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A modeling analysis of alternative primary and secondary US ozone standards in urban and rural areas

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HIGHLIGHTS

- CAMx HDDM used to calculate ozone sensitivity to US anthropogenic emissions.
- Emissions reductions determined to meet alternative US primary and secondary ozone standards.
- Scenarios for NOx-only, combined NOx and VOC, and VOC-only reductions for 22 cities and 20 rural sites across the US.
- Deep 2006 emission cuts needed to meet alternative standards in cities, secondary standard responds differently to cuts.
- 70 ppb primary standard is protective of 15 ppm-h secondary standard, and 60 ppb is protective of 7 ppm-h.

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ABSTRACT

This study employed the High-Order Decoupled Direct Method (HDDM) of sensitivity analysis in a photochemical grid model to determine US anthropogenic emissions reductions required from 2006 levels to meet alternative US primary (health-based) and secondary (welfare-based) ozone (O_3) standards. Applying the modeling techniques developed by Yarwood et al. (2013), we specifically evaluated sector-wide emission reductions needed to meet primary standards in the range of 60–75 ppb, and secondary standards in the range of 7–15 ppm-h, in 22 cities and at 20 rural sites across the US for NOx-only, combined NOx and VOC, and VOC-only scenarios. Site-specific model biases were taken into account by applying adjustment factors separately for the primary and secondary standard metrics, analogous to the US Environmental Protection Agency's (EPA) relative response factor technique. Both bias-adjusted and unadjusted results are presented and analyzed. We found that the secondary metric does not necessarily respond to emission reductions the same way the primary metric does, indicating sensitivity to their different forms. Combined NOx and VOC reductions are most effective for cities, whereas NOx-only reductions are sufficient at rural sites. Most cities we examined require more than 50% US anthropogenic emission reductions from 2006 levels to meet the current primary 75 ppb US standard and secondary 15 ppm-h target. Most rural sites require less than 20% reductions to meet the primary 75 ppb standard and less than 40% reductions to meet the secondary 15 ppm-h target. Whether the primary standard is protective of the secondary standard depends on the combination of alternative standard levels. Our modeling suggests that the current 75 ppb standard achieves a 15 ppm-h secondary target in most (17 of 22) cities, but only half of the rural sites; the inability for several western cities and rural areas to achieve the seasonally-summed secondary 15 ppm-h target while meeting the 75 ppb primary target is likely driven by higher background O_3 that is commonly reported in the western US. However, a 70 ppb primary standard is protective of a 15 ppm-h secondary standard in all cities and 18 of 20 rural sites we examined, and a 60 ppb primary standard is protective of a 7 ppm-h secondary standard in all cities and 19 of 20 rural sites. If EPA promulgates separate primary and secondary standards, exceedance areas will need to develop and demonstrate control strategies to achieve both. This HDDM analysis provides an illustrative screening assessment by which to estimate emissions reductions necessary to satisfy both standards.

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1. Introduction

Tropospheric ozone (O_3) is formed through complex photochemical reactions among emitted precursors including nitrogen oxides (NOx), volatile organic compounds (VOC), carbon monoxide and methane. Managing the amount of O_3 produced from anthropogenic precursor emissions in a particular geographic region is challenging due to non-linear responses to emission changes, uncertainties in emission estimates, large natural and anthropogenic background contributions, and a slow decay rate in the free troposphere that enables regional to global transport (Warneck, 2000; Zhang et al., 2011; Emery et al., 2012).

The US Environmental Protection Agency (EPA) regulates tropospheric O_3 as a criteria pollutant, for which National Ambient Air Quality Standards (NAAQS) are set for the nation. Primary NAAQS are established to protect human health, whereas secondary NAAQS are established to protect the public welfare (e.g., vegetative health and recreational/aesthetic values). The current primary and secondary standards are equivalent at 75 parts per billion (ppb) based on a 3-year average of the annual 4th highest maximum daily 8-hour average (H4MDA8) ambient concentration (Federal Register, 2008). EPA is considering lowering the health-based primary O_3 NAAQS within the range of 60–70 ppb (Federal Register, 2010), and also establishing a distinct welfare-based secondary O_3 standard for long-term vegetative exposure based on a cumulative index called W126. The W126 metric is defined as the highest three-month sum of hourly daytime (8 am–8 pm) O_3 concentrations weighted by a sigmoid function representing a hypothetical vegetation response (Lefohn and Runeckles, 1987). A W126 range of 7–15 parts per million hours (ppm-h) has been considered for the secondary standard. If EPA promulgates separate primary and secondary standards, areas exceeding these standards will need to develop emission control plans that are protective of both.

Photochemical grid models (PGMs) are necessary to assess local to regional O_3 response to emission reductions. PGMs simulate relevant physical and chemical processes in the troposphere and include non-linear O_3 chemistry. The high-order Decoupled Direct Method (HDDM; Hakami et al., 2003) is a PGM sensitivity technique that is gaining recognition by the air quality modeling community as an efficient way to evaluate a wide range O_3 responses to varying NOx and VOC levels in different environments (e.g., urban vs. rural). The method has advantages over the traditional "brute force" approach of successively repeating costly model simulations with altered emissions. HDDM tracks the spatial and temporal evolution of first- and second-order derivatives ("sensitivities") of O_3 with respect to NOx and VOC emissions. In a post-modeling step, the output sensitivities are used in an algebraic Taylor series to project O_3 concentration resulting from specific NOx and VOC changes. By employing first- and second-order sensitivities, non-linear emission impacts can be evaluated from a single PGM run.

Simon et al. (2012) describe an HDDM technique using the Community Multi-scale Air Quality (CMAQ; Byun and Schere, 2006; Foley et al., 2010) model, applied over the eastern US at a 12-km grid resolution during July and August of 2005. O_3 projections and performance against "brute force" modeling of domain and sector-wide anthropogenic NOx-only emission reductions were developed and analyzed at monitoring sites in Detroit, MI and Charlotte, NC. Simon et al. further developed regression models from raw hourly HDDM results to define "central tendencies" in O_3 sensitivity as a function of site, season, and hour of the day, from which to apply projections to O_3 observation data in any year. The Simon regression approach has been employed by the EPA (2014a) to support their draft health and welfare risk analyses of 15 US cities as part of the current O_3 NAAQS review. EPA ran CMAQ over the entire US at 12 km resolution for 8 months of 2007 to simulate sensitivity to US and sector-wide NOx-only and combined NOx/VOC emissions. Yarwood et al. (2013) describe the development of a similar HDDM approach using the Comprehensive Air quality Model with extensions (CAMx; ENVIRON, 2012). CAMx was applied over the entire US at 12-km grid resolution for the entire year of 2006. HDDM tracked hourly O_3 sensitivity to US and sector-wide anthropogenic emissions of both NOx and VOC. Model projections were evaluated against "brute force" simulations for several NOx and VOC scenarios in 22 US cities. The approach is further summarized in Section 2.

Using the results from Yarwood et al., Downey et al. (submitted for publication) conducted a detailed study of site-specific O_3 responses to US anthropogenic emission reductions in four US cities where the model exhibited low error in replicating hourly observations throughout 2006 at multiple sites per city. They specifically reported on the emission reductions needed to achieve 2006 H4MDA8 O_3 concentrations in the range 60–75 ppb among all monitoring sites in each city, and evaluated the evolution of 2006 hourly O_3 frequency distributions as a function of NOx and VOC reductions and associated changes in annual integrated O_3 concentrations as analogues for human exposure. They found that 2006 values of US anthropogenic NOx and VOC emissions must be reduced by large fractions in the four cities, by at least 70%, to meet the current 75 ppb standard and over 80% to meet a 60 ppb standard. Annual frequency distributions of hourly and MDA8 O_3 were noted to compress toward median values representative of the background O_3 range (25–40 ppb).

Whereas Downey et al. (submitted for publication) focus on meeting alterative primary O_3 standards in four US cities and ramifications for health risk estimates, this study further extends the HDDM results of Yarwood et al. to evaluate US emission reductions necessary to meet both primary and secondary alternative O_3 standards in 22 urban and 20 rural areas across the country. We tabulate where the model estimates that a primary standard is protective of a secondary standard over the ranges currently considered for the alternative primary and secondary levels, and discuss the effectiveness of NOx-only, VOC-only and combined NOx/VOC reductions. In addition, we account for model biases in replicating 2006 observed H4MDA8 and W126 O_3 metrics, a process not considered in the Yarwood et al. and Downey et al. studies.

2. Methods

The modeling setup for the 2006 North American HDDM application (Yarwood et al., 2013) included CAMx version 5.40 (ENVIRON, 2012) with the 2005 version of the Carbon Bond chemical mechanism (CB05; Yarwood et al., 2005), excluding aerosols. 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 the EPA for the Air Quality Model Evaluation International Initiative (AQMEII) program (Rao et al., 2011; Vautard et al., 2012; Pouliot et al., 2012). The modeling domain covered the conterminous US and portions of Canada and Mexico, with a grid resolution of 12 km (Fig. S1). Chemical boundary conditions were down-scaled from a 2006 global simulation using GEOS-Chem version 8-03-01 (Bey et al., 2001; Emery et al., 2012). CAMx model performance of the 2006 simulation has been previously documented by Emery et al. (2012) and Lefohn et al. (2014).

The CAMx HDDM algorithm follows Dunker et al. (2002) and Cohan et al. (2010). CAMx calculates first- and second-order sensitivities of O_3 with respect to changes in VOC and NOx emissions for every grid cell and every hour. The output sensitivities are used

to construct grid cell-specific Taylor series that project hourly O_3 estimates for any US anthropogenic NOx and VOC emission level between zero and 100%:

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

where

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

Coefficients ΔN and ΔV represent across-the-board US-wide percent reductions in anthropogenic NOx and VOC, respectively, allowing NOx and VOC emissions to be changed independently. Yarwood et al. (2013) and Simon et al. (2012) recommend running HDDM for several emission levels over the full emission range instead of just one (e.g., at "baseline" emissions) to improve O_3 estimation accuracy. Yarwood et al. conducted the CAMx HDDM simulations at 10% and 50% of US anthropogenic NOx and VOC emissions for 2006. Sensitivity coefficients from both runs were used to construct three algebraic response equations for the 0–15%, 15–25%, and 25–100% anthropogenic emission ranges. This approach is consistent, but not completely equivalent, with the technique developed by Simon et al. (2012). Comparisons of HDDM-predicted O_3 to brute force simulations showed that the HDDM performed better in warm than cold seasons, and at rural than urban locations. Nonetheless, overall results were in good agreement with brute force estimates, with a mean bias of less than 2 ppb and mean error of less than 3 ppb averaged over 22 cities in the US.

There are several inherent limitations in the Yarwood and Simon techniques. First, the O_3 response at each location reflects across-the-board reductions of all US anthropogenic emissions (although NOx and VOC can be altered separately). While not particularly realistic, we have not intended to simulate any of a large number of potential actual reduction strategies in this research exercise. Second, US sector-wide emission reductions needed to reach specific O_3 levels were determined independently for each of the 42 urban and rural areas. While O_3 at a specific location is not influenced by every source throughout the US, this simplifying assumption allows us to include the widest contributing regions possible according to 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.

Our selection of 22 cities follows from Yarwood et al. (2013) and includes 14 of the 15 cities that EPA is addressing in their risk and exposure analysis (EPA, 2014a) and 8 additional large cities in a wide variety of geographic and climatic environments. Since O_3 varies site-to-site, our analysis is based on city-wide peak H4MDA8 and W126 among all active monitoring sites reported in the EPA's Air Quality System (AQS; EPA, 2014b) in 2006. Twenty individual rural monitoring sites were also selected from the Clean Air Status and Trends Network (CASTNET; EPA, 2014c) based on several criteria, including completeness of measurement data in 2006, locations in forests or other vegetated areas (i.e., ignoring deserts and barren lands), high observed O_3 levels, adequate spatial representation across many climate zones of the US, and distance away from national borders to minimize the influence of uncertainty in foreign emission estimates. Site information is provided in Table S1.

We estimated US anthropogenic emission reductions from 2006 levels needed to meet primary H4MDA8 O_3 targets between 60 and 75 ppb within each city and at each rural site via three pathways: combined NOx and VOC, NOx-only and VOC-only. In the combined NOx and VOC case, both precursors were reduced in tandem; i.e., the same percent reduction was applied to both NOx and VOC. A city-wide peak could vary geographically site-to-site as emissions were reduced and chemical conditions evolved; consequently, emissions were reduced until the city-wide peak met a given primary target. We then determined whether these same emission reductions are sufficient to meet the secondary W126 O_3 targets, between 7 and 15 ppm-h, at the city-wide W126 peak site. Independent of primary targets, US anthropogenic emission reductions required to meet the secondary targets also were examined in two ways. First, we calculated specific emission reductions required to meet the secondary targets between 7 and 15 ppm-h within all cities and at all rural sites. Second, we produced US-wide spatial maps of the W126 surface at the model's native 12-km resolution for every 10% emission reduction interval between 0 and 100%.

All PGMs exhibit biases and errors. Using this same 2006 modeling database, Emery et al. (2012) compared predicted MDA8 against observations during spring and summer at 25 CASTNET sites across the US. CAMx tended to under predict O_3 levels in the west and over predict in the central and eastern US. Lefohn et al. (2014) extended the 2006 CAMx evaluation by comparing simulated hourly O_3 against observations at a mix of 23 urban and rural sites. Monthly model biases were found to be consistent with earlier multi-model studies (e.g., Reidmiller et al., 2009; Zhang et al., 2011). The high elevations sites tended toward under prediction, with some sites over predicting during the summer. Model performance at low-elevation sites tended toward larger under prediction biases in cool months (November–April) and larger over prediction biases in warm months (June–October), particularly for sites in the southern and eastern US. Another recent study has also reported W126 overestimates in the eastern US due to high bias of day-time O_3 from three global and regional chemical transport models (Lapina et al., 2014).

The preceding CAMx HDDM analyses reported by Downey et al. (submitted for publication) addressed O_3 responses at specific sites within four cities where the model exhibited minimal bias. In this study, we recognize that model bias is large in some locations, which could skew our estimates of emission reductions needed to reach various O_3 standards. For example, the model over predicted H4MDA8 O_3 in the city of Minneapolis, where the unadjusted HDDM response required over 30% emission reductions to reach the 75 ppb standard, whereas the actual 2006 observed H4MDA8 was only 72 ppb. We developed a bias adjustment factor (BAF) technique to reinforce our estimated O_3 responses in all 42 areas. The BAF is not applied to predictions of hourly O_3 throughout the year, but rather applied only to the single site-paired, time-unpaired H4MDA8 and W126 O_3 metrics analogous (but not equivalent) to the EPA's "relative response factor" modeling guidance (EPA, 2007).

Furthermore, we recognize that the causes for model error at 100% US anthropogenic emissions are potentially very different from sources of uncertainty related to background O_3 at 0% US anthropogenic emissions. However, we have no way to quantify model bias at background; measurements are insufficient as they always include some contribution from influences that are to be controlled. Applying a constant bias adjustment over the entire range of emission reductions implicitly assumes that bias is uniform over that range. But bias at background could be larger, smaller or even a different sign. The only guidance we have involves

model inter-comparisons. Previous work with this same CAMx modeling database shows that annual frequency distributions of hourly background O_3 range 25–40 ppb throughout the US, with higher concentrations at high altitudes in the west (Emery et al., 2012; Lefohn et al., 2014; Downey et al., submitted for publication). This range and the spatial patterns of US background over the continent are consistent with other independent modeling studies of background O_3, including that recently conducted by EPA (2014d) and referenced in EPA's current O_3 review (e.g., Zhang et al., 2011). Since we do not see a significant systematic bias relative to other background modeling studies, we have assumed zero bias in the background estimates so that O_3 projections down to zero emissions do not deviate from those of Emery et al. (2012). We consider this to be just as defensible as assuming a constant bias throughout the emissions range.

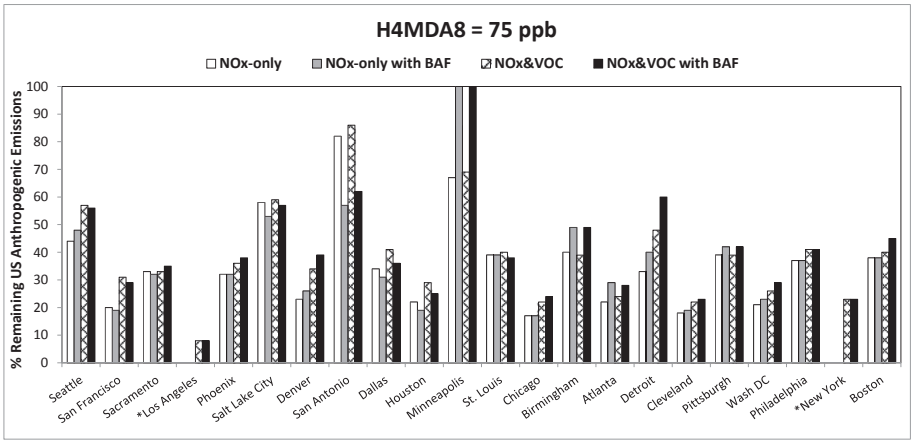
The BAF formulation is based on the ratio of observed H4MDA8 to the respective "base case" simulated H4MDA8 at 100% US anthropogenic emissions at each individual monitoring site (i), scaled linearly with percent remaining emissions (P):

$$\mathrm{BAF(i)_{H4\ MDA8}} = \frac{\mathrm{P}}{100} \times \left[\frac{\mathrm{H4\ MDA8(i)_{Obs}}}{\mathrm{H4\ MDA8(i)_{Model}}} - 1 \right] + 1 \qquad (2)$$

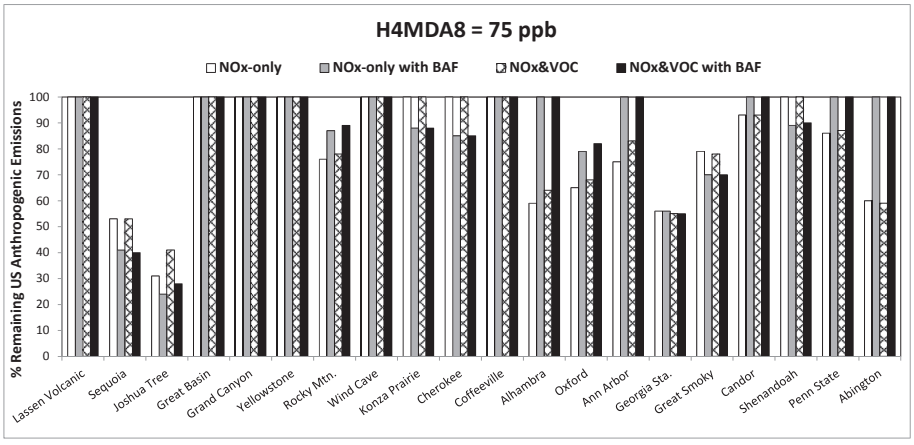
The BAF is applied at full strength at 100% anthropogenic emissions and scales linearly to one (no adjustment) at 0% anthropogenic emissions. BAF for W126 is derived in a similar manner (Table S2 lists observations, base case predictions, and respective BAF values by city and rural site for H4MDA8 and W126 metrics).

We acknowledge that our adjustment assumption is less appropriate for very remote rural sites, especially in the elevated terrain of the western US, where influences from anthropogenic emissions are small and the overall model bias is strongly dictated by uncertainty in characterizing the spatial and temporal evolution of background O_3 (Emery et al., 2012; Lefohn et al., 2014). We emphasize that those emission projections for such locations must be considered with caution.

While we present both unadjusted and BAF-adjusted results in our city and rural area analyses, our discussion focuses primarily on the adjusted results. Since BAF must be calculated from data at monitoring sites, there is not enough information to apply BAF in the national W126 maps without developing some approach to interpolate BAF values to the modeling grid. We felt this was a highly speculative and inappropriate extension of the adjustment technique, so the W126 maps were developed strictly from unadjusted HDDM projections.

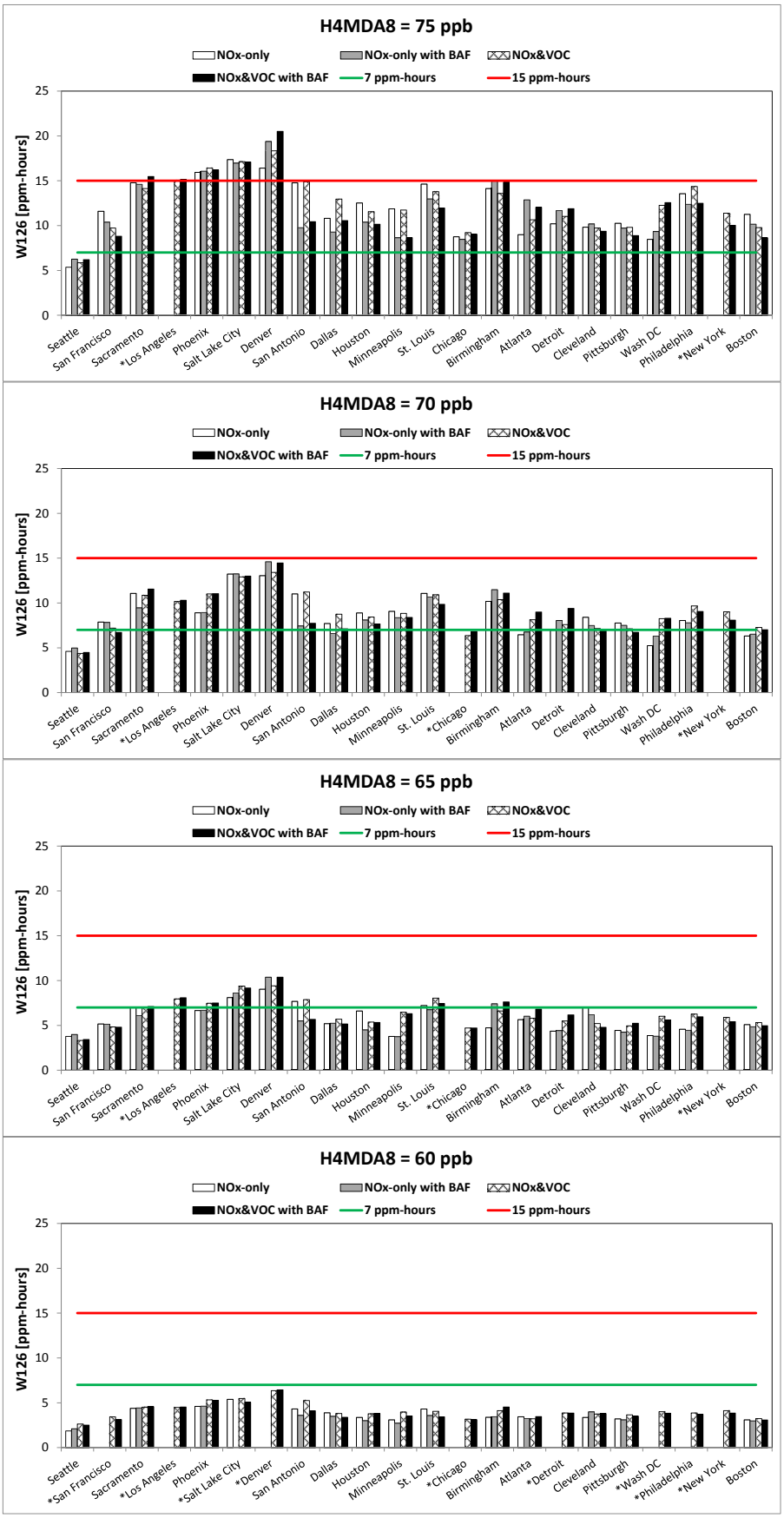


(a) Urban sites



(b) Rural sites

Fig. 1. Projections of 2006 remaining emissions that achieve H4MDA8 of 75 ppb (a) in 22 cities and (b) at 20 rural sites. Results from NOx-only and NOx/VOC combined reductions are shown, both unadjusted and adjusted for model bias (see text for details). Locations are ordered west to east. Cities labeled with asterisks (*) indicate that the standard was not reached after removing all US anthropogenic NOx emissions alone.


H4MDA8 = 75 ppb
NOx-only
NOx-only with BAF
NOx&VOC
NOx&VOC with BAF
7 ppm-hours
15 ppm-hours
W126 [ppm-hours]
0
5
10
15
20
25
Seattle
San Francisco
Sacramento
*Los Angeles
Phoenix
Salt Lake City
Denver
San Antonio
Dallas
Houston
Minneapolis
St. Louis
Chicago
Birmingham
Atlanta
Detroit
Cleveland
Pittsburgh
Wash DC
Philadelphia
*New York
Boston
H4MDA8 = 70 ppb
NOx-only
NOx-only with BAF
NOx&VOC
NOx&VOC with BAF
7 ppm-hours
15 ppm-hours
W126 [ppm-hours]
0
5
10
15
20
25
Seattle
San Francisco
Sacramento
*Los Angeles
Phoenix
Salt Lake City
Denver
San Antonio
Dallas
Houston
Minneapolis
St. Louis
*Chicago
Birmingham
Atlanta
Detroit
Cleveland
Pittsburgh
Wash DC
Philadelphia
*New York
Boston
H4MDA8 = 65 ppb
NOx-only
NOx-only with BAF
NOx&VOC
NOx&VOC with BAF
7 ppm-hours
15 ppm-hours
W126 [ppm-hours]
0
5
10
15
20
25
Seattle
San Francisco
Sacramento
*Los Angeles
Phoenix
Salt Lake City
Denver
San Antonio
Dallas
Houston
Minneapolis
St. Louis
*Chicago
Birmingham
Atlanta
Detroit
Cleveland
Pittsburgh
Wash DC
Philadelphia
*New York
Boston
H4MDA8 = 60 ppb
NOx-only
NOx-only with BAF
NOx&VOC
NOx&VOC with BAF
7 ppm-hours
15 ppm-hours
W126 [ppm-hours]
0
5
10
15
20
25
Seattle
*San Francisco
Sacramento
*Los Angeles
Phoenix
*Salt Lake City
*Denver
San Antonio
Dallas
Houston
Minneapolis
St. Louis
*Chicago
Birmingham
Atlanta
*Detroit
Cleveland
Pittsburgh
*Wash DC
*Philadelphia
*New York
Boston

3. Results

3.1. Meeting primary O_3 targets

HDDM modeling suggests most cities need deep cuts (>50%) in contributing regional emissions to attain the current 75 ppb H4MDA8 standard. Combined NOx and VOC reductions are more effective for cities than NOx-only reductions (Figs. 1a and S2). The central cores of large cities are often characterized by large NOx emissions and very low VOC:NOx ratios (VOC or radical-limited conditions), where NOx reductions can increase O_3 by relieving the destruction of O_3 via titration and the inhibition of radical generation for O_3 formation (often referred to as "NOx disbenefit"). Commensurate VOC reductions are effective in balancing or counteracting the NOx disbenefit.

Conversely, modeled VOC-only reductions have minimal influence on reducing H4MDA8 in cities (thus not shown) because city-wide peak H4MDA8 typically occurs in outer areas where VOC:NOx ratios are high and chemistry is NOx-sensitive. Using ambient measurement data, Blanchard et al. (2014) performed a generalized additive model (GAM) analysis that concluded that VOC-only reductions may be effective for reducing O_3 in the Atlanta metropolitan area. Our HDDM results suggest that VOC-only reductions can reduce 2006 O_3 in Atlanta but not to the current standard. Specifically, 100% VOC-only reductions decrease simulated H4MDA8 in Atlanta by 7%, or a reduction in the 2006 observed H4MDA8 from 99 ppb to 92 ppb. In fact, NOx and VOC controls are necessary and have occurred in reality (and will likely continue) to efficiently achieve O_3 reductions in highly polluted urban environments. Our combined NOx and VOC modeling results are consistent with this.

A numerical artifact was found to influence the modeled NOx-only cases for several cities requiring deep (>90%) emission reductions to reach H4MDA8 targets. Even at 10% remaining emissions NOx is abundant relative to VOC in the core of these cities and a strong NOx disbenefit continues to exist. In the extreme condition of 100% NOx-only reductions, large negative NOx sensitivities at 1 or 2 core sites increased peak H4MDA8 above the target, whereas mutual NOx and VOC reductions were able to achieve these targets. In these cases, the respective NOx-only results are not plotted (as noted in Figs. 1a and 2, S2 and S4a). EPA (2014a) reported similar numerical issues for Los Angeles and New York and they developed an ad hoc post-processing solution. An additional HDDM run at 0% emissions would be the best approach to address this issue.

Emission reductions estimated with BAF agree within 10 percentage points of the unadjusted projections in 19 cities, but relative differences extend to 31 points in Minneapolis and 24 points in San Antonio at the 75 ppb primary standard. Cities in which O_3 was over predicted (e.g., Atlanta and Minneapolis) need less emission reductions after BAF is applied. Conversely, application of BAF results in the need for more reductions in cities where O_3 was under predicted (e.g., Salt Lake City, San Antonio). Bias adjustment effects are larger when BAF is not scaled with emissions (i.e., unscaled BAF). Emission reductions estimated with unscaled BAF agree within 10 percentage points of the BAF projections in 17 cities, but relative differences extend to 25 points in Cleveland at the 75 ppb primary standard when reducing both NOx and VOC (Fig. S3).

O_3 formation in rural areas is NOx-limited; NOx-only reductions are as effective as combined NOx and VOC reductions (Figs. 1b and S2) in these areas. The rural sites show similar BAF effects as city sites but the impacts are greater. BAF results agree within 10 percentage points of unadjusted projections at 10 sites and within 20 percentage points at 18 sites. The largest differences arising from BAF-adjusted emission projections are 52% at Yellowstone (Wyoming) at the 60 ppb H4MDA8 target, and 41% at Abington (Connecticut) at the 75 ppb primary standard. The tendency for larger BAF-induced differences at rural areas may be due in part to projecting O_3 at only one monitoring site compared to multiple monitors per city, yielding stiffer urban responses to bias adjustments. With BAF, eleven rural sites do not need any reductions from 2006 emissions levels and five sites required less than 20% reductions to meet a primary standard of 75 ppb. Unscaled BAF results agree within 10 percentage points of BAF projections except at Sequoia for the 75 ppb primary standard when reducing both NOx and VOC (Fig. S3).

3.2. W126 after meeting primary O_3 targets

We evaluated whether projected emissions reductions needed to meet the primary O_3 targets in 2006 are sufficient to attain the secondary targets. In the NOx and VOC scenario with BAF, most cities we examined meet a W126 target of 15 ppm-h after meeting the H4MDA8 standard of 75 ppb (Fig. 2); five western cities fail, including Denver, Los Angeles, Phoenix, Sacramento, and Salt Lake City. All cities achieve 15 ppm-h when H4MDA8 meets 70 ppb, and achieve 7 ppm-h when H4MDA8 meets 60 ppb.

Only half of rural sites meet a W126 of 15 ppm-h after meeting the H4MDA8 of 75 ppb (Fig. 3) based on the NOx and VOC scenario with BAF. Notwithstanding, four of the sites not meeting 15 ppm-h do not need any reductions to meet 75 ppb and again all of these occur in the west (Grand Canyon [Arizona], Lassen [California], Great Basin [Nevada], and Wind Cave [South Dakota]). All rural sites achieve 15 ppm-h when H4MDA8 meets 70 ppb except Grand Canyon and Wind Cave, two rural sites that have relatively poor model performance. The model under predicts O_3 at these sites, so more emission reductions are needed (via BAF) than the unadjusted model results would suggests. Only Grand Canyon fails to reach 7 ppm-h after H4MDA8 meets 60 ppb and only by 0.3 ppm-h. In Section 4 we discuss implications related to the difficulty of western areas to attain a W126 of 15 ppm-h, and the possible reasons for the urban-rural disparity in meeting W126 targets.

3.3. Meeting secondary O_3 targets

HDDM projections with BAF indicate that most cities need more than 50–70% cuts in 2006 regional emission contributions of NOx and VOC to meet a W126 of 15 ppm-h (Figs. 4a and S4). Even deeper cuts are necessary in Los Angeles and Denver, where 93% and 76% reductions are required. Five cities (Boston, Chicago, Detroit, Minneapolis, and Seattle) already attain the 15 ppm-h without any further reductions. Seven rural sites require no reductions to meet 15 ppm-h with BAF. However, Sequoia (California), Joshua Tree (California), Rocky Mountain (Colorado), Georgia Station (Georgia), and Great Smokey Mountains (Tennessee) require a range of 20–70% emission reductions to meet 15 ppm-h (Fig. 4b). All of these sites are heavily influenced by local urban emissions from the San Joaquin Valley, Los Angeles, Denver, and Atlanta areas, respectively. At rural sites, NOx-only reduction is as effective as combined NOx and VOC reductions and the agreement between the two paths is within 3 percentage points. To attain a W126 target

Fig. 2. Projections of 2006 W126 (ppm-h) when H4MDA8 meets 60, 65, 70, and 75 ppb in 22 cities. Results from NOx-only and NOx/VOC combined reductions are shown, both unadjusted and adjusted for model bias (see text for details). Locations are ordered west to east. Cities labeled with asterisks (*) indicate that the H4MDA8 target was not reached after removing all US anthropogenic NOx emissions alone.

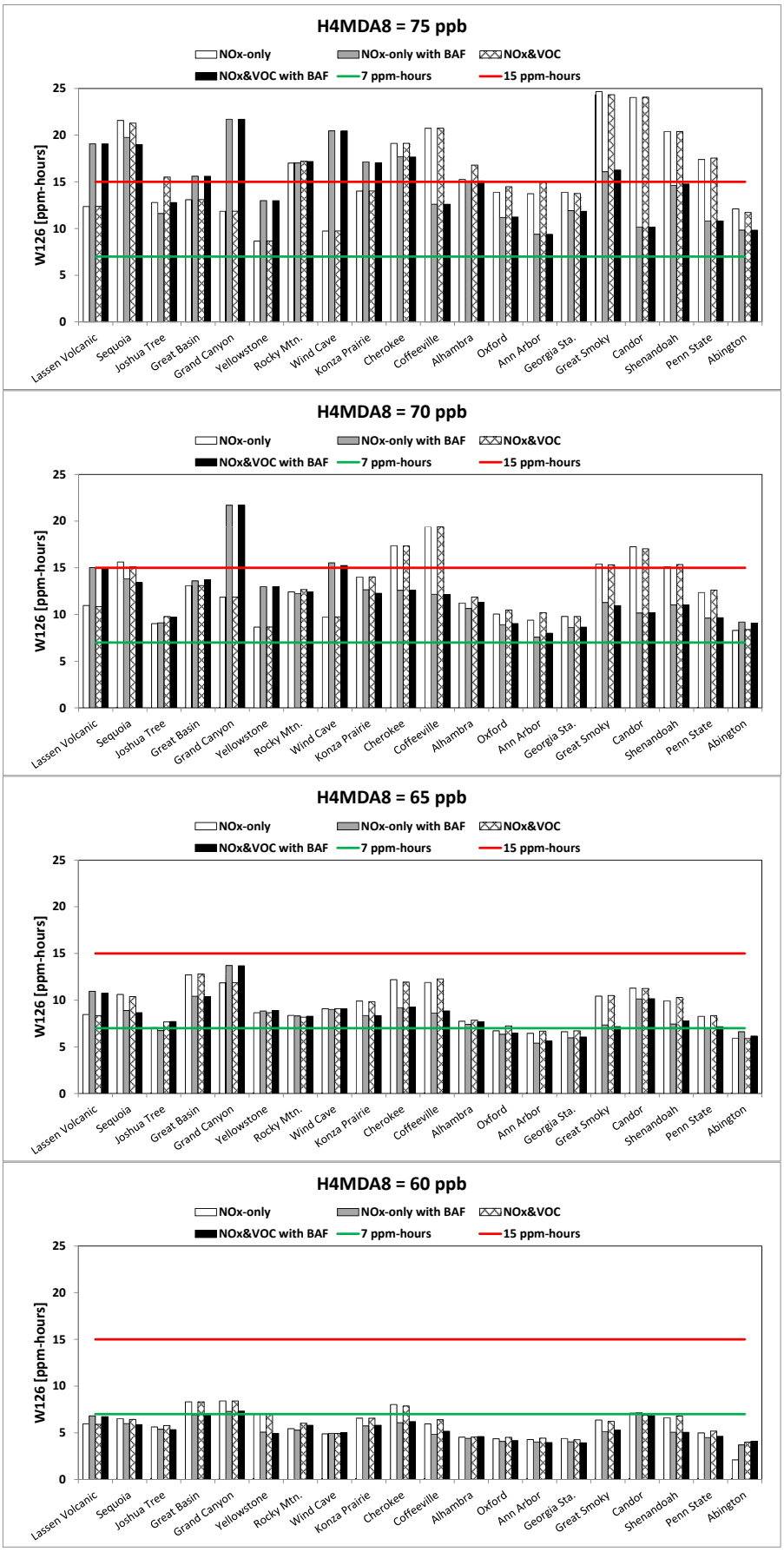
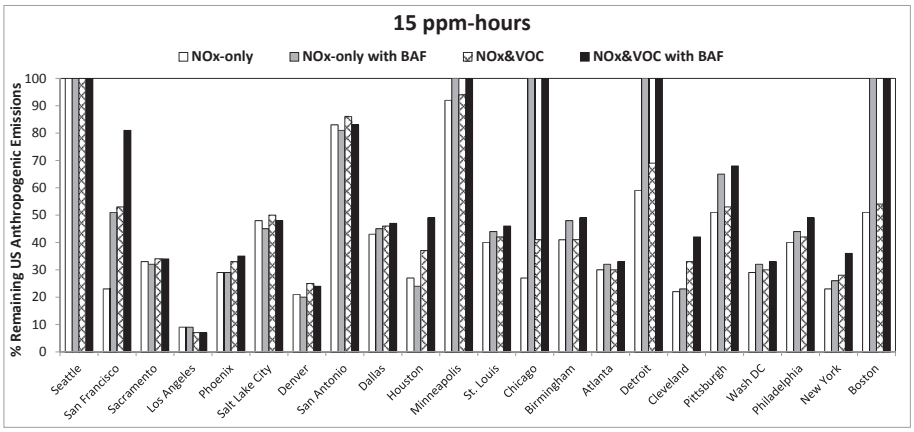
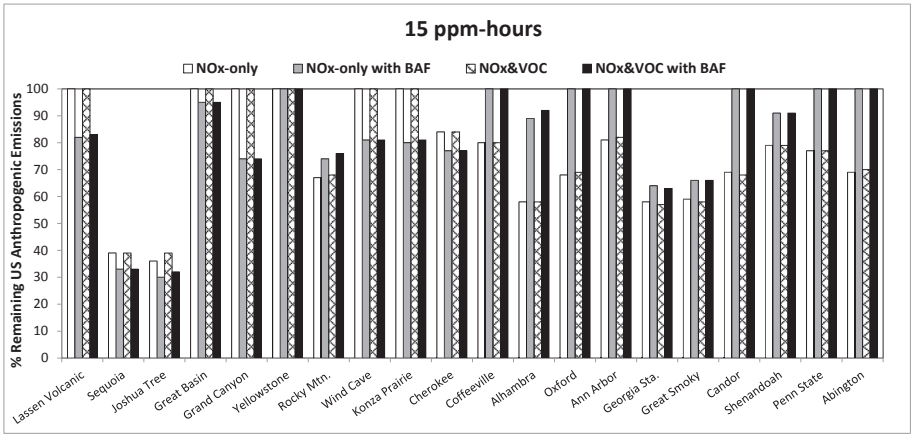


Fig. 3. As in Fig. 2, but at 20 rural sites.



(a) Urban sites



(b) Rural sites

Fig. 4. Projections of 2006 remaining emissions that achieve a W126 of 15 ppm-h (a) in 22 cities and (b) at 20 rural sites. Results from NOx-only and NOx/VOC combined reductions are shown, both unadjusted and adjusted for model bias (see text for details). Locations are ordered west to east.

of 7 ppm-h, most cities need more than 70% reductions, while most rural sites need less than 70% emissions reductions from 2006 levels (Fig. S4).

The CAMx model over estimated W126 in most cities we examined but with BAF the predicted emission reductions required to meet 15 ppm-h agree to within 10 percentage points (BAF vs. unadjusted) in 16 of 22 cities. The largest differences in emission reduction estimates with and without BAF are up to 59 points in Chicago for 15 ppm-h and 12 points in Minneapolis for 7 ppm-h. The model also over estimated W126 at rural sites in the eastern US, but under estimated in the western US. Emission reduction differences to meet 15 ppm-h with and without BAF are within 10 percentage points at only eight rural sites. The largest differences are up to 34% at Alhambra (Illinois) for 15 ppm-h and 26% at Wind Cave (South Dakota) for 7 ppm-h. The emissions reductions projected to meet 15 ppm-h are within 10 percentage points between the BAF and unscaled BAF scenarios at all rural sites and in 17 of 22 cities (Fig. S5).

Spatial maps of W126 across the entire modeling domain (Fig. 5) show that at 100% US anthropogenic NOx and VOC emissions, California and most of the eastern US exceed 15 ppm-h. It is important to note again that these maps are influenced by model biases, including over predictions of W126 in the eastern US and under predictions in the intermountain west. With 30% anthropogenic emission reductions (i.e., 70% remaining) most heavily populated areas in the US continue to exceed 11 and 15 ppm-h and most areas of the US continue to exceed 7 ppm-h. Most areas need more than 50% anthropogenic emission reductions to achieve 7 ppm-h, although California, the intermountain western US (despite under prediction bias tendencies), the northeast US O_3 transport corridor (Washington DC through Boston), and many other major cities require additional reductions relative to 2006 emissions levels. Note that remaining W126 locations greater than 7 ppm-h in the 0% anthropogenic emission case are caused by wildfires that occurred during the summer of 2006.

4. Discussion

We have compared the results presented in Section 3 to those of Simon et al. (2012) and EPA (2014a) where possible. Our results for Detroit are comparable to both studies. CAMx HDDM modeling suggests that Detroit needs 67% (no BAF) or 60% (with BAF) NOx-only reductions from 2006 levels to attain the 75 ppb H4MDA8 standard. Based on CMAQ HDDM modeling of July and August 2005, Simon et al. report that 62% NOx-only reductions are needed to reach a 75 ppb H4MDA8 (an approach similar to our “no BAF” scenario). That reduction is moderated to a 55% NOx reduction when Simon et al. apply their regression-based “central tendency” model to July–August 2005 observations. EPA (2014a) reports that a 59% NOx-only reduction is needed for Detroit to reach a 3-year

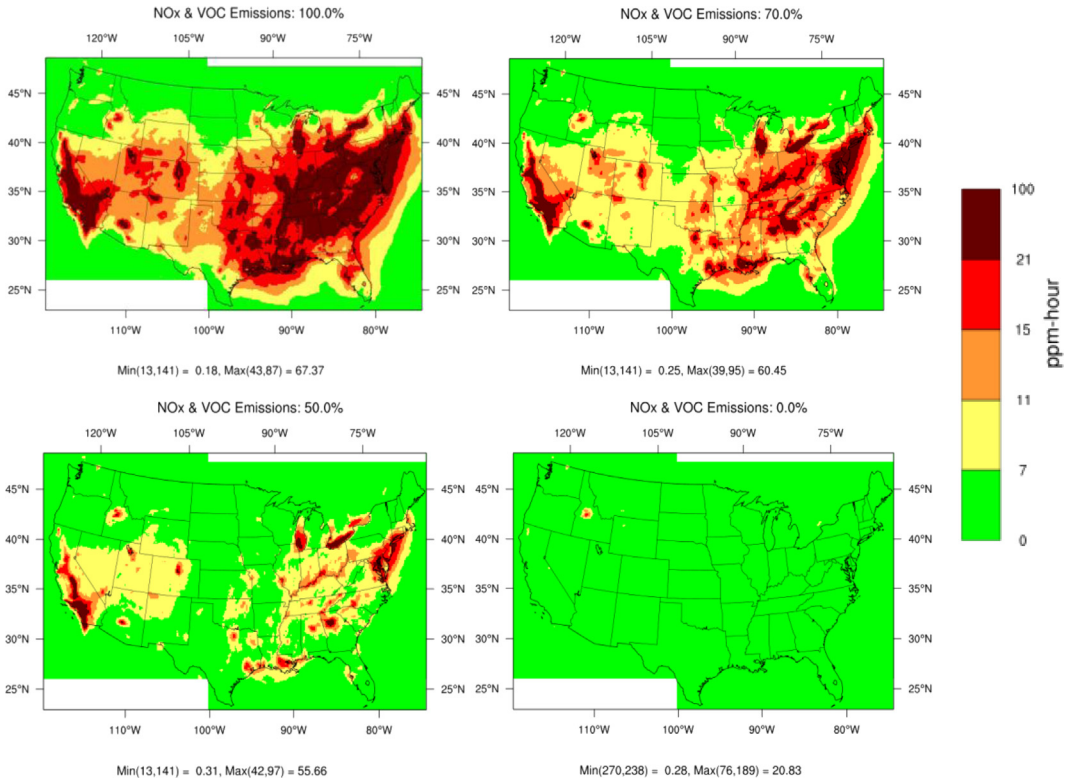


Fig. 5. HDDM-predicted W126 without bias adjustments at 0%, 50%, 70%, and 100% NOx and VOC US anthropogenic emission levels. The model tended to over predict W126 in the eastern US, but under predict in the western US. Note that remaining locations greater than 7 ppm-h in the 0% anthropogenic emission case are caused by wildfires that occurred during the summer of 2006.

average 75 ppb H4MDA8 when their 2007-based HDDM/regression modeling technique is applied to 2006–2008 observations. Comparisons for Charlotte were not possible because that city was not included in our analysis or in EPA's health risk assessment. We qualitatively inter-compared our NOx-only results to those tabulated by EPA (2014a) for 12 overlapping cities (disregarding Los Angeles and New York) but refrain from an extensive quantitative comparison given the draft status of that document at the time of this writing. The comparison reveals that the two modeling approaches result in wide variations among the 12 cities in the amount of NOx emission reductions necessary to meet the current 75 ppb standard, and that our estimates consistently require deeper reductions. These differences highlight the inter-annual and methodological sensitivities inherent among these emission reduction estimates. In particular, observed peak O_3 trended lower in 2007 and 2008 relative to 2006 throughout much of the US (EPA, 2014a), which is a primary reason for the smaller NOx reductions reported by EPA. The use of regression models formed from HDDM output also appears to mitigate the estimated NOx reductions, possibly by reducing hour-by-hour HDDM variability to “central tendency” slopes.

BAF-estimated reductions of 2006 NOx and VOC emissions agree to within 10 percentage points of the unadjusted results in 53 of 84 combined cases (63%) of meeting 75 ppb H4MDA8 and 15 ppm-h W126 in all cities and at all rural sites analyzed. Agreement improves when this comparison is extended to lower standard targets because further emission reductions result in smaller differences between unadjusted and adjusted projections. However, larger discrepancies in estimated emission reductions are seen at some sites, up to 31 points (urban Minneapolis H4MDA8), 59 points (urban Chicago W126), 52 points (rural Yellowstone H4MDA8) and 34 points (rural Alhambra W126). W126-related emission cuts do not necessarily respond to BAF the same way H4MDA8-related cuts do, which is a result of the different forms of these metrics. Specifically, the H4MDA8 BAF is determined by how well the model matches the single-day H4MDA8 observation,

Table 1
Number of cities (top) and rural sites (bottom) projected to exceed W126 targets in 2006 after satisfying H4MDA8 targets in the NOx and VOC emission reduction scenario with BAF.

W126 (ppm-h)	H4MDA8 (ppb)			
	75	70	65	60
Urban (22 total)				
16	3	0	0	0
15	5	0	0	0
14	6	1	0	0
13	6	1	0	0
12	9	2	0	0
11	11	5	0	0
10	15	6	1	0
9	17	9	2	0
8	21	13	3	0
7	21	18	7	0
Rural (20 total)				
16	8	1	0	0
15	10	2	0	0
14	11	3	0	0
13	11	5	1	0
12	14	10	1	0
11	16	12	1	0
10	18	14	4	0
9	20	18	6	0
8	20	19	11	0
7	20	20	16	1[a]

[a] W126 at Grand Canyon after meeting an H4MDA8 of 60 ppb is 7.3 ppm-h.

whereas the W126 BAF is based on how well the model matches the sum of all higher (sigmoidal-weighted) summer mid-day O_3 values. In San Antonio, for example, BAF has large effects on H4MDA8-related cuts (24%), but small effects (<3%) on W126-related cuts. The model performs better in replicating San Antonio's peak-site summer-average daytime O_3 (W126) than the upper tail of the peak-site annual frequency distribution (H4MDA8). Although the BAF takes into consideration model performance, it is certainly not a panacea. In cases where projections using BAF are widely different from unadjusted projections, it is likely that model performance issues degrade the robustness of our analysis in those regions and caution should be taken in interpreting either result.

Combined NOx and VOC reductions are most effective in reaching O_3 targets in cities. At rural sites, NOx-only reductions are sufficient because of limited NOx sources and abundant biogenic VOCs, yielding NOx-sensitive chemistry. VOC-only reductions are insufficient for most cases. Cities require more reductions to meet H4MDA8 and W126 targets than rural sites. However, rural sties have a lower likelihood of meeting the secondary targets once a primary target is met. Table 1 shows that 17 of 22 cities meet a W126 of 15 ppm-h after meeting an H4MDA8 of 75 ppb, but only 10 of 20 rural sites achieve both targets (NOx and VOC scenario with BAF). The majority of cities (15 of 20), compared to only a few rural sites (4 of 20), meet a W126 of 7 ppm-h after meeting an H4MDA8 of 65 ppb. After meeting an H4MDA8 of 60 ppb, only Grand Canyon fails to meet a W126 of 7 ppm-h with BAF by 0.3 ppm-h; note that model under predictions and the associated large BAF increase uncertainty at Grand Canyon.

The reasons for this urban-rural disparity in meeting W126 and H4MDA8 targets are related to their very different forms. The W126 sigmoidal weighting function effectively removes low O_3 values (<40 ppb) and makes the 3-month O_3 sum sensitive to daily O_3 reductions at the high end of the frequency distribution. In urban areas, the diurnal O_3 pattern is highly variable and typically exhibits some hours below 40 ppb due to NOx-inhibited O_3 chemistry, and some daytime peak hours well above 40 ppb. Meeting primary H4MDA8 targets in urban areas requires deep emission reductions that are effective at reducing O_3 in the highest portion of the frequency distribution, and by ignoring the low O_3 hours, W126 responds well at urban sites. In rural areas, the diurnal O_3 pattern is less variable with many more daytime hours at or above 40 ppb (just around the unaffected O_3 background) with relatively moderate daytime peaks. Meeting primary H4MDA8 targets in rural areas need smaller or zero emission reductions, so the overall frequency distribution is less impacted and W126 is less responsive.

All of the cities and several rural sites that do not meet a W126 of 15 ppm-h while meeting an H4MDA8 of 75 ppb is located in the western US. This implies a common thread, and we suggest that it is related to high year-round background O_3. High background has been noted for all five cities (Los Angeles, Sacramento, Phoenix, Salt Lake City, and Denver) and all western rural areas according to previous modeling investigations (Zhang et al., 2011; Emery et al., 2012; Lefohn et al., 2014, the latter two of which employed the same modeling database as our HDDM projections). In particular, cities in the inter-mountain west, including Denver and Salt Lake City, were found to be influenced by high O_3 concentrations in the mid to upper troposphere, which include contributions from international transport and natural sources such as wildfires, lightning NOx, and stratospheric intrusion. Deep vertical circulations induced by complex topography are effective in transporting these high concentrations to the elevated surface and maintaining higher background levels (reaching 50–60 ppb) than occur in the eastern US. As discussed above, higher background O_3 exceeding about 40 ppb maintains higher values of seasonally-averaged metrics such as W126.

5. Conclusions

This study used CAMx instrumented with the HDDM method of sensitivity analysis (Yarwood et al., 2013) to determine emissions reductions required from 2006 levels to meet alternative O_3 primary standards (60–75 ppb) and secondary standards (7–15 ppm-h) at urban and rural sites for NOx-only, combined NOx and VOC, and VOC-only scenarios. Model biases were taken into account by applying a bias adjustment factor separately for H4MDA8 and W126 metrics, analogous to the EPA's modeled relative response factor technique. These adjustments resulted in differences in emissions reductions required to meet H4MDA8 targets mostly to within 10 percentage points of unadjusted levels, and up to 31% and 52% for cities and rural sites, respectively. W126 does not necessarily respond to bias adjustments the same way H4MDA8 does, indicating its sensitivity to different formulations of H4MDA8 and W126.

Combined NOx and VOC reductions were most effective for cities, whereas NOx-only reductions were sufficient at rural sites. However, ozone responses to NOx-only cuts in several cities requiring deep reductions (>90%) were unreasonable and likely biased as a result of extremely large NOx-disbenefit sensitivity in the presence of 100% VOC emissions. A comparison between the efficacy of NOx-only and VOC and NOx controls in such cases is not appropriate. Most cities we examined require more than 50% US anthropogenic emission reductions from 2006 levels to meet the primary 75 ppb standard and secondary 15 ppm-h target. Most rural sites require less than 20% reductions to meet the primary 75 ppb standard and less than 40% reductions to meet the secondary 15 ppm-h target. Whether the primary standard is protective of the secondary standard depends on the combination of alternative standard levels. Based on our modeling of 2006, the current 75 ppb standard achieves a 15 ppm-h W126 target in most (17 of 22) cities, but only half of the rural sites. Meeting an H4MDA8 of 70 ppb protects a W126 of 15 ppm-h, and meeting an H4MDA8 of 60 ppb protects a W126 of 7 ppm-h, in all cities we examined. Rural sites in our analysis must achieve an H4MDA8 of 70 ppb to achieve a W126 of 15 ppm-h at all but two poor-performing sites (Grand Canyon, Arizona and Wind Cave, South Dakota), and an H4MDA8 of 60 ppb to achieve a W126 of 7 ppm-h at all but Grand Canyon. The inability for several western cities and rural areas to achieve various W126 targets while meeting H4MDA8 targets is related to the different forms of these metrics, and likely driven by higher background O_3 that is commonly reported in the western US, which tends to maintain high levels of W126.

If EPA promulgates separate primary and secondary standards, exceedance areas will need to develop and demonstrate control strategies to achieve both. This HDDM analysis provides an illustrative screening assessment by which to estimate emissions reductions necessary to satisfy both standards. There is a large array of potential emission control pathways to reach air quality goals that involve local, regional, and national programs, as well as sector-specific regulations. We have not intended to simulate actual reduction strategies in this research exercise because our approach involves reductions applied at the national level and across all source sectors. In addition, the analysis is performed for only one year (2006). Refinement of this technique would be necessary to better address local city/regional/source-specific emission sensitivity at finer scales and perhaps over multiple years.

Acknowledgments

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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.2014.09.062.

References

Bey, I., Jacob, D.J., Yantosca, R.M., Logan, J.A., Field, B.D., Fiore, A.M., Li, Q., Liu, H.Y., Mickley, L.J., Schultz, M., 2001. Global modeling of tropospheric chemistry with assimilated meteorology: model description and evaluation. J. Geophys. Res. 106, 23073–23096.

Blanchard, C.L., Hidy, G.M., Tanenbaum, S., 2014. NMOC, ozone, and organic aerosol in the southeastern United States, 1999–2007: 2. Ozone trends and sensitivity to NMOC emissions in Atlanta, Georgia. Atmos. Environ. 88, 192–200. http://dx.doi.org/10.1016/j.atmosenv.2014.02.006.

Byun, D., Schere, K.L., 2006. Review of the governing equations, computational algorithms, and other components of the models-3 Community Multiscale Air Quality (CMAQ) modeling system. Appl. Mech. Rev. 59 (1–6), 51–77.

Cohan, D.S., Koo, B., Yarwood, G., 2010. Influence of uncertain reaction rates on ozone sensitivity to emissions. Atmos. Environ. 44, 3101–3109.

Downey, N., Emery, C., Jung, J., Sakulyanontvittaya, T., Hebert, L., Blewitt, D., Yarwood, G., 2014. Emission Reductions and Urban Ozone Responses Under More Stringent US Standards (submitted for publication).

Dunker, A.M., Yarwood, G., Ortmann, J.P., Wilson, G.M., 2002. The decoupled direct method for sensitivity analysis in a three-dimensional air quality model—implementation, accuracy, and efficiency. Environ. Sci. Technol. 36, 2965–2976.

Emery, C., Jung, J., Downey, N., Johnson, J., Jimenez, J., Yarwood, G., Morris, R., 2012. Regional and global modeling estimates of policy relevant background ozone over the United States. Atmos. Environ. 47, 206–217. http://dx.doi.org/10.1016/j.atmosenv.2011.11.012.

ENVIRON, 2012. User's Guide for the Comprehensive Air Quality Model with Extensions (CAMx). Version 5.4. http://www.camx.com.

Environmental Protection Agency, 2014a. Health Risk and Exposure Assessment for Ozone. Report No. EPA-452/R-14-004a. EPA Office of Air Quality Planning and Standards, Research Triangle Park, NC.

Environmental Protection Agency, 2014b. http://www.epa.gov/ttn/airs/airsaqs.

Environmental Protection Agency, 2014c. www.epa.gov/castnet/.

Federal Register, 2008. 40 CRS Parts 50 and 58. National Ambient Air Quality Standards for Ozone; Final Rule, vol. 73. No. 60, 16436-16514 (EPA-HQ-OAR-2005-0172;FRL-8544-3), Available at: http://www.gpo.gov/fdsys/pkg/FR-2008-03-27/html/E8-5645.htm.

Environmental Protection Agency, August 2014d. Policy Assessment for the Review of the Ozone National Ambient Air Quality Standards. Report No. EPA-452/R-14-006. EPA Office of Air Quality Planning and Standards, Research Triangle Park, NC.

Federal Register, 2010. 40 CRS Parts 50 and 58. National Ambient Air Quality Standards for Ozone; Final Rule, vol. 75. No. 11, 16436-16514 (EPA-HQ-OAR-2005-0172;FRL-9102-1), Available at: http://www.gpo.gov/fdsys/pkg/FR-2010-01-19/pdf/2010-340.pdf.

Foley, K.M., Roselle, S.J., Appel, K.W., Bhave, P.V., Pleim, J.E., Otte, T.L., Mathur, R., Sarwar, G., Young, J.O., Gilliam, R.C., 2010. Incremental testing of the Community Multiscale Air Quality (CMAQ) modeling system version 4.7. Geosci. Model Dev. 3 (1), 205–226.

Hakami, A., Odman, M.T., Russell, A.G., 2003. High-order, direct sensitivity analysis of multidimensional air quality models. Environ. Sci. Technol. 37, 2442–2452.

Lapina, K., Henze, D.K., Milford, J.B., Huang, M., Lin, M., Fiore, A.M., Carmichael, G., Pfister, G.G., Bowman, K., 2014. Assessment of source contributions to seasonal vegetative exposure to ozone in the U.S. J. Geophys. Res. 119, 324–340. http://dx.doi.org/10.1002/2013JD020905.

Lefohn, A., Runeckles, V., 1987. Establishing a standard to protect vegetation-ozone exposure/dose considerations. Atmos. Environ. 21, 561–568.

Lefohn, A.S., Emery, C., Shadwick, D., Wernli, H., Jung, J., Oltmans, S.J., 2014. Estimates of background surface ozone concentrations in the United States based on model-derived source apportionment. Atmos. Environ. 84, 275–288. http://dx.doi.org/10.1016/j.atmosenv.2013.11.033.

Pouliot, G., Pierce, T., Denier van der Gon, H., Schaap, M., Moran, M., Nopmongcol, U., 2012. Comparing emission inventories and model-ready emission datasets between Europe and North America for the AQMEII project. Atmos. Environ. 53, 4–14. http://dx.doi.org/10.1016/j.atmosenv.2011.12.041.

Rao, S.T., Galmarini, S., Puckett, K., 2011. Air Quality Model Evaluation International Initiative (AQMEII): advancing state-of-science in regional photochemical modeling and its applications. Bull. Am. Meteorol. Soc. http://dx.doi.org/10.1175/2010BAMS3069.1.

Reidmiller, D.R., Fiore, A.M., Jaffe, D.A., Bergmann, D., Cuvelier, C., Dentener, F.J., Duncan, B.N., Folberth, G., Gauss, M., Gong, S., Hess, P., Jonson, J.E., Keating, T., Lupu, A., Marmer, E., Park, R., Schultz, M.G., Shindell, D.T., Szopa, S., Vivanco, M.G., Wild, O., Zuber, A., 2009. The influence of foreign vs. North American emissions on surface ozone in the US. Atmos. Chem. Phys. 9, 5027–5042. http://dx.doi.org/10.5194/acp-9-5027-2009.

Simon, H., Baker, K.R., Akhtar, F., Napelenok, S.L., Possiel, N., Wells, B., Timin, B., 2012. A direct sensitivity approach to predict hourly ozone resulting from compliance with the National Ambient Air Quality Standard. Environ. Sci. Technol. 47 (5), 2304–2313. http://dx.doi.org/10.1021/es30674e.

Vautard, R., Moran, M., Solazzo, E., Gilliam, R., Matthias, V., Bianconi, R., Chemel, C., Ferreira, J., Geyer, B., Hansen, A., Jericevic, A., Prank, M., Segers, A., Silver, J., Werhahn, J., Wolke, R., Rao, S.T., Galmarini, S., 2012. Evaluation of the meteorological forcing used for the Air Quality Model Evaluation International Initiative (AQMEII) air quality simulations. Atmos. Environ. 53, 1352–2310. http://dx.doi.org/10.1016/j.atmosenv.2011.10.065.

Warneck, P., 2000. Chemistry of the Natural Atmosphere, second ed. Academic Press.

Yarwood, G., Emery, C., Jung, J., Nopmongcol, U., Sakulyanontvittaya, T., 2013. A method to represent ozone response to large changes in precursor emissions using high-order sensitivity analysis in photochemical models. Geosci. Model Dev. 6, 1601–1608. http://dx.doi.org/10.5194/gmd-6-1601-2013.

Yarwood, G., Rao, S., Yocke, M., Whitten, G., 2005. Updates to the Carbon Bond Chemical Mechanism: CB05. report, Rpt. RT-0400675. US EPA, Research Triangle Park, NC.

Zhang, L., Jacob, D.J., Downey, N.V., Wood, D.A., Blewitt, D., Carouge, C.C., van Donkelaar, A., Jones, D.B.A., Murray, L.T., Wang, Y., 2011. Improved estimate of the policy-relevant background ozone in the United States using the GEOS-Chem global model with 1/2 × 2/3 horizontal resolution over North America. Atmos. Environ. 45, 6769–6776. http://dx.doi.org/10.1016/j.atmosenv.2011.07.054.