

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

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Received: 7 May 2014 / Accepted: 7 July 2014  
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**Abstract** Ozone (O<sub>3</sub>) has harmful effects on human health and ecosystems. In the USA, significant reductions of O<sub>3</sub> precursors—nitrogen oxides (NO<sub>x</sub>) and volatile organic compounds (VOCs)—have not yielded proportionate decreases in O<sub>3</sub>. NO<sub>x</sub> is a major precursor of O<sub>3</sub> as well as a quencher of O<sub>3</sub> through NO<sub>x</sub> titration, which is especially important during the night and wintertime. In this study, we investigated the potential dual impact of NO<sub>x</sub> concentration decreases on recent O<sub>3</sub> trends by season and time of day. We analyzed hourly O<sub>3</sub> and NO<sub>x</sub> measurement data between 1994 and 2010 in the continental USA. Nationally, hourly O<sub>3</sub> concentrations decreased by as much as −0.38 ppb/year with a standard error of 0.05 ppb/year during the warm season mid-day, but increased by as much as +0.30±0.04 ppb/year during the cold season. High O<sub>3</sub> 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<sub>x</sub> decreases as less O<sub>3</sub> is quenched. These O<sub>3</sub> increases, or “penalties”, related to NO<sub>x</sub> reductions remained robust at a wide range of O<sub>3</sub> 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 O<sub>3</sub> penalties across rural, suburban, and urban areas. Nonetheless, peak O<sub>3</sub> concentrations (99.9th percentile) were mitigated by NO<sub>x</sub> reductions. In addition, there was some

suggestive evidence that VOC reductions have been more effective in reducing O<sub>3</sub>.

**Keywords** Ozone · Nitrogen oxides · Air pollution · Trends

## Introduction

Ground-level ozone (O<sub>3</sub>) 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<sub>3</sub> precursors, such as nitrogen oxides (NO<sub>x</sub>=NO<sub>2</sub>+NO) and volatile organic compounds (VOCs) (US EPA 2012). However, decreasing O<sub>3</sub> trends have leveled off in recent years and low O<sub>3</sub> 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<sub>3</sub> standard (US EPA 2012). This warrants investigation on the efficacy of O<sub>3</sub> precursor reductions and the underlying chemical mechanisms that influence the responsiveness of O<sub>3</sub>.

Among NO<sub>x</sub> species, NO<sub>2</sub> is a major precursor of O<sub>3</sub> in the presence of sunlight, while NO is an important scavenger of O<sub>3</sub> during the night and wintertime (NO+O<sub>3</sub>→NO<sub>2</sub>+O<sub>2</sub>) (Sillman 1999). During the winter, the removal of O<sub>3</sub> through NO<sub>x</sub> titration is enhanced by less efficient NO<sub>x</sub> transport from the boundary layer as well as a slower rate of photochemical O<sub>3</sub> production (Parrish et al. 1999). Currently, there are limited studies on the extent to which this dual role of NO<sub>x</sub> as an O<sub>3</sub> precursor and quencher affects the efficacy of NO<sub>x</sub> emission reductions for O<sub>3</sub> mitigation. One study noted that the increase in lower hourly O<sub>3</sub> 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<sub>x</sub> emission reductions did not have a

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substantial impact on annual O<sub>3</sub> trends, but also did not directly quantify the NO<sub>x</sub> impact (Wilson et al. 2012).

In this study, we presented a statistical framework to create an O<sub>3</sub> penalty term that quantifies the effect of NO<sub>x</sub> reductions on O<sub>3</sub> trends. We estimated recent O<sub>3</sub> trends in the USA (1994–2010), with and without adjusting for NO<sub>x</sub> concentrations, as the difference between these trends reflects the impact of NO<sub>x</sub> decreases. By analyzing trends by time of day, we provided a more holistic view on O<sub>3</sub> trends compared to prior studies, which have primarily focused on trends based on daily or seasonal metrics. In particular, NO<sub>x</sub> contributes to the diurnal variation of O<sub>3</sub>, 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<sub>x</sub> decreases on O<sub>3</sub> trends.

## Materials and methods

### Data collection

We gathered hourly O<sub>3</sub>, hourly NO<sub>x</sub>, 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<sub>x</sub> concentration data thereafter, and selected 437 O<sub>3</sub> monitoring sites, which operated year-round (Jan–Dec) for at least 10 years; among these sites, 133 also measured NO<sub>x</sub>. The collocated O<sub>3</sub>-NO<sub>x</sub> 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<sub>3</sub> and NO<sub>x</sub> 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<sub>3</sub>, 8-h max O<sub>3</sub>, and 24-h NO<sub>x</sub> metrics to analyze their monthly time series. The 24-h O<sub>3</sub> and 24-h NO<sub>x</sub> metrics were created on days with at least 12 out of 24 hourly valid measurements. The 8-h max O<sub>3</sub> 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<sub>3</sub>, 8-h max O<sub>3</sub>, and 24-h NO<sub>x</sub>. 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<sub>3</sub> trend analysis

To estimate national hourly O<sub>3</sub> trends, we first estimated regional O<sub>3</sub> 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<sub>3</sub> concentrations (intercept). The following model was applied iteratively by region, season, and hour with the statistical package, SAS (version 9.3):

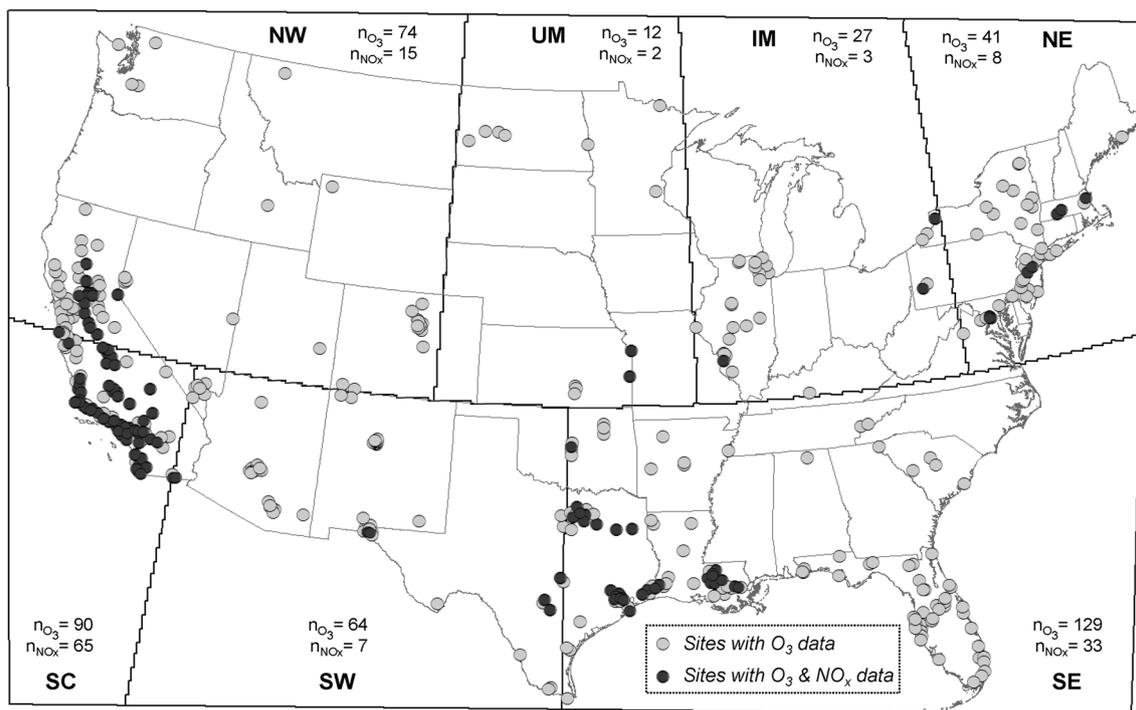
$$(O_3)_{ij} = (\beta_0 + b_{0i}) + (\beta_1 + b_{1i})\text{year}_{ij} + \gamma \text{month}_{ij} + \delta \text{weekday}_{ij} + \varepsilon_{ij} \quad (1)$$

where, (O<sub>3</sub>)<sub>ij</sub> is the O<sub>3</sub> concentration at site *i* and date *j*; β<sub>1</sub> estimates the annual O<sub>3</sub> change (ppb/year) in 1994–2010 for a specific season, region, and hour of day; *b*<sub>0*i*</sub> and *b*<sub>1*i*</sub> are the random site-specific effects for the intercept (β<sub>0</sub>) and slope (β<sub>1</sub>), respectively; and γ and δ are vectors of coefficients that represent monthly and weekday variability of O<sub>3</sub> concentrations, respectively. We meta-analyzed the regional O<sub>3</sub> trends obtained from model (1) to estimate national trends.

### Ozone penalty calculation

To assess the impact of NO<sub>x</sub> emission reductions on O<sub>3</sub> trends, we estimated actual and NO<sub>x</sub>-adjusted O<sub>3</sub> trends. Here, we applied generalized additive models (GAMs) (Hastie and Tibshirani 1990) to adjust for the nonlinear relationship between O<sub>3</sub> and NO<sub>x</sub>. 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 O<sub>3</sub>, NO<sub>x</sub>-adjusted O<sub>3</sub>, and NO<sub>x</sub> were calculated for each region, season, and time of day from the following GAMs, using the statistical package R (<http://www.r-project.org>):

$$(O_3)_{ij} = \beta_0 + \beta_{1,\text{actual}}\text{year}_{ij} + \gamma \text{month}_{ij} + \delta \text{weekday}_{ij} + \varepsilon_{ij} \quad (2)$$



**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)

$$(O_3)_{ij} = \beta_0 + \beta_{1,\text{adjusted}} \text{year}_{ij} + \gamma \text{month}_{ij} + \delta \text{weekday}_{ij} + s((NO_x)_{ij}) + \varepsilon_{ij} \quad (3)$$

$$(NO_x)_{ij} = \beta_0 + \beta_{1,NO_x} \text{year}_{ij} + \gamma \text{month}_{ij} + \delta \text{weekday}_{ij} + \varepsilon_{ij} \quad (4)$$

where,  $(O_3)_{ij}$  and  $(NO_x)_{ij}$  represent  $O_3$  and  $NO_x$  concentrations, respectively, at site  $i$  and on date  $j$  and;  $\beta_{1,\text{actual}}$ ,  $\beta_{1,\text{adjusted}}$ , and  $\beta_{1,NO_x}$  estimate regional trends of  $O_3$ ,  $NO_x$ -adjusted  $O_3$ , 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  $O_3$  and  $NO_x$  concentrations. To estimate the impact of  $NO_x$  changes on  $O_3$  trends, we obtained the difference between actual and  $NO_x$ -adjusted  $O_3$  trends, and refer to this as a “penalty” henceforth:

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

A positive penalty ( $\beta_{1,\text{actual}} > \beta_{1,\text{adjusted}}$ ) indicates an increase in  $O_3$  concentrations associated with  $NO_x$  decreases during the study period, whereas a negative penalty ( $\beta_{1,\text{actual}} < \beta_{1,\text{adjusted}}$ ) reflects a decrease in  $O_3$  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  $O_3$  trends,  $NO_x$ -adjusted  $O_3$  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  $O_3$  trends, we estimated the difference between  $O_3$  trends adjusted for smoothing functions of both  $NO_x$  and VOC, and  $NO_x$ -adjusted  $O_3$  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  $O_3$  penalty, we estimated  $O_3$  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  $O_3$  concentrations (5th to 99.9th percentile) by applying quantile regression methods (Koenker and Bassett 1978). For each co-located  $O_3$ - $NO_x$  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 O<sub>3</sub> 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,  $\beta$ . 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

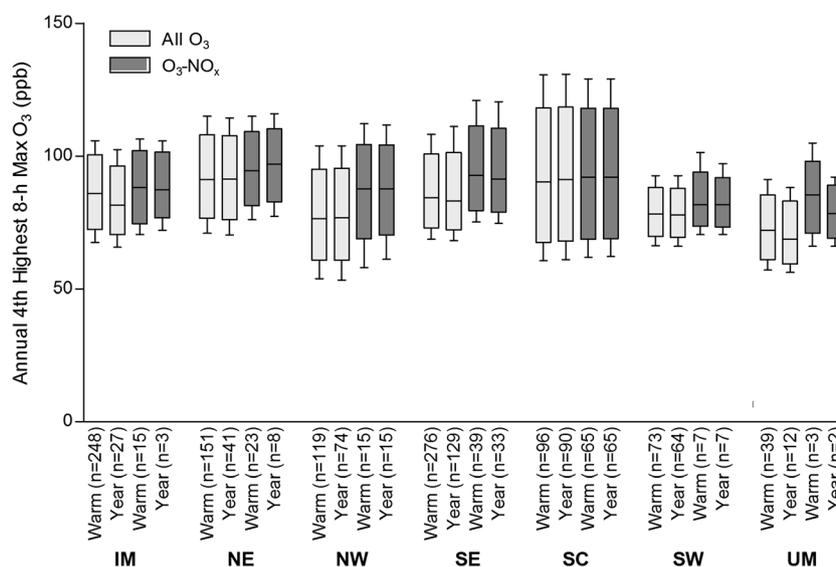
### Monthly and seasonal time series of O<sub>3</sub> and NO<sub>x</sub>

Selecting for year-round sites yielded 437 O<sub>3</sub> monitoring sites and 133 co-located O<sub>3</sub>-NO<sub>x</sub> 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 O<sub>3</sub> concentration (Fig. 2). To assess overall observed trends, we estimated national monthly averages of 24-h O<sub>3</sub>, 8-h max O<sub>3</sub>, and 24-h NO<sub>x</sub> as well as cold (Nov–Apr) and

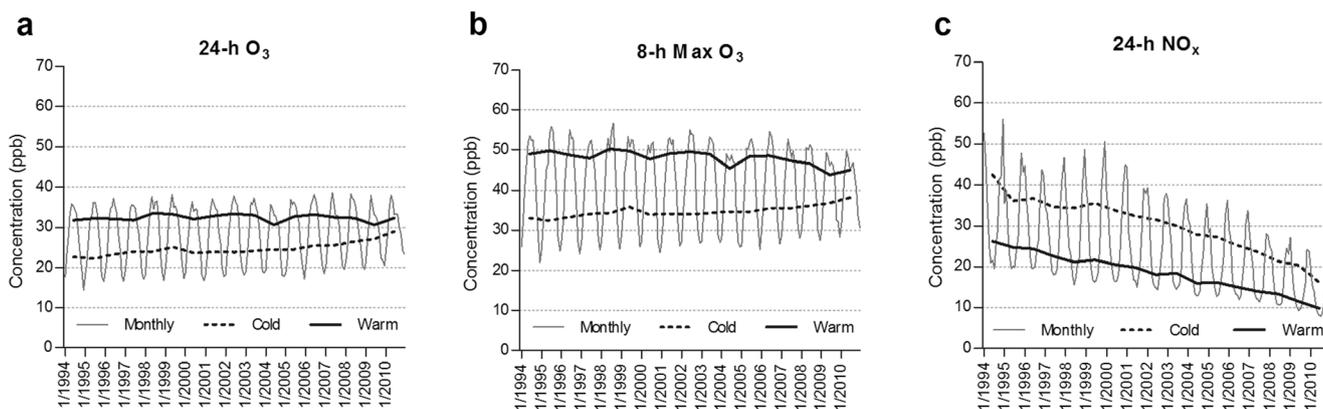
warm (May–Oct) season averages (Fig. 3). Despite substantial NO<sub>x</sub> decreases (over 60 %) in both warm and cold months, we did not observe proportionate decreases in O<sub>3</sub>. During the cold season, NO<sub>x</sub> decreased considerably from 42 to 16 ppb, but both 8-h max and 24-h O<sub>3</sub> increased from 33 to 38 and 23 to 29 ppb, respectively. In the warm season, 8-h max O<sub>3</sub> decreased from 49 to 45 ppb, while 24-h O<sub>3</sub> did not change appreciably. Therefore, the downward trends of warm season 8-h max O<sub>3</sub> were not representative of the remaining 16 h excluded from this metric. Other studies have also observed that O<sub>3</sub> trends are sensitive to exposure metric selection, with greater decreases in 8-h max O<sub>3</sub> than 24-h O<sub>3</sub> (Bell et al. 2005). Therefore, the 8-h max metric may not provide a holistic perspective on recent O<sub>3</sub> trends. This warrants closer investigation on diurnal differences in O<sub>3</sub> trends.

### O<sub>3</sub> trends by season and time of day

Given suggestive evidence for diurnally and seasonally varying O<sub>3</sub> trends in Fig. 3, we analyzed the full hourly O<sub>3</sub> data (437 sites) and employed regression methods to estimate national O<sub>3</sub> trends by season and time of day (Fig. 4). The four seasons were dichotomized to warm and cold seasons, as hourly O<sub>3</sub> 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) O<sub>3</sub> declined with a maximum decrease at 2 pm of  $-0.38$  ppb/year



**Fig. 2** Distribution of the annual fourth highest 8-h max O<sub>3</sub> concentrations by region, site selection criteria (warm season vs. year-round), and data type (all O<sub>3</sub> sites vs. co-located O<sub>3</sub>-NO<sub>x</sub> sites). Whiskers represent 5th and 95th percentile concentrations.

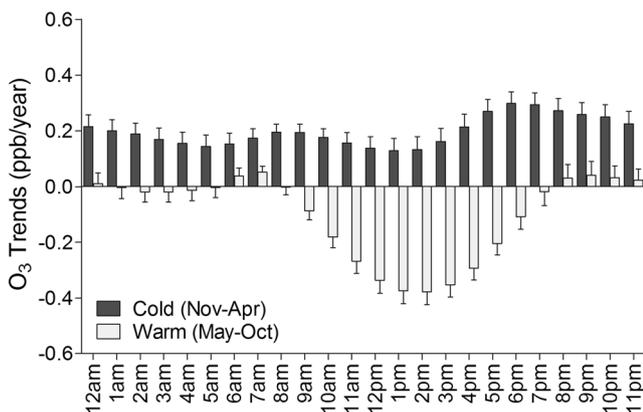


**Fig. 3** a–c National monthly mean concentration time series of O<sub>3</sub> and NO<sub>x</sub> metrics. National averages of 24-h O<sub>3</sub> (a), 8-h max O<sub>3</sub> (b), and 24-h

NO<sub>x</sub> (c) are shown. The cold season (Nov–Apr) and warm season (May–Oct) monthly means were averaged to estimate seasonal time series

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 O<sub>3</sub> concentrations rose during all hours of the day, as much as  $+0.30 \pm 0.04$  ppb/year. Recent studies have also found that O<sub>3</sub> increases were much more common in the winter and springtime, especially among low- to mid-O<sub>3</sub> percentile levels (e.g., 5th and 50th percentiles) (Cooper et al. 2012).

All seven NMMAPS regions exhibited warm season mid-day 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 O<sub>3</sub> increases during the warm season nighttime in the Northwest, Industrial Midwest, and Southern California. The cold season and nighttime rise in O<sub>3</sub> concentrations suggested that NO<sub>x</sub> titration reactions—an important chemical mechanism precisely when photochemical activity is reduced—may have played a role.

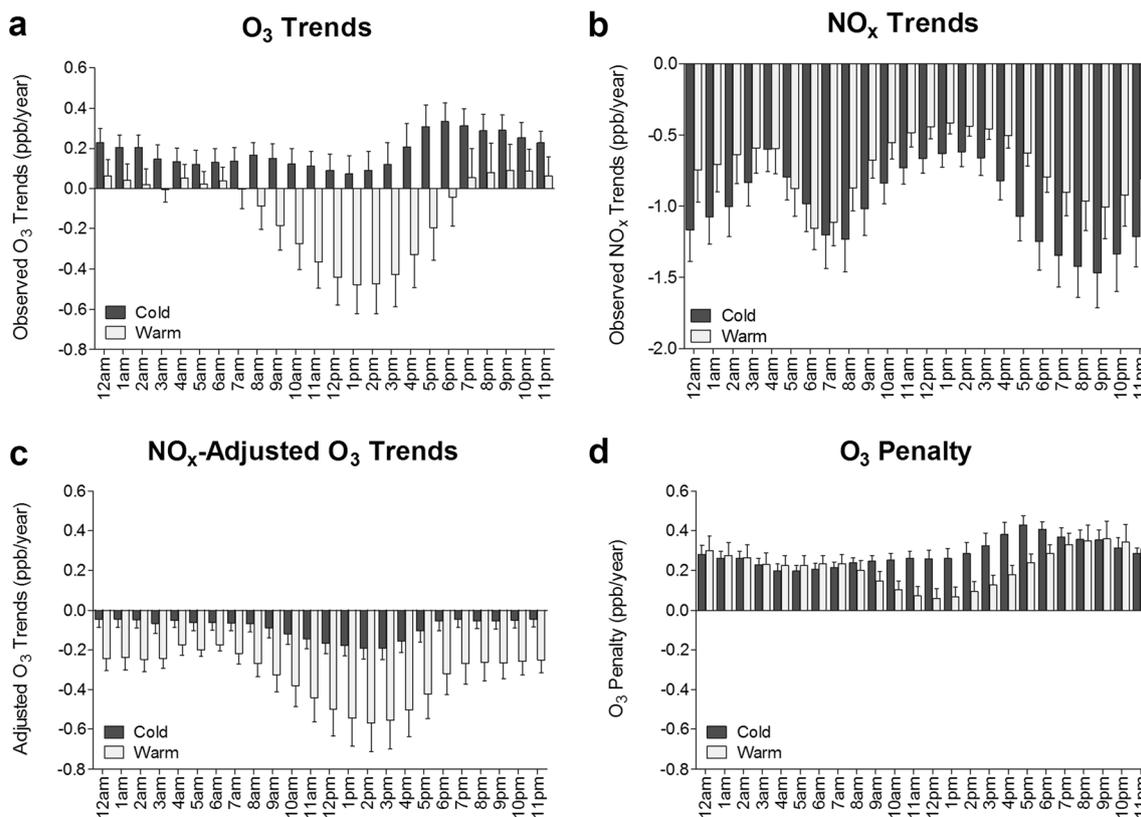


**Fig. 4** National O<sub>3</sub> trends by season and time of day. National trends were estimated by meta-analyzing regional trends derived from all O<sub>3</sub> data (437 sites). Standard errors are shown

O<sub>3</sub> and NO<sub>x</sub> trends in subset of sites

We quantified the impact of NO<sub>x</sub> emission reductions on O<sub>3</sub> trends using co-located hourly O<sub>3</sub> and NO<sub>x</sub> 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 O<sub>3</sub> dataset (Fig. 5a). However, warm season nighttime O<sub>3</sub> increases were greater, which may result from differences in the characteristics of sites that also measure NO<sub>x</sub>. Co-located O<sub>3</sub>-NO<sub>x</sub> sites had slightly higher annual fourth highest 8-h max O<sub>3</sub> concentrations in many regions (Fig. 2). In addition, these sites are more likely to have higher initial NO<sub>x</sub> concentrations, as NO<sub>x</sub> monitoring sites are strategically chosen. Consequently, the magnitude of NO<sub>x</sub> decreases could be greater in areas where NO<sub>x</sub> was monitored. This is consistent with the elevated nighttime O<sub>3</sub> increases in these sites (Fig. 5a), since less O<sub>3</sub> would have been quenched by NO<sub>x</sub> due to greater NO<sub>x</sub> reductions. While an enhanced NO<sub>x</sub> decrease may lead to an overestimate of the impact of NO<sub>x</sub> on O<sub>3</sub> trends, we analyze a fairly even distribution of rural ( $n=35$ ), suburban ( $n=55$ ), and urban ( $n=42$ ) sites, which differ in baseline NO<sub>x</sub> levels and magnitude of NO<sub>x</sub> decreases.

We also estimated trends of NO<sub>x</sub>, which decreased during all times of the day in both seasons ranging from  $-0.42 \pm 0.08$  to  $-1.47 \pm 0.24$  ppb/year (Fig. 5b). Normalizing these trends to the initial NO<sub>x</sub> concentrations eliminated the seasonal and diurnal variability of trends. In summary, hourly trends of NO<sub>x</sub> and O<sub>3</sub> were consistent with time series results in Fig. 3, as they showed that NO<sub>x</sub> decreased in both seasons while O<sub>3</sub> increased in the cold season and had mixed warm season trends.



**Fig. 5** **a–d** Trends and O<sub>3</sub> penalties. Regression results of O<sub>3</sub> trends (**a**), NO<sub>x</sub> trends (**b**), NO<sub>x</sub>-adjusted O<sub>3</sub> trends (**c**), and O<sub>3</sub> penalties (**d**) using data from co-located O<sub>3</sub>-NO<sub>x</sub> sites (133 sites). Standard errors are shown

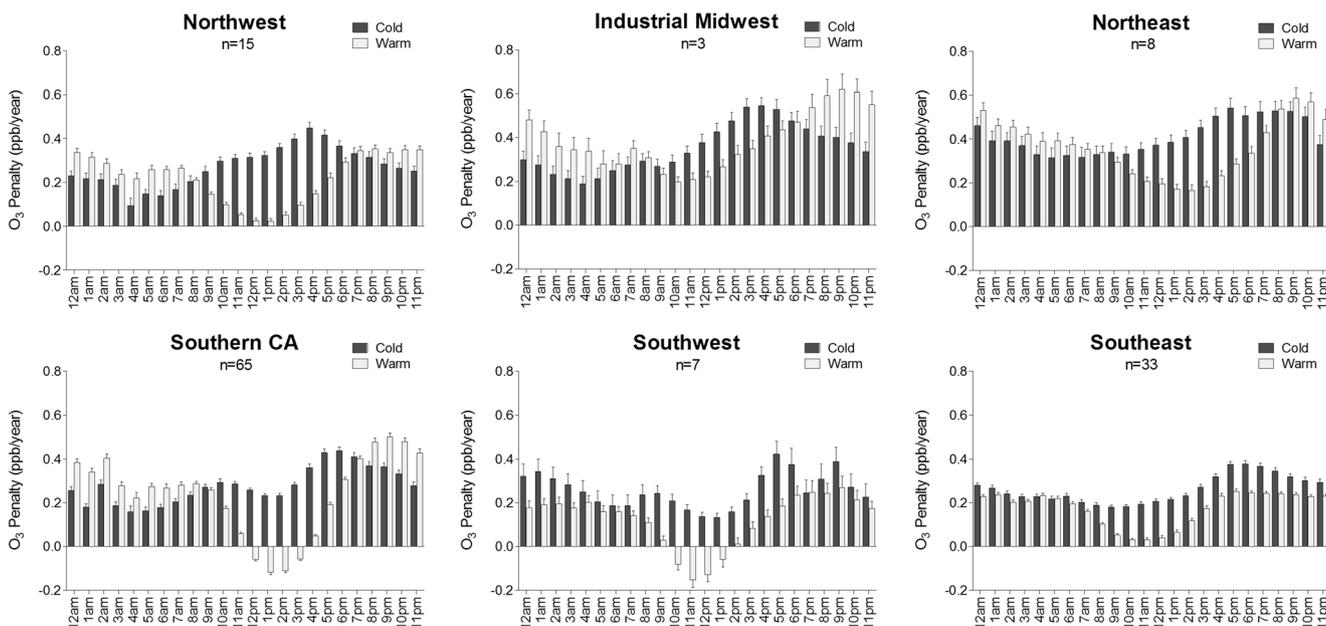
### O<sub>3</sub> penalty

We estimated O<sub>3</sub> trends that were adjusted for NO<sub>x</sub>, in order to characterize O<sub>3</sub> trends that assume NO<sub>x</sub> concentrations remained constant (i.e., without influence of regulations). The NO<sub>x</sub>-adjusted O<sub>3</sub> trends demonstrated that if NO<sub>x</sub> concentrations did not decrease, O<sub>3</sub> concentrations during the warm season nighttime and cold season would have decreased instead (Fig. 5c). Therefore, NO<sub>x</sub> concentration decreases were associated with an increase, or “penalty”, in O<sub>3</sub> concentrations. While we are primarily interested in the impact of NO<sub>x</sub> changes on O<sub>3</sub> trends rather than explaining the variability of O<sub>3</sub> concentrations, we found that adjusting for NO<sub>x</sub> 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 O<sub>3</sub> and NO<sub>x</sub> 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<sub>x</sub> concentration decreases were associated with higher O<sub>3</sub> 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 O<sub>3</sub>

increases. Penalty values can be greater than the magnitude of O<sub>3</sub> increases in cases where O<sub>3</sub> would have decreased instead (i.e., where NO<sub>x</sub>-adjusted O<sub>3</sub> trends are negative). Therefore, NO<sub>x</sub> concentration decreases significantly influenced O<sub>3</sub> trends by suppressing the scavenging of O<sub>3</sub> through NO<sub>x</sub> titration; this phenomenon was largely responsible for O<sub>3</sub> increases during the cold season and warm season nighttime. The NO<sub>x</sub>-related O<sub>3</sub> penalties were slightly greater during the more recent 8 years (2003–2010), after the implementation of EPA’s NO<sub>x</sub> Budget Trading Program that targeted NO<sub>x</sub> emissions from power plants in the Eastern USA. This warrants continued vigilance on the impact of future NO<sub>x</sub> decreases on nonpeak O<sub>3</sub> concentrations in the USA.

Even the warm season O<sub>3</sub> decreases during the midday were largely insensitive to NO<sub>x</sub> decreases, suggesting that other factors were more effective at mitigating O<sub>3</sub> (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 O<sub>3</sub> year-round. However, some benefits of NO<sub>x</sub> decreases were observed on a regional scale. Southwest and Southern California exhibited benefits of NO<sub>x</sub> reductions (as much as  $-0.15 \pm 0.03$  ppb/year) during the warm season midday, when NO<sub>x</sub> predominantly acts as a photochemical precursor rather than a quencher of O<sub>3</sub> (Fig. 6). These benefits,



**Fig. 6** O<sub>3</sub> penalties by region, season, and time of day. Upper Midwest not shown due to nonsignificant penalties. Standard errors are shown

however, were much smaller in magnitude than nighttime O<sub>3</sub> penalties, which were as high as  $+0.62 \pm 0.07$  ppb/year. An important consideration is that the limited availability of NO<sub>x</sub> 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 O<sub>3</sub>-NO<sub>x</sub> monitors that are located in some of the most populated areas and places where O<sub>3</sub> concentrations are higher (Fig. 2).

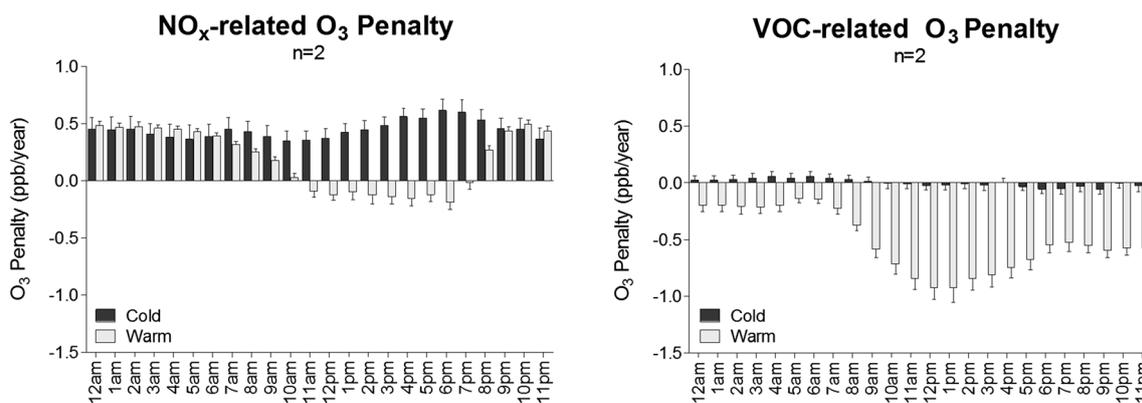
Many modeling and trend analysis studies have illustrated that NO<sub>x</sub> emission controls led to decreases in O<sub>3</sub> concentrations (Bloomer et al. 2010; Butler et al. 2011; Gégó et al. 2007). However, they either primarily focused on high O<sub>3</sub> levels (e.g., warm season 8-h max) or simply compared O<sub>3</sub> trends from periods before and after implementation of the NO<sub>x</sub> Budget Trading Program (e.g., 1997–1999 vs. 2006–2008). Here, we *directly* quantified the impact of NO<sub>x</sub> decreases on O<sub>3</sub> trends, rather than make qualitative comparisons; we also illustrated a more holistic perspective by considering regional, seasonal, and diurnal differences in O<sub>3</sub> 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 O<sub>3</sub> trends

National penalties were lowest and nearly zero during the warm season midday. The insensitivity of warm season O<sub>3</sub> decreases to NO<sub>x</sub> adjustment suggested that NO<sub>x</sub> reductions may not be responsible for the observed decreases. Instead, mitigation of other O<sub>3</sub> 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 O<sub>3</sub>, NO<sub>x</sub>, and total nonmethane organic carbons (NMOCs, representing ambient concentrations rather than emissions); prior studies have used NMOC measurements to assess the relationship between O<sub>3</sub> 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 O<sub>3</sub> trends, we obtained the difference between the impacts of NO<sub>x</sub> decreases and both NO<sub>x</sub> and NMOCs decreases on O<sub>3</sub> trends. Despite data limitations, these results suggested that NMOC reductions were more effective in reducing O<sub>3</sub> 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<sub>x</sub> where VOC is the limiting reactant can actually *increase* O<sub>3</sub> 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<sub>x</sub> emission reductions can increase O<sub>3</sub> production efficiency and actually increase 8-h max O<sub>3</sub> in VOC-limited areas (Reynolds et al. 2003). Lastly, unlike NO<sub>x</sub> reductions, NMOC decreases had minimal impact on nighttime and cold season O<sub>3</sub> levels. Therefore, VOC reductions achieved more meaningful benefits by mitigating warm season daytime O<sub>3</sub> 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



**Fig. 7** NO<sub>x</sub>- and VOC-related O<sub>3</sub> penalties by season and time of day in the Northeast. Standard errors are shown

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 O<sub>3</sub> mitigation.

#### Penalties in urban and rural sites

As atmospheric compositions of NO<sub>x</sub> and VOCs differ between urban, suburban, and rural areas, we also analyzed the impact of reducing NO<sub>x</sub> in these areas separately. Rural sites ( $n=35$ ) showed the greatest O<sub>3</sub> decreases and the least NO<sub>x</sub> decreases compared to urban ( $n=42$ ) and suburban ( $n=55$ ) sites. Benefits of reducing NO<sub>x</sub> were observed in rural sites during the warm season midday (11 am–3 pm), with a maximum benefit of  $-0.14 \pm 0.03$  ppb/year. However, this was only a fraction of the actual O<sub>3</sub> decrease of  $-0.63 \pm 0.19$  ppb/year, again suggesting that other factors led to the majority of O<sub>3</sub> decreases. Furthermore, statistically significant positive O<sub>3</sub> penalties were observed in the nighttime and cold season in rural sites. Therefore, NO<sub>x</sub>-related O<sub>3</sub> penalties were not confined to urban areas.

#### Meteorological impacts on trends and penalties

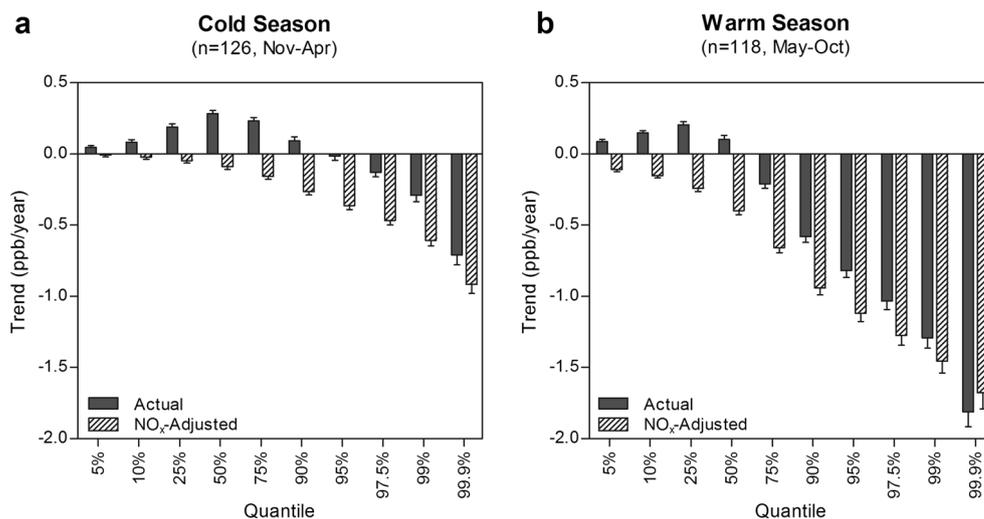
In addition to NO<sub>x</sub> and VOCs, weather conditions also significantly affect O<sub>3</sub> levels; for instance, high temperature, low humidity, and low wind speed conditions favor O<sub>3</sub> formation (The National Academies Press 1991). To assess the influence of weather, we compared the impact of NO<sub>x</sub> reductions on O<sub>3</sub> trends with and without adjusting for temperature, wind speed, and water vapor pressure. Changes in these meteorological parameters during our study period had *mitigated* O<sub>3</sub> 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 O<sub>3</sub> removal during the night and wintertime. Second, as a result of weather changes, NO<sub>x</sub> did not decrease as much as it would have otherwise. In other words, without the influence of meteorological changes, O<sub>3</sub> penalties would have been even higher not only due to greater NO<sub>x</sub> decreases, but also due to less favorable condition for O<sub>3</sub> removal. In summary, O<sub>3</sub> penalties were robust to meteorological adjustment and the penalty values we reported earlier in Fig. 5d were conservative estimates.

#### Quantile regression of hourly O<sub>3</sub>

To examine the impact of NO<sub>x</sub> on a wider range of O<sub>3</sub> concentrations, we applied the quantile regression method. Nationally, the 95th quantile O<sub>3</sub> 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 O<sub>3</sub> increased. We analyzed a subset of sites with co-located O<sub>3</sub> and NO<sub>x</sub> data to estimate trends of 5th, 10th, 25th, 50th, 75th, 90th, 95th, 97.5th, 99th, and 99.9th quantiles of hourly O<sub>3</sub> concentrations and compared these trends to those that were adjusted for hourly NO<sub>x</sub> concentrations (Fig. 8). In the cold season, 5th to 90th quantile O<sub>3</sub> levels increased, and the NO<sub>x</sub>-adjusted quantile trends showed that O<sub>3</sub> would have decreased if NO<sub>x</sub> concentrations had remained constant (Fig. 8a). In the warm season, higher O<sub>3</sub> levels ( $\geq 75$ th quantiles) decreased, but lower quantile O<sub>3</sub> levels increased (Fig. 8b), indicating a shift towards mid-O<sub>3</sub> concentrations. Consistent with the positive penalties we reported earlier in Fig. 5d, NO<sub>x</sub> reductions were associated with an increase in a wide range of O<sub>3</sub> concentrations, even during the warm season. This is also

**Fig. 8 a,b** Actual and NO<sub>x</sub>-adjusted O<sub>3</sub> quantile trends. Quantile trends in the cold season (a) and warm season (b) using data from co-located O<sub>3</sub>-NO<sub>x</sub> sites (133 sites). Standard errors are shown



consistent with our VOC analysis, which suggested that our atmosphere is more VOC-limited—an environment in which photochemical production of O<sub>3</sub> can increase with NO<sub>x</sub> reduction. However, benefits of NO<sub>x</sub> reductions were observed at the 99.9th quantile level in the warm season, illustrating that NO<sub>x</sub> decreases mitigated extreme O<sub>3</sub> episodes.

## Conclusion

Important progress has been made in mitigating high O<sub>3</sub> concentrations. Our analyses showed significant decreases in O<sub>3</sub> during the warm season midday and at peak levels ( $\geq 75$ th quantile). However, there were significant increases in non-peak O<sub>3</sub> concentrations, which occurred primarily during the cold season and nighttime. As a result, the gap between the highest and lowest O<sub>3</sub> concentrations has been narrowing.

While many factors impact O<sub>3</sub> trends, the dual influence of NO<sub>x</sub> emission reductions has been largely under-investigated. We found suggestive evidence that NO<sub>x</sub> reductions mitigated the highest O<sub>3</sub> concentrations (99.9th percentile). However, substantial increases in non-peak O<sub>3</sub> concentrations were associated with NO<sub>x</sub> decreases, which were driven by two mechanisms. First, decreasing NO<sub>x</sub> reduces the amount of O<sub>3</sub> quenched through NO<sub>x</sub> titration, leading to an apparent increase in O<sub>3</sub> concentrations, especially during the night and wintertime. Second, we found suggestive evidence that the atmosphere may be more VOC-limited; in such conditions, NO<sub>x</sub> reductions can increase O<sub>3</sub> 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 O<sub>3</sub> concentrations.

It is important to recognize other factors that also influence O<sub>3</sub> 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 O<sub>3</sub> levels (Fiore et al. 2003; Wang et al. 2009). Additionally, while we show that NO<sub>x</sub> reductions yielded penalties to O<sub>3</sub> in recent years, reducing NO<sub>x</sub> also mitigated particle pollution (US EPA 2009c) and prevented adverse health effects related to NO<sub>x</sub> exposure (Burnett et al. 2004; Samoli et al. 2006). Therefore, the decreases in NO<sub>x</sub> are a critical public health achievement.

Continued decreases in NO<sub>x</sub> may eventually lead to more meaningful O<sub>3</sub> reductions in the future. However, the level of NO<sub>x</sub> decreases necessary to achieve this is uncertain. In the meanwhile, more effective O<sub>3</sub> mitigation strategies are needed and future air quality management efforts should assess ways to capitalize on the significant NO<sub>x</sub> reductions that have already been achieved.

**Acknowledgments** This work was made possible by the Harvard School of Public Health Scholarship and the US EPA grant RD-834798-01. Its contents are solely the responsibility of the grantee and do not necessarily represent the official views of the US EPA. Further, the US EPA does not endorse the purchase of any commercial products or services mentioned in the publication. We thank Choong-Min Kang for his assistance with creating the dataset, Marianthi Kioumourtzoglou for her help with the bootstrap method development, and Elena Austin for her help with the quantile regression method. We also thank Joel Schwartz for his input on statistical analyses.

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