact of NO_x changes on O₃ trends, we obtained the difference between actual and NO_x-adjusted O₃ trends, and refer to this as a “penalty” henceforth:

$$\text{Penalty (ppb/year)} = \beta_{1,actual} - \beta_{1,adjusted} \quad (5)$$

A *positive* penalty ($\beta_{1,actual} > \beta_{1,adjusted}$) indicates an *increase* in O₃ concentrations associated with NO_x decreases during the study period, whereas a *negative* penalty ($\beta_{1,actual} < \beta_{1,adjusted}$) reflects a *decrease* in O₃ associated with NO_x decreases. Standard errors of the trends and trend differences (penalties) were estimated by utilizing a block bootstrap procedure (Politis 2003). Briefly, this involved creating 100 pseudo-datasets by resampling the original dataset in 20-day blocks for each region, season, and time of day (33,600 bootstrap datasets total). Then, models (2), (3), and (5) were iteratively applied to each bootstrap dataset to calculate O₃ trends, NO_x-adjusted O₃ trends, and their difference (penalty). Standard errors were estimated as the standard deviation of the distribution of 100 parameter estimates for each region, season, and hour. Subsequently, these regional trends and penalties were meta-analyzed to estimate national averages.

To assess the impact of VOC reductions on O₃ trends, we estimated the difference between O₃ trends adjusted for smoothing functions of both NO_x and VOC, and NO_x-adjusted O₃ trends derived from model (3) for each region, season, and hour of day. To assess the impact

of weather variation on the NO_x-related O₃ penalty, we estimated O₃ trends adjusted for meteorological parameters (i.e., smoothing functions of temperature, wind speed, and water vapor pressure) with and without controlling for NO_x and their difference (i.e., meteorology-adjusted penalty). The trends of daily VOCs and meteorological parameters were estimated by applying models analogous to models (2) and (4).

Quantile regression

We estimated the impact of NO_x decreases on a wider range of hourly O₃ concentrations (5th to 99.9th percentile) by applying quantile regression methods (Koenker and Bassett 1978). For each co-located O₃-NO_x site, we estimated quantile trends with and without adjusting for hourly NO_x concentrations by applying models that controlled for year, month, and weekday, analogous to models (2) and (3). We also estimated quantile trends for all 437 O₃ monitoring sites by applying a model analogous to model (2). For site i at the k th quantile, $\tau_k = \{0.05, 0.10, 0.25, 0.50, 0.75, 0.90, 0.95, 0.975, 0.99, \text{ and } 0.999\}$, solutions were obtained using the quantreg package in R, which minimizes:

$$\arg \min \left\{ \sum_{y_i > X_i' \beta} (\tau_k) |y_i - X_i' \beta| + \sum_{y_i < X_i' \beta} (1 - \tau_k) |y_i - X_i' \beta| \right\} \quad (6)$$

where, $|y_i - X_i' \beta|$ represents the site-specific absolute value of predicted errors for a vector of estimated regression coefficients, β . The standard errors of the coefficients were obtained by using the Powell kernel estimator of the covariance matrix. The site-specific quantile trends were meta-analyzed to compute the national quantile trends.

Results and discussion

Monthly and seasonal time series of O₃ and NO_x

Selecting for year-round sites yielded 437 O₃ monitoring sites and 133 co-located O₃-NO_x monitoring sites (Fig. 1); excluding warm season (May–Sept), monitoring sites did not significantly alter the distribution of the annual fourth highest 8-h max O₃ concentration (Fig. 2). To assess overall observed trends, we estimated national monthly averages of 24-h O₃, 8-h max O₃, and 24-h NO_x as well as cold (Nov–Apr) and warm (May–Oct) season averages (Fig. 3). Despite substantial NO_x decreases (over 60 %) in both warm and cold months, we did not observe proportionate decreases in O₃. During the cold season, NO_x decreased considerably from 42 to 16 ppb, but both 8-h max and 24-h O₃ increased from 33 to 38 and 23 to 29 ppb, respectively. In the warm season, 8-h max O₃ decreased from 49 to 45 ppb, while 24-h O₃ did not change appreciably. Therefore, the downward trends of warm season 8-h max O₃ were not representative of the remaining 16 h excluded from this metric. Other studies have also observed that O₃ trends are sensitive to exposure metric selection, with greater decreases in 8-h max O₃ than 24-h O₃ (Bell et al. 2005). Therefore, the 8-h max metric may not provide a holistic perspective on recent O₃ trends. This warrants closer investigation on diurnal differences in O₃ trends.

O₃ trends by season and time of day

Given suggestive evidence for diurnally and seasonally varying O₃ trends in Fig. 3, we analyzed the full hourly O₃ data (437 sites) and employed regression methods to estimate national O₃ trends by season and time of day (Fig. 4). The four seasons were dichotomized to warm and cold seasons, as hourly O₃ trends in May to October exhibited a distinct diurnal pattern with decreases during the midday, whereas trends in November through April exhibited increases throughout the day. Nationally, warm season daytime (8 am–6 pm) O₃ declined with a maximum decrease at 2 pm of -0.38 ppb/year with a standard error of 0.05 ppb/year, and there were no statistically significant changes during the nighttime (7 pm–5 am). In contrast, cold season O₃ concentrations rose during all hours of the day, as much as $+0.30 \pm 0.04$ ppb/year. Recent studies have also found that O₃ increases were much more common in the winter and springtime, especially among low- to mid-O₃ percentile levels (e.g., 5th and 50th percentiles) (Cooper et al. 2012).

All seven NMMAPS regions exhibited warm season midday decreases and cold season increases. Warm season decreases were greater in the Southern regions, whereas cold season increases were greater in the Northern regions. There were also statistically significant O₃ increases during the warm season nighttime in the Northwest, Industrial Midwest, and Southern California. The cold season and nighttime rise in O₃ concentrations suggested that NO_x titration reactions—an important chemical mechanism precisely when photochemical activity is reduced—may have played a role.

O₃ and NO_x trends in subset of sites

We quantified the impact of NO_x emission reductions on O₃ trends using co-located hourly O₃ and NO_x data from 133 year-round sites; selecting for year-round sites eliminated 34 warm season monitoring sites. Warm season daytime decreases and cold season increases in the co-located sites were similar in magnitude to those of the full O₃ dataset (Fig. 5a). However, warm season nighttime O₃ increases were greater, which may result from differences in the characteristics of sites that also measure NO_x. Co-located O₃-NO_x sites had slightly higher annual fourth highest 8-h max O₃ concentrations in many regions (Fig. 2). In addition, these sites are more likely to have higher initial NO_x concentrations, as NO_x monitoring sites are strategically chosen. Consequently, the magnitude of NO_x decreases could be greater in areas where NO_x was monitored. This is consistent with the elevated nighttime O₃ increases in these sites (Fig. 5a), since less O₃ would have been quenched by NO_x due to greater NO_x reductions. While an enhanced NO_x decrease may lead to an overestimate of the impact of NO_x on O₃ trends, we analyze a fairly even distribution of rural ($n=35$), suburban ($n=55$), and urban ($n=42$) sites, which differ in baseline NO_x levels and magnitude of NO_x decreases.

We also estimated trends of NO_x, which decreased during all times of the day in both seasons ranging from -0.42 ± 0.08 to -1.47 ± 0.24 ppb/year (Fig. 5b). Normalizing these trends to the initial NO_x concentrations eliminated the seasonal and diurnal variability of trends. In summary, hourly trends of NO_x and O₃ were consistent with time series results in Fig. 3, as they showed that NO_x decreased in both seasons while O₃ increased in the cold season and had mixed warm season trends.

O₃ penalty

We estimated O₃ trends that were adjusted for NO_x, in order to characterize O₃ trends that assume NO_x concentrations remained constant (i.e., without influence of regulations). The NO_x-adjusted O₃ trends demonstrated that if NO_x concentrations did not decrease, O₃ concentrations during the warm season nighttime and cold season would have decreased instead (Fig. 5c). Therefore, NO_x concentration decreases were associated with an increase, or “penalty”, in O₃ concentrations. While we are primarily interested in the impact of NO_x changes on O₃ trends rather than explaining the variability of O₃ concentrations, we found that adjusting for NO_x in the regression model significantly improved model fit. On average, the r^2 values increased from 0.24 to 0.60 in the cold season and 0.12 to 0.30 in the warm season. The improvement in model fit suggested that the relationship between O₃ and NO_x was adequately modeled.

We meta-analyzed regional penalty values (Fig. 6) to obtain a national summary (Fig. 5d). National penalties were all positive, which indicated that, on average, NO_x concentration decreases were associated with higher O₃ concentrations during both warm and cold seasons. Penalties during the cold season and nighttime ($+0.20 \pm 0.03$ to $+0.43 \pm 0.05$ ppb/year) were comparable to, if not greater than, corresponding O₃ increases. Penalty values can be greater than the magnitude of O₃ increases in cases where O₃ would have decreased instead (i.e., where NO_x-adjusted O₃ trends are negative). Therefore, NO_x concentration decreases significantly influenced O₃ trends by suppressing the scavenging of O₃ through NO_x titration; this phenomenon was largely responsible for O₃ increases during the cold season and warm season nighttime. The NO_x-related O₃ penalties were slightly greater during the more recent 8 years (2003–2010), after the implementation of EPA’s NO_x Budget Trading Program that targeted NO_x emissions from power plants in the Eastern USA. This warrants continued vigilance on the impact of future NO_x decreases on nonpeak O₃ concentrations in the USA.

Even the warm season O₃ decreases during the midday were largely insensitive to NO_x decreases, suggesting that other factors were more effective at mitigating O₃ (this will be further explored in the next section). The warm season penalties remained robust even when we included the 34 co-located sites (12 IM, 15 NE, 6 SE, and 1 UM sites) that did not measure O₃ year-round. However, some benefits of NO_x decreases were observed on a regional scale. Southwest and Southern California exhibited benefits of NO_x reductions (as much as -0.15 ± 0.03 ppb/year) during the warm season midday, when NO_x predominantly acts as a photochemical precursor rather than a quencher of O₃ (Fig. 6). These benefits, however, were much smaller in magnitude than nighttime O₃ penalties, which were as high as $+0.62 \pm 0.07$ ppb/year. An important consideration is that the limited availability of NO_x measurements restricted our analyses to sites located in 11 states (CA, DC, IL, KS, LA, MA, NJ, NY, OK, PA, and TX). While our results may not be generalizable to other areas in the USA, we analyzed data from O₃-NO_x monitors that are located in some of the most populated areas and places where O₃ concentrations are higher (Fig. 2).

Many modeling and trend analysis studies have illustrated that NO_x emission controls led to decreases in O₃ concentrations (Bloomer et al. 2010; Butler et al. 2011; Gégó et al. 2007). However, they either primarily focused on high O₃ levels (e.g., warm season 8-h max) or

simply compared O₃ trends from periods before and after implementation of the NO_x Budget Trading Program (e.g., 1997–1999 vs. 2006–2008). Here, we *directly* quantified the impact of NO_x decreases on O₃ trends, rather than make qualitative comparisons; we also illustrated a more holistic perspective by considering regional, seasonal, and diurnal differences in O₃ chemistry. In addition, we conducted further analyses to take into account the influence of VOC reductions, meteorology, and urbanicity, which showed the robustness of our results.

Impact of VOC reduction on O₃ trends

National penalties were lowest and nearly zero during the warm season midday. The insensitivity of warm season O₃ decreases to NO_x adjustment suggested that NO_x reductions may not be responsible for the observed decreases. Instead, mitigation of other O₃ precursors may have led to these decreases. Our analysis using a limited set of VOC data provided evidence that this was indeed the case. Only 21 sites (two NW, two NE, seven SC, one SW, and nine SE sites) had at least 10 years of year-round data on O₃, NO_x, and total nonmethane organic carbons (NMOCs, representing ambient concentrations rather than emissions); prior studies have used NMOC measurements to assess the relationship between O₃ and VOCs (Blanchard et al. 2010a, 2010b). In addition, NMOCs measurements were only available as daily averages rather than hourly data. In these 21 sites, 24-h NMOCs were reduced by −12.5 and −9.2 ppb/year in the cold and warm seasons, respectively.

To deduce NMOC impacts on O₃ trends, we obtained the difference between the impacts of NO_x decreases and both NO_x and NMOCs decreases on O₃ trends. Despite data limitations, these results suggested that NMOC reductions were more effective in reducing O₃ in the five regions we analyzed, especially during the warm season midday and in the Northeast (Fig. 7). This reflects characteristics of a VOC-limited atmospheric environment. Reducing NO_x where VOC is the limiting reactant can actually *increase* O₃ due to nonlinear relationships (Sillman 1999); this is consistent with the positive penalties during the warm season daytime we reported in Fig. 5d. A previous study also noted that NO_x emission reductions can increase O₃ production efficiency and actually increase 8-h max O₃ in VOC-limited areas (Reynolds et al. 2003). Lastly, unlike NO_x reductions, NMOC decreases had minimal impact on nighttime and cold season O₃ levels. Therefore, VOC reductions achieved more meaningful benefits by mitigating warm season daytime O₃ without yielding penalties in other times. Unfortunately, reducing VOCs is challenging, as biogenic VOC emissions make up a large proportion of total VOC emissions (US EPA 2009b). While biogenic VOCs play an important role, anthropogenic VOCs account for the majority of the VOC reactivity in many urban areas (Chameides et al. 1992). Therefore, further research is needed to demonstrate the efficacy of targeting anthropogenic VOCs for O₃ mitigation.

Penalties in urban and rural sites

As atmospheric compositions of NO_x and VOCs differ between urban, suburban, and rural areas, we also analyzed the impact of reducing NO_x in these areas separately. Rural sites ($n=35$) showed the greatest O₃ decreases and the least NO_x decreases compared to urban ($n=42$) and suburban ($n=55$) sites. Benefits of reducing NO_x were observed in rural sites during the warm season midday (11 am–3 pm), with a maximum benefit of -0.14 ± 0.03 ppb/

year. However, this was only a fraction of the actual O₃ decrease of -0.63 ± 0.19 ppb/year, again suggesting that other factors led to the majority of O₃ decreases. Furthermore, statistically significant positive O₃ penalties were observed in the nighttime and cold season in rural sites. Therefore, NO_x-related O₃ penalties were not confined to urban areas.

Meteorological impacts on trends and penalties

In addition to NO_x and VOCs, weather conditions also significantly affect O₃ levels; for instance, high temperature, low humidity, and low wind speed conditions favor O₃ formation (The National Academies Press 1991). To assess the influence of weather, we compared the impact of NO_x reductions on O₃ trends with and without adjusting for temperature, wind speed, and water vapor pressure. Changes in these meteorological parameters during our study period had *mitigated* O₃ penalties by up to 0.13 ppb/year during the cold season. We identified two reasons for this. First, wind speed decreased in all seven regions (by -0.4 m/s on average) during both seasons over the study period. A more stagnant atmosphere is favorable for O₃ removal during the night and wintertime. Second, as a result of weather changes, NO_x did not decrease as much as it would have otherwise. In other words, without the influence of meteorological changes, O₃ penalties would have been even higher not only due to greater NO_x decreases, but also due to less favorable condition for O₃ removal. In summary, O₃ penalties were robust to meteorological adjustment and the penalty values we reported earlier in Fig. 5d were conservative estimates.

Quantile regression of hourly O₃

To examine the impact of NO_x on a wider range of O₃ concentrations, we applied the quantile regression method. Nationally, the 95th quantile O₃ concentration in the warm season significantly declined from 70.5 to 60.0 ppb in 1994–2010, whereas the 5th to 75th quantiles of cold season O₃ increased. We analyzed a subset of sites with co-located O₃ and NO_x data to estimate trends of 5th, 10th, 25th, 50th, 75th, 90th, 95th, 97.5th, 99th, and 99.9th quantiles of hourly O₃ concentrations and compared these trends to those that were adjusted for hourly NO_x concentrations (Fig. 8). In the cold season, 5th to 90th quantile O₃ levels increased, and the NO_x-adjusted quantile trends showed that O₃ would have decreased if NO_x concentrations had remained constant (Fig. 8a). In the warm season, higher O₃ levels (75th quantiles) decreased, but lower quantile O₃ levels increased (Fig. 8b), indicating a shift towards mid-O₃ concentrations. Consistent with the positive penalties we reported earlier in Fig. 5d, NO_x reductions were associated with an increase in a wide range of O₃ concentrations, even during the warm season. This is also consistent with our VOC analysis, which suggested that our atmosphere is more VOC-limited—an environment in which photochemical production of O₃ can increase with NO_x reduction. However, benefits of NO_x reductions were observed at the 99.9th quantile level in the warm season, illustrating that NO_x decreases mitigated extreme O₃ episodes.

Conclusion

Important progress has been made in mitigating high O₃ concentrations. Our analyses showed significant decreases in O₃ during the warm season midday and at peak levels (75th quantile). However, there were significant increases in non-peak O₃ concentrations,

which occurred primarily during the cold season and nighttime. As a result, the gap between the highest and lowest O₃ concentrations has been narrowing.

While many factors impact O₃ trends, the dual influence of NO_x emission reductions has been largely under-investigated. We found suggestive evidence that NO_x reductions mitigated the highest O₃ concentrations (99.9th percentile). However, substantial increases in non-peak O₃ concentrations were associated with NO_x decreases, which were driven by two mechanisms. First, decreasing NO_x reduces the amount of O₃ quenched through NO_x titration, leading to an apparent increase in O₃ concentrations, especially during the night and wintertime. Second, we found suggestive evidence that the atmosphere may be more VOC-limited; in such conditions, NO_x reductions can increase O₃ even during the daytime. While further investigation on the latter mechanism is necessary, our analyses suggested that the two mechanisms combined have led to increases in O₃ concentrations.

It is important to recognize other factors that also influence O₃ concentrations, such as pollution transport from Asia and Europe (Fiore et al. 2002; Jaffe and Ray 2007; Lin et al. 2012), climate change (US EPA 2009a), stratospheric-tropospheric exchange (Langford et al. 2012; Lefohn et al. 2001, 2011, 2012, 2014; Lin et al. 2012), and increasing background O₃ levels (Fiore et al. 2003; Wang et al. 2009). Additionally, while we show that NO_x reductions yielded penalties to O₃ in recent years, reducing NO_x also mitigated particle pollution (US EPA 2009c) and prevented adverse health effects related to NO_x exposure (Burnett et al. 2004; Samoli et al. 2006). Therefore, the decreases in NO_x are a critical public health achievement.

Continued decreases in NO_x may eventually lead to more meaningful O₃ reductions in the future. However, the level of NO_x decreases necessary to achieve this is uncertain. In the meanwhile, more effective O₃ mitigation strategies are needed and future air quality management efforts should assess ways to capitalize on the significant NO_x reductions that have already been achieved.

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Fig. 1.

Monitoring site locations. Number of O_3 and NO_x monitoring sites are noted by n_{O_3} and n_{NO_x} , respectively (*NW* Northwest, *UM* Upper Midwest, *IM* Industrial Midwest, *NE* Northeast, *SC* Southern California, *SW* Southwest, *SE* Southeast)

Fig. 2. Distribution of the annual fourth highest 8-h max O₃ concentrations by region, site selection criteria (warm season vs. year-round), and data type (all O₃ sites vs. co-located O₃-NO_x sites). Whiskers represent 5th and 95th percentile concentrations.

Fig. 3.

a–c National monthly mean concentration time series of O₃ and NO_x metrics. National averages of 24-h O₃ (**a**), 8-h max O₃ (**b**), and 24-h NO_x (**c**) are shown. The cold season (Nov–Apr) and warm season (May–Oct) monthly means were averaged to estimate seasonal time series

Fig. 4. National O₃ trends by season and time of day. National trends were estimated by meta-analyzing regional trends derived from all O₃ data (437 sites). Standard errors are shown

Fig. 5. **a–d** Trends and O₃ penalties. Regression results of O₃ trends (**a**), NO_x trends (**b**), NO_x-adjusted O₃ trends (**c**), and O₃ penalties (**d**) using data from co-located O₃-NO_x sites (133 sites). Standard errors are shown

Fig. 6.
O₃ penalties by region, season, and time of day. Upper Midwest not shown due to nonsignificant penalties. Standard errors are shown

Fig. 7.
NO_x- and VOC-related O₃ penalties by season and time of day in the Northeast. Standard errors are shown

Fig. 8.

a, b Actual and NO_x-adjusted O₃ quantile trends. Quantile trends in the cold season (**a**) and warm season (**b**) using data from co-located O₃-NO_x sites (133 sites). Standard errors are shown