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Emission reductions and urban ozone responses under more stringent US standards

Nicole Downey [a, *], Chris Emery [b], Jaegun Jung [b], Tanarit Sakulyanontvittaya [b], Laura Hebert [a], Doug Blewitt [a], Greg Yarwood [b]

[a] Earth System Sciences, LLC, P.O. Box 7565, Houston, TX 77270, USA
[b] ENVIRON International Corporation, 775 San Marin Dr., Novato, CA 94945, USA

HIGHLIGHTS

- Emission reductions of 60–92% required to reduce 4th highest MDA8 to 75 ppb.
- Emission reductions of 80–97% required to reduce 4th highest MDA8 to 60 ppb.
- Emission reductions lead to frequency distributions tending toward background O_3.
- Significant integrated O_3 remains after elimination of domestic precursor emissions.

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ABSTRACT

We use a photochemical grid model instrumented with the high-order Decoupled Direct Method (HDDM) to evaluate the response of ozone (O_3) to reductions in US-wide anthropogenic emissions, and to estimate emission reductions necessary to meet more stringent National Ambient Air Quality Standards (NAAQS) for O_3. We simulate hourly O_3 response to nationwide reductions in nitrogen oxides (NOx) and volatile organic compound (VOC) emissions throughout 2006 and compare O_3 responses in 4 US cities: Los Angeles, Sacramento, St. Louis, and Philadelphia. We compare O_3 responses between NOx-rich, O_3-inhibited urban core sites and NOx-sensitive, higher O_3 suburban sites and analyze projected O_3 frequency distributions, which can be used to drive health effect models. We find that 2006 anthropogenic NOx and VOC emissions must be reduced by 60–70% to reach annual 4th highest (H4) maximum daily 8-h (MDA8) O_3 of 75 ppb (the current US standard) in Sacramento, St. Louis, and Philadelphia, and by 80–85% to reach an H4 MDA8 of 60 ppb. Los Angeles requires larger emissions reductions and achieves an H4 MDA8 of 75 ppb with 92% reductions and 60 ppb with 97% reductions. As emissions are reduced, hourly and MDA8 frequency distributions tend toward mid-level background distributions. Mid-level O_3 exposure is an important driver of O_3 health impacts calculated by epidemiological models. A significant fraction (at least 48%) of summertime integrated MDA8 O_3 at all sites remains after complete elimination of US anthropogenic NOx and VOC emissions, implying that mid-level O_3 exposure due to background will become more important as domestic precursor emissions are controlled.

1. Introduction

Tropospheric ozone (O_3) is regulated by the US Environmental Protection Agency (EPA) as a criteria pollutant (EPA, 2006). O_3 is unique among criteria pollutants because it is formed in the atmosphere rather than directly emitted and because surface O_3 concentrations include a relatively large contribution from a combination of natural precursors and international transport (US background O_3) (Warneck, 2000; Lefohn et al., 2001; Fiore et al., 2002; Cooper et al., 2011; Zhang et al., 2011; Emery et al., 2012; Lin et al., 2012). Tropospheric O_3 is produced by photochemical reactions among a multitude of directly emitted precursor compounds including nitrogen oxides (NO_x = NO + NO_2), volatile organic compounds (VOC), carbon monoxide (CO), and methane (CH_4). Changing NOx emissions can produce strong non-linear responses in O_3 depending on the local relative abundance of NOx and VOCs (Warneck, 2000). Under high NOx, low VOC conditions such as in urban core areas, O_3 production is inhibited and

* Corresponding author.
E-mail address: nicole.downey@earthsystemsciences.com (N. Downey).

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reductions of NOx can increase local O_3 (often referred to as a NOx "dis-benefit"). In the opposite case such as suburban and rural areas, O_3 production is more efficient and reductions of NOx will decrease O_3. In general, NOx emissions from urban core areas are transported toward suburban and rural areas leading to higher peak ozone downwind.

The current US National Ambient Air Quality Standard (NAAQS) for O_3 is 75 ppb based on a 3-year average of the annual 4th highest (H4) maximum daily 8-h average (MDA8) concentrations (Federal Register, 2008). EPA is currently considering lowering the O_3 standard into the 60–70 ppb range in its ongoing NAAQS review (EPA, 2014b). During this process EPA evaluates the public health risk associated with O_3 and estimates changes in risk at progressively lower standards. The non-linear chemistry of O_3 formation coupled with its relatively high background and uncertainties in precursor emissions make it difficult to estimate *a priori* what emission reductions will be needed to meet a given level of the standard. Photochemical grid models include the relevant science to compute O_3 responses to emission changes. However, models are computationally costly and traditional "brute-force" approaches, in which specific NOx and VOC emission scenarios are simulated, are inefficient for estimating emissions reductions needed to meet a range of proposed standards across vastly different urban environments.

Many photochemical models are now instrumented with efficient and accurate "sensitivity" algorithms, such as the Decoupled Direct Method (DDM) (Dunker et al., 2002) and the adjoint method (Menut et al., 2000). Adjoints of photochemical models calculate the first order response of O_3 to changes in precursor emissions and thereby cannot capture non-linear effects, limiting their applicability to a relatively narrow range of emissions. High-order DDM (or HDDM) offers advantages over both brute-force and adjoint modeling because a wider range of emission responses can be estimated from a limited set of model runs (Hakami et al., 2003). HDDM calculates first and second order derivatives (sensitivity coefficients) of O_3 with respect to NOx and VOC emissions, which can then be used in an algebraic Taylor series to estimate hourly ambient O_3 concentrations resulting from specific NOx and VOC changes. A wide range of emission levels can be examined with a single Taylor series yielding a useful tool for (1) generating realistic annual frequency distributions of hourly O_3 concentrations at alternative standards for use in health risk calculations and (2) evaluating the magnitude of emission reductions needed to meet targeted O_3 standards.

EPA used HDDM in the current NAAQS review to estimate annual O_3 distributions in 15 US cities meeting a range of proposed standards between 60 and 75 ppb (EPA, 2014a). In developing EPA's technique, Simon et al. (2012) applied the Community Multi-scale Air Quality (CMAQ) model (Byun and Schere, 2006; Foley et al., 2010) over the eastern US at 12 km grid resolution over 2 months (July and August 2005). Three cases were simulated with HDDM involving anthropogenic NOx reductions of 0%, 50%, and 75% across the eastern US. Simon et al. did not address O_3 sensitivity to VOC emissions. Hourly sensitivities generated from each of the three runs were input to a set of three linked "step-wise" equations that represented O_3 response over the full range of NOx reductions between 0 and 100%. Simon et al. further developed sensitivity regression relationships from which to calculate O_3 "central tendency" responses by season, hour of the day, and monitoring site so that O_3 projections could be extended to hourly observation data in any year. O_3 projections and performance against "brute force" results were developed and analyzed for monitoring sites in Detroit, MI and Charlotte, NC. Predictions of O_3 response to changes in emissions outside of July and August 2005 were not evaluated. On the basis of newer CMAQ/HDDM runs of the entire US at 12 km resolution over 8 months of 2007, the EPA has applied the Simon et al. technique for all monitoring sites in 15 US cities as part of their Risk and Exposure Assessment (EPA, 2014a). However, results from the full 15 city analyses have not been published in journal literature.

Yarwood et al. (2013) describe a similar HDDM technique that applied the Comprehensive Air quality Model with extensions (CAMx; ENVIRON, 2012) over the entire US at 12 km grid resolution for the entire year of 2006. Details of the approach are described in Section 2. HDDM tracked hourly O_3 sensitivity to US-wide anthropogenic emissions of both NOx and VOC, and the model projections were evaluated against "brute force" simulations of several NOx and VOC scenarios in 22 US cities. Whereas Simon et al. (2012) and Yarwood et al. (2013) describe the development of two similar HDDM techniques and present initial evaluations (Simon for two cities over a two-month summer application in 2005, Yarwood for 22 cities over the entire year 2006), in this analysis we have extended the HDDM results of Yarwood et al. (2013) to study in detail the O_3 response in four specific US cities to nationwide anthropogenic emission reductions. Specifically, we estimate emission reductions needed to achieve 2006 H4 MDA8 O_3 concentrations in the range 60–75 ppb at all monitoring sites in each city. From these simulations we calculate the annual O_3 frequency distributions as a function of NOx and VOC reductions at both high O_3 concentration sites and NOx-inhibited sites and present changes in seasonal and annual integrated hourly and MDA8 O_3 concentrations.

2. Methods

Yarwood et al. (2013) performed 2006 North American HDDM photochemical modeling with CAMx version 5.40 at 12 km resolution using the 2005 version of the Carbon Bond chemical mechanism, excluding aerosols (Yarwood et al., 2005). Model configuration and inputs were developed for a previous study of North American Background O_3 (Emery et al., 2012) using meteorological and emissions data prepared by EPA for the Air Quality Model Evaluation International Initiative (AQMEII) program (Rao et al., 2011; Vautard et al., 2012; Pouliot et al., 2012). Chemical boundary conditions for the modeling grid (Fig. S1) were downscaled from a 2006 global simulation using GEOS-Chem version 8-03-01 (Bey et al., 2001; Emery et al., 2012). Statistical model-observation performance comparisons at rural and urban monitoring sites across the US have been previously reported (Emery et al., 2012; Lefohn et al., 2014).

The CAMx HDDM treatment follows the approach of Dunker et al. (2002) and Cohan et al. (2010). CAMx was configured to generate hourly O_3 sensitivity to US-wide anthropogenic NOx and VOC for every grid cell across the entire model domain. The resulting sensitivity coefficients were used to construct algebraic Taylor series from which to generate annual frequency distributions of hourly O_3 at any location and for any US anthropogenic NOx and VOC emission scenario between zero and 100%:

$$\Delta O_3 = \Delta N S_N^{(1)} + \frac{1}{2}\Delta N^2 S_N^{(2)} + \Delta V S_V^{(1)} + \frac{1}{2}\Delta V^2 S_V^{(2)} + \Delta N \Delta V S_{NV}^{(2)},$$

where

$$S_N^{(1)} = \partial O_3 / \partial \mathrm{NOx}$$
$$S_V^{(1)} = \partial O_3 / \partial \mathrm{VOC}$$
$$S_N^{(2)} = \partial^2 O_3 \Big/ \partial \mathrm{NOx}^2$$
$$S_V^{(2)} = \partial^2 O_3 \Big/ \partial \mathrm{VOC}^2$$
$$S_{NV}^{(2)} = \partial^2 O_3 \Big/ \partial \mathrm{NOx}\, \partial \mathrm{VOC}$$

HDDM requires an *a priori* definition of the spatial area and source sector to be tracked by the sensitivity coefficients, and in this case the coefficients ΔN and ΔV represent across-the-board US-wide percent reductions in anthropogenic NOx and VOC, respectively. We can thus examine the site-specific response of O_3 to US-wide changes in NOx and VOC emissions independently. Recent HDDM publications (Simon et al., 2012; Yarwood et al., 2013) recommend applying HDDM at several points over the full emissions range to ensure accuracy under extreme emission reduction cases. For this analysis, annual CAMx simulations were conducted with HDDM at 10% and 50% of 2006 US NOx and VOC anthropogenic emissions. Sensitivity coefficients from both cases were combined to yield a 3-equation algebraic response model applied to the 0–15%, 15–25%, and 25–100% anthropogenic emission ranges.

Yarwood et al. (2013) compared O_3 predictions from the HDDM model to brute force CAMx simulations, and reported that HDDM predictions tended to more accurately replicate brute force results in warm rather than cold seasons, at rural rather than urban locations, and with 100% rather than zero anthropogenic emissions. These results stem from the strongly non-linear response of O_3 to NOx concentrations under specific emission and meteorological conditions (e.g., urban, cold/stagnant). This particular HDDM technique was able to reproduce zero and 100% brute force modeled emission scenarios to within 2–3 ppb averaged over all monitoring sites in 22 cities.

We selected cities for this analysis based on several criteria to minimize influences of model error. First, we started with 12 cities that EPA addressed in their risk and exposure analysis (EPA, 2014a). We examined CAMx model performance in replicating the 2006 observed city-wide peak H4 MDA8 values within each city statistical area (as defined by EPA). We selected only cities where the unpaired modeled and observed peak H4 MDA8 values agreed to within 10% (the site with peak simulated H4 MDA8 was not necessarily the same site with peak observed H4 MDA8). Of the cities meeting our first criterion we then compared simulated and observed annual frequency distributions of hourly O_3 (binned by 5 ppb) among all monitoring sites. To characterize total error across these distributions, we summed the absolute model-observation error over all bins, and retained cities with less than 25% cumulative error at a minimum of four sites that represented both urban core NOx rich and suburban high O_3 concentration regimes. This ensured that we chose cities where the model performed well over a broad range of chemical conditions and across the entire hourly frequency distribution. Four cities met these specifications: Philadelphia, PA; Los Angeles, CA; St. Louis, MO; and Sacramento, CA (Table S1, Figs. S2–S5).

For each city we calculated the city-wide peak H4 MDA8 as a function of US anthropogenic NOx and VOC emissions, which were reduced equally from 100% (2006 baseline) to 0% (US background). Hence, sensitivity coefficients calculated by our HDDM model runs represent the sensitivity of O_3 at a particular location to emission reductions across the entire US, which is similar to those calculated by Simon et al. (2012) and those used by EPA (2014a). Clearly O_3 in a given city is not influenced by every source throughout the US but rather by local to regional contributions, which diminish with distance depending on specific multi-scale environments and influences from the upstream fetch. Thus when we speak of US-wide reduction impacts to city/site-specific O_3, we are effectively referring to the dominant influence from respective contributing regions. For example, O_3 in Los Angeles and Sacramento is primarily formed from local emissions in their respective basins (SCAQMD, 2013; SMAQMD, 2013), whereas O_3 in St. Louis and Philadelphia forms from a mix of local and regional emissions over much larger fetches (MDNR, 2010; PDEP, 2007).

In each city, we chose a high peak O_3 concentration site and a lower O_3 concentration NOx-rich site with good model performance (Figs. S2–S5), as described above, to examine the evolution of the annual frequency distributions of hourly and MDA8 O_3 as precursor emissions are reduced. We then time-integrated these distributions over the entire year (ppb-hours) and over May to September to estimate the net effect of emissions reductions on total O_3 response (hourly) and on O_3 response during the most photochemically active portion of the day (MDA8). These time-integrated metrics can be thought of a surrogate for exposure to ambient O_3 at a particular monitoring site.

3. Results and discussion

The CAMx HDDM model suggests that 2006 US anthropogenic emissions must be reduced by 60–70% to achieve a 2006 annual H4 MDA8 of 75 ppb in Sacramento, St. Louis and Philadelphia (Table 1, Fig. 1). To reduce the H4 MDA8 to 60 ppb requires approximately 85% emissions reductions. Los Angeles requires 92% emissions reductions to bring the H4 MDA8 down to 75 ppb and 97% reductions to achieve 60 ppb (Table 1, Fig. 1). Los Angeles shows a very slight NOx dis-benefit (increasing H4 MDA8 with decreasing emissions) down to about 50% of 2006 emissions and then a marked decrease in H4 MDA8 below 25% of 2006 emissions (Fig. 1). These results are broadly consistent with those reported by EPA in their Health Risk and Exposure Assessment (EPA, 2014a). The city-wide peak site varied geographically site-to-site as emissions were reduced and chemical conditions evolved, further highlighting the complex spatial response of ambient O_3 to broad precursor controls.

The estimated precursor emission controls needed to reduce simulated 2006 H4 MDA8 O_3 to the 60–75 ppb range are substantial in all four cities analyzed here (Table 1), and large reductions in NOx and VOC emissions have occurred since 2006. For example, EPA estimates that NOx emissions have decreased by 25% and VOC emissions have decreased by 23% between 2006 (Pouliot et al., 2012) and 2011 (EPA Trends, 2014d). Nevertheless, many areas of the US continue to exceed the 75 ppb standard (EPA, 2011), which is consistent with our results. EPA projects additional decreases in NOx emissions by 2018, for total NOx reductions of 60% and VOC reductions of 41% between 2006 and 2018 (EPA, 2014c).

Given the large (>90%) reductions in 2006 emissions simulated to meet the current and proposed O_3 standard in Los Angeles, we compared our projections against the latest air quality management plan developed for Southern California (SCAQMD, 2013) to ensure that they were reasonable. In that analysis, NOx reductions of 75% relative to a projected 2023 emission inventory will be needed to reach 75 ppb at the Crestline monitoring station in the Los Angeles airshed. NOx reductions of 80–88% would be needed relative to 2023 to meet 60–70 ppb standards. These reductions are in addition to those that are expected to occur out to 2023. SCAQMD (2013) also notes that concurrent VOC reductions would moderate the needed NOx reductions.

Table 1
Projected US-wide emission reductions relative to 2006 necessary to achieve a 4th highest MDA8 between 60 and 75 ppb in each city.

4th highest MDA8	% Reductions in US-wide 2006 emissions			
	Los Angeles, CA	Sacramento, CA	St. Louis, MO	Philadelphia, PA
75 ppb	92%	68%	62%	62%
70 ppb	94%	75%	70%	73%
65 ppb	95%	82%	77%	79%
60 ppb	97%	87%	85%	84%

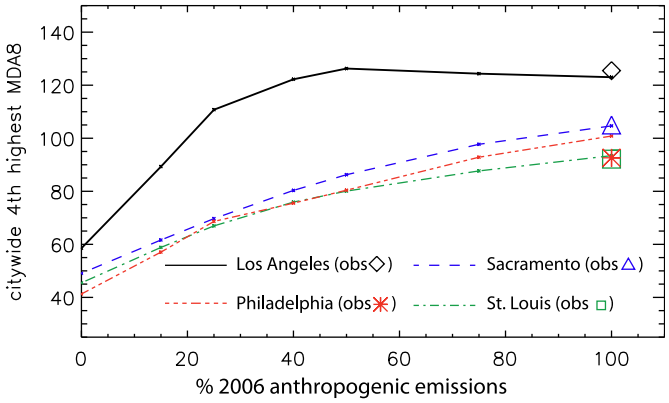

Fig. 1. Projected city-wide peak annual 4th highest (H4) maximum daily 8-h average (MDA8) O_3 as a function of US anthropogenic NOx and VOC emissions. 100% represents the 2006 baseline emissions scenario. For this analysis NOx and VOC emissions were reduced by equal proportions. Large symbols are observed peak 2006 H4 MDA8 for each city.

Examining changes in the frequency distributions for both NOx-rich and high O_3 sites for each city (Figs. 2 and 3, S6, S7) shows several interesting features. As O_3 precursor emissions are reduced the entire frequency distribution tends toward the distribution of less variable US background O_3 (Zhang et al., 2011; Emery et al., 2012, Lefohn et al., 2014). Hours with very low O_3 due to NOx scavenging tend toward higher O_3 concentrations (NOx-disbenefit) and hours with high O_3 tend toward lower O_3 concentrations. This is a direct result of the non-linear chemical response of O_3 production to changes in NOx emissions and the reduction in variability from anthropogenic influences. May to September MDA8 ozone shows the largest shift toward lower ozone, while the full-year hourly data shows the largest NOx disbenefit. May to September is generally the period over which O_3 is highest and has the largest measured impacts on health (EPA, 2014a). Observations suggest that this type of behavior is occurring in the atmosphere, as the frequency of both high and low O_3 days has decreased, while mid-level O_3 levels have both increased and decreased (Russell et al., 2014; Simon et al., 2014).

O_3 health risk models generally fall into two classes, clinical-based models of health impacts (such as lung function decrements; i.e. McDonnell et al., 2007; McDonnell et al., 2010, 2012) and epidemiological models of morbidity and mortality impacts (i.e. Bell et al., 2006; Smith et al., 2009; Jerrett et al., 2009). Clinical-based models tend to be driven by higher O_3 concentrations, and it is clear from Figs. 1–3 that emission reductions lead to reductions in peak O_3, which would lead to lower estimates of risk for endpoints based on clinical trials. However, the epidemiological models referenced above assume that the concentration response function, and thus risk, is linear down to zero O_3, an approach that EPA is following in their current NAAQS review (EPA, 2014a). Such an assumption is equivalent to integrated O_3, so it is useful to examine the response of integrated O_3 to changes in emissions as a possible indicator of impacts to epidemiological based risk estimates. Epidemiological models show the most significant relationships between O_3 and health endpoints during warmer months (Ren et al., 2008) and we have evaluated trends in hourly (full day) and MDA8 (daytime) integrated O_3 for both the full year and the warm season (May to September).

We calculated changes in integrated O_3 as the ratio of integrated O_3 at current emission levels to that at progressively lower levels of domestic anthropogenic emissions (Table S2). For the cities we examined, we saw between a 52% decrease and a 57% increase in integrated O_3 after domestic anthropogenic precursor emissions were eliminated, depending on the averaging time and period of year considered (Fig. 4, Table S2). In Philadelphia, St. Louis and Sacramento, we observed a fairly shallow slope in annual integrated MDA8 O_3 down to ~25% emissions (Fig. 4), after which emissions reductions yielded larger changes. May to September integrated O_3 decreased nearly linearly as emissions were reduced, and in all cases the total decrease in integrated O_3 was largest for the May to September MDA8 O_3 case. High O_3 sites tended to show larger decreases in integrated O_3 as emissions were reduced. The NOx rich site in Los Angeles consistently showed an increase in integrated O_3 with emission reductions (a NOx-disbenefit), regardless of the period of year or averaging time considered. In all cases, a significant portion of the integrated exposure for May to September MDA8 O_3 (at least 48%) remained after complete elimination of domestic precursor emissions. This is driven by increases in the frequency of mid-level O_3 as domestic anthropogenic emissions are reduced, ultimately reflecting US background O_3 (EPA, 2013) as domestic anthropogenic emissions go to zero. It is clear that the response among all sites in a given city will not be identical and that there will be large intra-city spatial variability in O_3 change due to interactions with NOx. Based on our results and those of others (i.e. Digar et al., 2011), the choice of daily and seasonal averaging time in health effects models is a key variable.

Our results are subject to several limitations. Photochemical modeling includes errors introduced by emission and meteorological inputs, model algorithms, space/time discretization, and other factors. Such sources of uncertainty are not attributable to HDDM or specific to CAMx but they impact model performance in replicating observed baseline O_3 patterns and influence simulated O_3 response to emission changes. The grid resolution employed in this continental-scale application (12 km) is toward the upper range typically used for city-specific regulatory modeling assessments in the US (more typically 4 km), but is consistent with regional modeling to support nationwide rulemaking (EPA, 2011). We attempted to minimize the effects of model performance issues on our results by limiting our site selection to those with good performance both at replicating the 2006 observed peak H4 MDA8 in a city and at replicating the entire frequency distribution of hourly O_3 across many sites in each city (Figs. S2–S5). These criteria are intended to make our results as robust as possible for the modeled year. Some analyses have suggested that photochemical models are not responsive enough to changes in emissions (Gilliland et al., 2008; Godowitch et al., 2010; Zhou et al., 2013), which may lead to an overestimate in the emission reductions necessary to meet alternative standards.

We also note that the O_3 response to emissions reductions at a given monitoring site reflects lowering the entire US anthropogenic emissions inventory by single across-the-board factors for NOx and VOC irrespective of location, time, or source sector. We recognize that this broad assumption is not particularly realistic and we do not intend our approach to reflect actual attainment strategies. However this approach is consistent with that employed by EPA (2014a). The emission reductions we estimate are likely broadly representative of the emission reductions that would be necessary to achieve lower US standards but our modeled hourly and MDA8 O_3 responses are specific to the year 2006 and cannot be applied to observed O_3 frequency distributions in other years. Therefore, since the form of the O_3 standard involves a 3-year average we cannot estimate the emissions reductions necessary to attain a specific 3-year standard. Due to the complex nature of O_3 chemistry and the influence of inter-annual variability of meteorology and emissions, HDDM-based projections determined for one year should not be extrapolated to other years without thorough validation of any technique used.

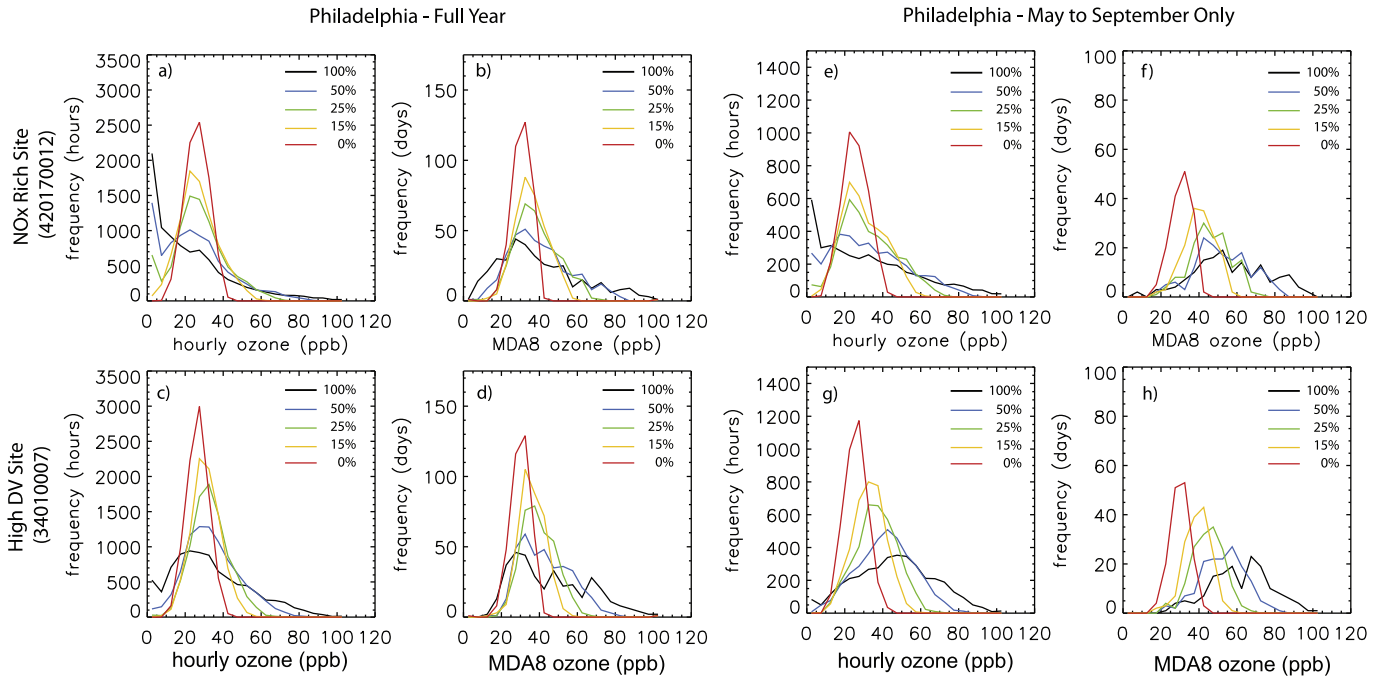

Fig. 2. Projected annual frequency distributions of hourly and MDA8 O_3 at fractions of 2006 US anthropogenic NOx and VOC emissions levels for a NOx-rich site (top) (AQS ID 420170012) and a high O_3 concentration site (bottom) (AQS ID 34010007) in Philadelphia, PA. Data in panels a–d are modeled data covering 1/1/2006 to 12/30/2006. Data in panels e–h are modeled data covering 5/1/2006 to 9/30/2006. Notice that as emissions are reduced, the distributions tend toward median values, which at 0% emissions is equivalent to US background O_3 (EPA, 2013). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

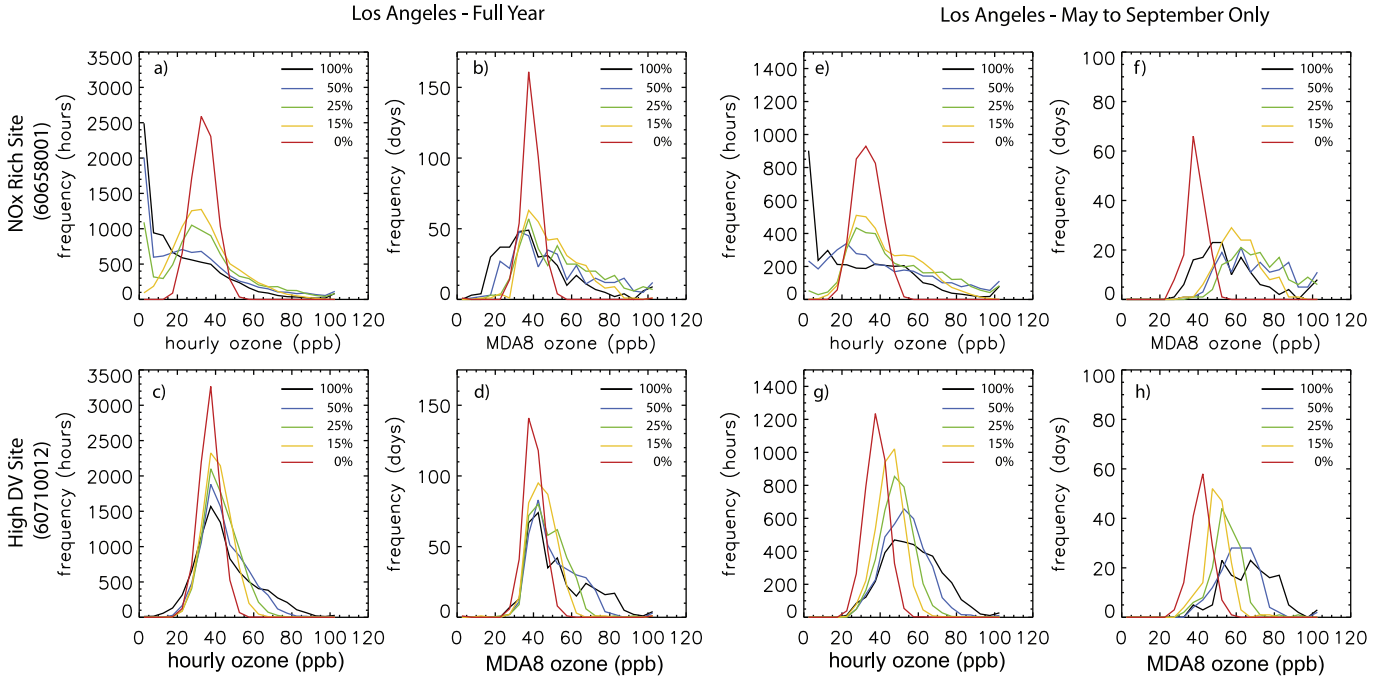

Fig. 3. Projected annual frequency distributions of hourly (left) and MDA8 (right) O_3 at fractions of 2006 US anthropogenic NOx and VOC emissions levels for a NOx-rich site (top) (AQS ID 60658001) and a high O_3 concentration site (bottom) (AQS ID 60710012) in Los Angeles, CA. Data in panels a–d are modeled data covering 1/1/2006 to 12/30/2006. Data in panels e–h are modeled data covering 5/1/2006 to 9/30/2006. Notice that as emissions are reduced the distributions tend toward median values, which at 0% emissions is equivalent to US background O_3 (EPA, 2013). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusion

We used the CAMx photochemical grid model instrumented with HDDM as described by Yarwood et al. (2013) to estimate US anthropogenic emissions reductions necessary to meet lower ambient O_3 standards in four cities, and their impact on O_3 frequency distributions and integrated O_3. We find that very large domestic emissions reductions are necessary in all cities to reduce

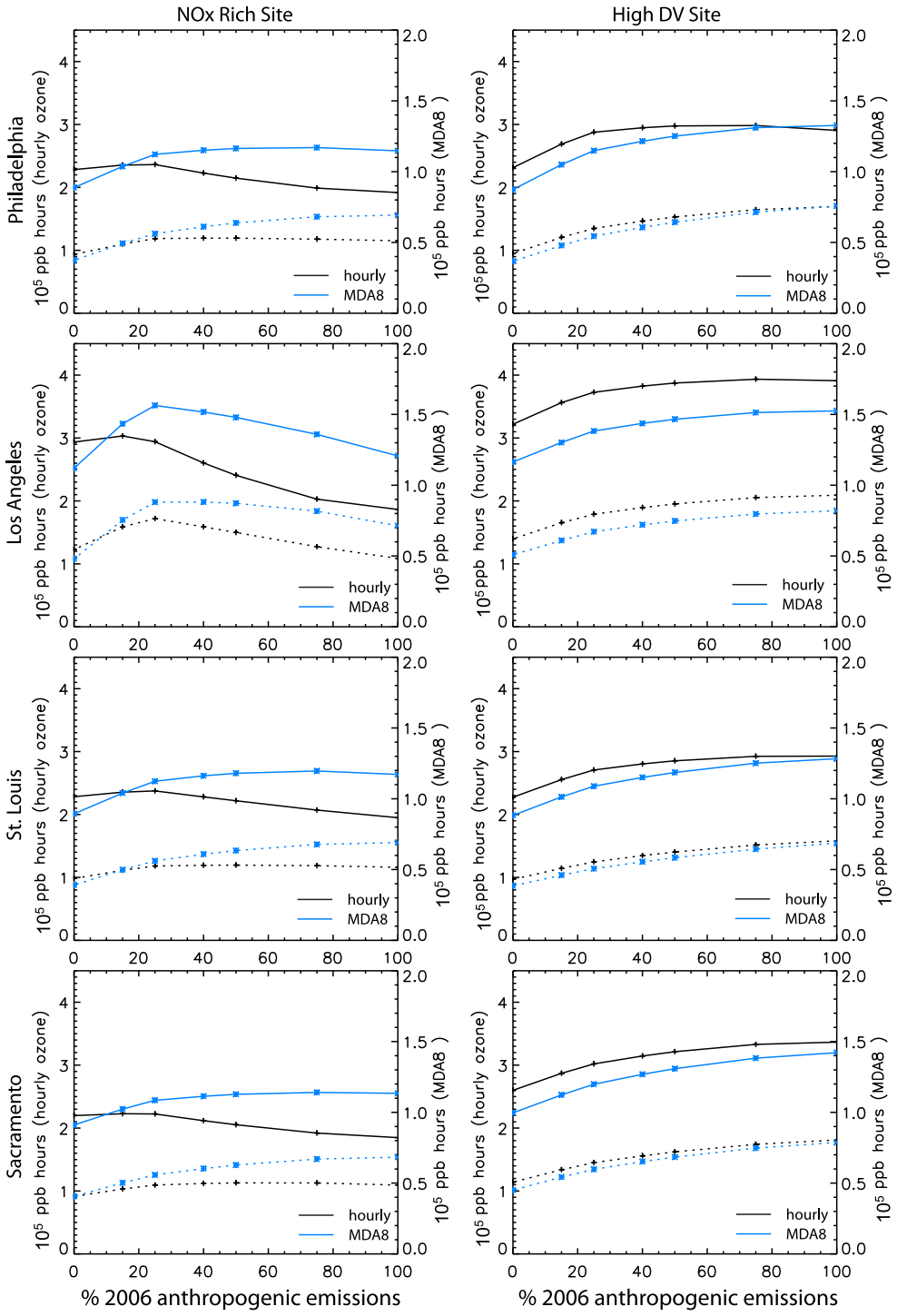

Fig. 4. Integrated O_3 as a function of 2006 US anthropogenic NOx and VOC emissions for NOx rich sites (left column) and high design value sites (right column) in Philadelphia, Los Angeles, St. Louis and Sacramento. Solid lines represent modeled integrated O_3 over the full year for hourly O_3 (black) and MDA8 O_3 (blue). Dashed lines represent modeled integrated O_3 over May to September for hourly O_3 (black) and MDA8 O_3 (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the 2006 H4 MDA8 into the range of 60–75 ppb. There are predicted to be large reductions in US-wide NOx and VOC emissions by 2018, as discussed in section 3, but these reductions may not be sufficient to reduce the H4 MDA8 to 75 ppb in any of the 4 cities examined here. Our emission reduction estimates are noteworthy as EPA is currently considering revising the NAAQS to 60–70 ppb (EPA, 2014b).

The complex nature of O_3 chemistry leads to complex spatial and temporal patterns in O_3 response to precursor controls. The strongest downward shift in O_3 frequency distributions occurs for May–Sept MDA8 ozone. Hourly full-year frequency distributions are less uniform, with some sites experiencing a downward shift and others experiencing an increase in O_3 (a NOx disbenefit). In general, there are smaller decreases or net increases in integrated

O_3 at NOx rich urban core sites relative to more suburban, less NOx saturated sites. Both the magnitude and the direction of O_3 responses can depend on the averaging time (hourly vs. MDA8) and portion of year (full-year vs. warm season) considered. This sensitivity to averaging time suggests that contemporary epidemiological health effects models should carefully consider which O_3 levels and portions of the day or year drive health impacts, as the sign of modeled health endpoints may change depending on these assumptions. We note that significant integrated May–September MDA8 O_3 remains at all sites (between 48% and 67%, Table S2) after elimination of all US anthropogenic precursor emissions, which is due to background O_3. The relative importance of background ozone to total exposure will increase as domestic precursor emissions are reduced.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2014.11.018.

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