Modeled response of ozone to electricity generation emissions in the northeastern United States using three sensitivity techniques

Evan Couzo[a,b], James McCann[a,c], William Vizuete[a], Seth Blumsack[d], and J. Jason West[a]

[a]Environmental Sciences & Engineering, University of North Carolina, Chapel Hill, North Carolina, USA; [b]Department of Education, University of North Carolina at Asheville, Asheville, North Carolina, USA; [c]Ramboll Environ, Arlington, Virginia, USA; [d]Energy and Mineral Engineering, Penn State University, University Park, Pennsylvania, USA

ABSTRACT

Electrical generation units (EGUs) are important sources of nitrogen oxides (NO_x) that contribute to ozone air pollution. A dynamic management system can anticipate high ozone and dispatch EGU generation on a daily basis to attempt to avoid violations, temporarily scaling back or shutting down EGUs that most influence the high ozone while compensating for that generation elsewhere. Here we investigate the contributions of NO_x from individual EGUs to high daily ozone, with the goal of informing the design of a dynamic management system. In particular, we illustrate the use of three sensitivity techniques in air quality models—brute force, decoupled direct method (DDM), and higher-order DDM—to quantify the sensitivity of high ozone to NO_x emissions from 80 individual EGUs. We model two episodes with high ozone in the region around Pittsburgh, PA, on August 4 and 13, 2005, showing that the contribution of 80 EGUs to 8-hr daily maximum ozone ranges from 1 to >5 ppb at particular locations. At these locations and on the two high ozone days, shutting down power plants roughly 1.5 days before the 8-hr ozone violation causes greater ozone reductions than 1 full day before; however, the benefits of shutting down roughly 2 days before the high ozone are modest compared with 1.5 days. Using DDM, we find that six EGUs are responsible for >65% of the total EGU ozone contribution at locations of interest; in some locations, a single EGU is responsible for most of the contribution. Considering ozone sensitivities for all 80 EGUs, DDM performs well compared with a brute-force simulation with a small normalized mean bias (–0.20), while this bias is reduced when using the higher-order DDM (–0.10).

Implications: Dynamic management of electrical generation has the potential to meet daily ozone air quality standards at low cost. We show that dynamic management can be effective at reducing ozone, as EGU contributions are important and as the number of EGUs that contribute to high ozone in a given location is small (<6). For two high ozone days and seven geographic regions, EGUs would best be shut down or their production scaled back roughly 1.5 days before the forecasted exceedance. Including online sensitivity techniques in an air quality forecasting model can provide timely and useful information on which EGUs would be most beneficial to shut down or scale back temporarily.

PAPER HISTORY

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Introduction

Electrical power generation in the United States has been growing every year since 1950 and is projected to grow by another 24% between 2013 and 2040 (Energy Information Administration [EIA], 2013). Nearly 70% of all net U.S. electricity generation during 2011 was from fossil-fuel sources, with 42% of that electricity produced from coal combustion (EIA, 2012). In many areas of the United States, coal-fired power plants will continue to comprise the majority of generating sources (EIA, 2013), even as environmental regulations become more stringent and coal faces increasing competition from other fuels. During coal combustion, many atmospheric pollutants are formed including oxides of nitrogen (NO_x = NO + NO_2). Electrical generation units (EGUs) accounted for 13% of all US anthropogenic NO_x emissions in 2011, 86% of which resulted from electricity generation from coal (EPA, 2014). Emissions of NO_x from EGUs are a major contributor to the formation of tropospheric ozone (O_3) in many regions (Gego et al., 2008), which is a concern for air quality in the United States and elsewhere for its effects on health and the environment.

CONTACT J. Jason West jasonwest@unc.edu Department of Environmental Sciences & Engineering, University of North Carolina, CB#7431, Chapel Hill, NC 27599, USA.

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The United States now routinely forecasts daily air quality using state-of-the-art air quality models, projecting episodes of high ozone and other pollutants 48 hr in advance (Eder et al., 2010; National Oceanic and Atmospheric Administration [NOAA], 2013). As air quality forecasting continues to mature, the information it provides can increasingly be used to support daily actions to reduce emissions, and this dynamic approach to air quality management can help reduce exceedances of air quality standards in a way that would reduce the need for more permanent emission reductions from sources (National Research Council [NRC], 2004). In particular, the electric power sector can potentially contribute to a daily dynamic management system to avoid daily exceedances of the 8-hr ozone standard. Electric utilities and transmission system operators already make electricity generation scheduling decisions on a day-ahead basis, redispatching power plants as demand changes and as generators, transmission lines, and other equipment in the electric grid are taken off line (e.g., for maintenance). EGUs that most strongly influence a projected ozone exceedance could potentially reduce their output or be shut down, with that generation compensated for by increases in generation elsewhere where there is no high ozone forecast. Flexible pollution control units (on plants so equipped) could also be activated in response to anticipated ozone exceedances, with a corresponding increase in production cost. While ozone mitigation strategies are employed periodically by owners of EGUs, such as by turning on control units, air pollution concerns do not influence daily electrical dispatching decisions on a widespread or routine basis (National Association of Clean Air Agencies [NACAA], 2015).

Although the potential for a dynamic air quality management system that focuses on daily ozone exceedances by influencing daily electrical generation commitment and dispatch decisions may be limited by our current ability to accurately predict high ozone episodes, such dynamic management can be informed through the use of sensitivity techniques that quantify the sensitivities of high ozone to emissions from individual power plants. Actions to shift generation can then target the power plants that most influence the high ozone concentrations in particular locations. Current air quality models contain online sensitivity techniques that allow estimation of the sensitivity of output parameters (concentrations) to input parameters (emissions), in addition to modeling pollutant concentrations. One such method, the direct decoupled method (DDM), uses the underlying atmospheric diffusion equations within an air quality model to produce sensitivity coefficients, which can then be used to estimate the sensitivity to changes in emissions, background concentrations, and chemical reaction rates (Dunker, 1984). DDM significantly reduces run time versus other methods that obtain similar results (Dunker, 1984; Yang et al., 1997).

DDM has been used previously to estimate the relative impacts of domain-wide reductions in anthropogenic NO_x and VOCs on ozone concentrations (Simon et al., 2013). Dunker et al. (2002) implemented DDM in the Comprehensive Air Quality Model with Extensions (CAMx) to show that first-order sensitivity coefficients accurately describe model response to domain-wide area-source NO_x perturbations up to 40% when compared to brute-force calculations, and this finding was supported by Zhang et al. (2005) and Cohan et al. (2005). DDM was enhanced to include higher order terms to account for nonlinearities in ozone production, referred to as the higher order direct decoupled method (HDDM), which was shown to also agree well with brute force for up to a 50% perturbation in domain-wide anthropogenic emissions (Hakami et al., 2003; Hakami et al., 2004; Simon et al., 2013). DDM and the brute-force method compare well for smaller NO_x perturbations for hypothetical single source impacts on downwind ozone (Kelly et al., 2015).

Several approaches have been used to isolate the impacts of single sources on downwind ozone in photochemical grid models, including DDM (Baker and Kelly, 2014; Bergin et al., 2008; Cohan et al., 2005; Cohan et al., 2006; Kelly et al., 2015), brute-force sensitivity (Baker and Kelly, 2014; Bergin et al., 2008; Cohan et al., 2005; Kelly et al., 2015; Zhou et al., 2012), and source apportionment (Baker and Kelly, 2014). Modeled sensitivities of ozone to emissions from specific facilities are generally similar using DDM and brute-force techniques, at 4 to 12 km resolution (Cohan et al., 2006). While DDM has been implemented to address the effect of the power generation sector as a whole and the effect of a single point source on ozone, DDM has not been used to track the downwind impacts of a large number of individual point sources simultaneously. In such a case, every grid cell may show ozone sensitivity to several point sources that may be local or far away. Due to nonlinear ozone formation, total ozone concentrations may not equal the sum of zero-out contributions from all sources (Cohan et al., 2005).

In this paper, we aim to explore several choices in implementing a dynamic management system. We configure DDM to estimate the sensitivity of peak ozone concentrations to emissions of NO_x from 80

EGUs simultaneously. In particular, we investigate these topics:

1. (1) The contributions of power plants to high ozone episodes, to bound the maximum effectiveness of dynamic management.
2. (2) The time scales over which power plant emissions contribute to an ozone exceedance (i.e., we compare the response of ozone to emissions from the day before versus 2 days before the exceedance), which would be useful information for electric grid operators who face operational constraints in the ramp-up and ramp-down of EGUs.
3. (3) The contributions of individual power plants to high ozone, using DDM and HDDM, to estimate the extent to which high ozone is responsive to emissions from a few EGUs versus many EGUs and over what spatial scales.
4. (4) The accuracy of DDM and HDDM sensitivities compared to a brute force approach.

We explore these questions by analyzing a region of the northeastern United States focused on Pittsburgh, PA, and nearby cities, for two days in which Pittsburgh is modeled to have exceeded the 8-hr ozone standard, August 4 (81.6 ppb) and August 13 (81.0 ppb), 2005. Our main purpose is to inform choices in the development of a dynamic management system, in which online sensitivity techniques are used as part of air quality forecast modeling. In addition, this work may be useful in demonstrating the use of DDM for tracking the sensitivity of ozone to multiple point sources simultaneously, as well as in understanding the effects of smokestack emissions on ozone more broadly. The full design and administration of a dynamic system will be addressed in a separate paper. Because of the patchwork nature of how the electric grid is operated in the United States, with system administrative boundaries that do not always correspond to jurisdictions (such as state lines), our analysis may be useful for identifying opportunities for cooperative action by multiple electric grid operators to improve local air quality.

Methods

Air quality model

CAMx version 5.30 (Environ, 2011) with the Carbon Bond 2005 chemical mechanism (CB05; Yarwood et al., 2005) was used to evaluate the effect of emissions perturbations on regional ozone on August 4 and 13, 2005. These dates had simulated high ozone episodes across Pittsburgh, PA, and surrounding areas. The eastern United States modeling domain used in CAMx simulations has a horizontal grid resolution of 12 km × 12 km, extending from Texas to Maine (Figure 1), and has 14 vertical layers from the surface to 100 millibar, though only ground-layer concentrations are presented here. All analysis of EGU emissions and ozone concentrations was performed in a subdomain of 151 × 151 grid cells and centered on Pittsburgh, PA. In this paper, all times are reported in Eastern Standard Time (EST). The model was run in Coordinated Universal Time (UTC), which is +5 hr from EST. As a result, the two analysis days, August 4 and 13, end 5 hr prematurely (at 7:00 p.m. EST), but we verified in the full summer simulation that this time period captures the full 8-hr maximum ozone window for each analysis region described in the Results section.

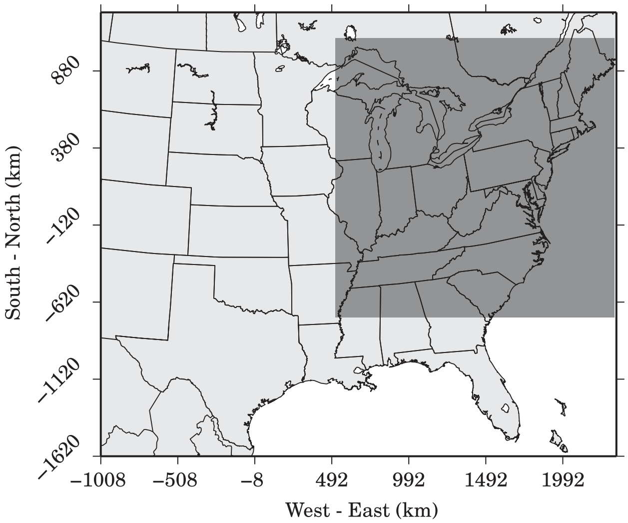

Figure 1. The 12-km modeling domain and the smaller analysis region (shaded). Only concentrations and sensitivities within the analysis domain are considered.

Within CAMx, DDM calculates seminormalized first-order sensitivity coefficients ($S^{(1)} = \delta C/\delta E$) of modeled species concentrations, C, to perturbations in a set of input parameters such as normalized emissions, E (Dunker, 1984). Here, we consider the effect of point source NO_x emission perturbations on predicted ozone. An estimated system response can be calculated with DDM sensitivity coefficients as a Taylor-series expansion:

$$C_{E=\Delta E} = C_{E=E_0} + \lambda S^{(1)} \tag{1}$$

where $C_{E=E_0}$ is the base case modeled concentration, $S^{(1)}$ is the first-order sensitivity coefficient, and λ is the fractional emission perturbation ($\Delta E/E_0$). Zero-out contributions (ZOC) estimated by DDM (Cohan et al., 2005) can be expressed as

$$C_{E=0} = C_{E=E_0} + \lambda S^{(1)} \tag{2}$$

$$ZOC_{DDM} = C_{E=E_0} - C_{E=0} = S^{(1)} \tag{3}$$

where $\lambda = -1$ for a 100% EGU NO_x emissions reduction. Total sensitivity to all tracked facilities can be calculated as a sum of these ZOC_{DDM} for each perturbed facility. Additionally, Cohan et al. (2006) found that DDM within a 12-km grid resolution could largely reproduce ozone response features.

HDDM (Koo et al., 2008) generates a second-order sensitivity coefficient, which partially accounts for nonlinear model processes relating to ozone production (Cohan et al., 2005). Within CAMx, the second-order sensitivity coefficient ($S^{(2)} = \delta^2 C/\delta E^2$), representing the second partial derivative of ozone with respect to NO_x emissions, is calculated alongside the first-order sensitivity. Considering this second-order term in the Taylor series, a second-order ZOC is

$$C_{E=0} = C_{E=E_0} + \lambda S^{(1)} + 0.5\lambda^2 S^{(2)} \tag{4}$$

$$ZOC_{HDDM} = C_{E=E_0} - C_{E=0} = S^{(1)} - 0.5S^{(2)} \tag{5}$$

where $\lambda = -1$ for a 100% EGU NO_x emissions reduction.

Model inputs and episodes

The EPA developed model inputs for a base-case 2005 simulation for its analysis of the final Transport Rule (TR) (EPA, 2009). This includes refined meteorological and emissions fields for 2005 across the eastern United States. The Pennsylvania State University/National Center for Atmospheric Research Mesoscale Model (MM5) produced gridded meteorological data with the same projection and resolution as the CAMx configuration. Boundary conditions were derived from a larger CAMx simulation encompassing the lower 48 states with 36 × 36 km horizontal resolution. The meteorological inputs are further detailed by the EPA (2011b), as are the emission inventories used (EPA, 2011c). The EPA (2011b) thoroughly evaluated model performance, which exceeded all regulatory metrics for adequate use as a regulatory application. It should be noted, however, that the EPA (2007) recommends that air quality models be used in a relative sense, and performance metrics may not adequately evaluate a model's suitability for use in an absolute sense, such as correctly identifying concentrations above the threshold.

We conducted a full summer 2005 simulation using inputs provided by the EPA. From this simulation, we selected two days that had high ozone in Pittsburgh, PA, to be the focus of this study—August 4, 2005, and August 13, 2005. August 4 had high ozone concentrations across the northeastern United States, as 21% of all grid cells in the analysis domain exceeded the 75 ppb National Ambient Air Quality Standard for 8-hr ozone (Figure 2). High ozone concentrations on August 13 were not as widespread as on August 4, with only 7.2% of grid cells with a daily maximum 8-hr ozone average above 75 ppb. On August 13, two clusters of grid cells in western Pennsylvania exceeded 75 ppb, and much of the analysis on this day focused on these two regions, New Castle and Pittsburgh. Measurements confirm that the Pittsburgh region had high ozone on these two analysis days, with measured daily maximum 8-hr ozone concentrations of 81.6 ppb on August 4 and 81.0 on August 13 (Table 1).

Power grid operators aim to satisfy electricity demand at the lowest possible cost, a process known as "economic dispatch" or "merit order dispatch." In many portions of the United States, including the subdomain considered here, the process of matching supply and demand involves multiple decision points, because electricity cannot be stored sufficiently at reasonable cost. The power grid operator schedules (or "commits") EGUs to be available to produce electricity

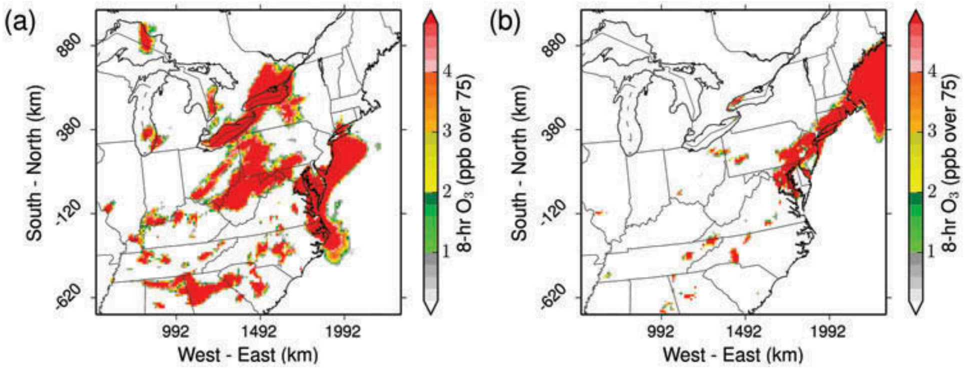

Figure 2. Daily maximum 8-hr ozone concentrations exceeding 75 ppb on August 4 (a) and August 13 (b). Grid cells without color did not exceed 75 ppb. The color of the shaded grid cells shows by how much the 75 ppb threshold was exceeded.

Table 1. Measured and simulated maximum daily 8-hr ozone concentrations (ppb), showing the average of all monitored values within the county of interest (reported by the EPA AQS database, https://aqs.epa.gov/api), and the average of simulated concentrations over an area of 3 × 3 grid cells centered on each urban region.

	August 4, 2005			August 13, 2005		
	Measured	Simulated	NME (%)	Measured	Simulated	NME (%)
Pittsburgh, PA	81.6	80.8	1.0	81.0	70.9	12.5
Columbus, OH	67.8	78.9	16.4	65.3	68.0	4.1
New Castle, PA	67.5	78.2	15.9	63.9	75.5	18.2
Altoona, PA	80.3	72.8	9.3	75.3	67.8	10.0
Friendsville, MD	82.9	91.5	10.4	73.8	60.1	18.6

Note: For Pittsburgh, PA, (Allegheny County) and Columbus, OH, (Franklin County), four monitoring stations provided data and were averaged; Altoona, PA (Blair County), New Castle, PA (Lawrence County), and Friendsville, MD (Garrett County), show measurements for one monitoring station each; Butler, PA, (Butler County), and Clarksburg, WV (Harrison), were not included here because no measurements were reported in these counties on August 4 and August 13, 2005.

more than 24 hr ahead of real-time production. Between the scheduling decision and the real-time dispatch decision, adjustments to EGU commitments may be made (adjusting with demand and unplanned malfunctions), and final dispatch instructions are issued to individual EGUs between 5 and 30 min ahead of real-time demand. Both the scheduling decisions and the final real-time dispatch decisions rely on optimization routines that minimize electricity production costs while keeping supply and demand in balance.

We use a comprehensive database of power substation locations and fuel types developed by Energy Visuals, Inc., which is derived from the Multiregional Modeling Working Group (MMWG) that is part of the North American Electric Reliability Corporation (NERC). In total, 338 substations listed coal as their fuel type and were selected for analysis. Substation locations do not necessarily match those of individual EGUs, but these locations are generally within close proximity. We matched substation locations with corresponding point sources related to EGUs in the CAMx input file by identifying all model point sources within 750 m of the 338 substations. This resulted in the identification of 302 point sources within the modeled domain that we refer to as EGU point sources.

To illustrate dynamic management for this paper, we first chose a set of EGUs for which we model sensitivities, requiring us to balance the number of EGUs with computational costs. We set a NO_x emissions rate threshold of 1000 mol/hr on the analysis day (August 4 or 13) to separate likely EGU point sources from other non-EGU NO_x point sources. (There could be multiple point sources with the same coordinates, so we required that at least one individual point source at a given location meet the 1000-mol/hr threshold to be considered.) After the threshold was applied, we selected the 80 EGUs closest to Pittsburgh, PA, which we determined to be adequate to capture most of the sensitivities as other EGUs were too distant to have significant influences. Once the 80 locations were determined, all individual point sources at each location were aggregated and considered as a single EGU facility. These 80 facilities are all within 700 km of Pittsburgh, PA (Figure 3),and have modeled average hourly NO_x emissions rates on August 4, 2005, ranging from 34.9 kg/hr to 2412.1 kg/hr. Since EGUs are not generally large sources of CO or VOCs, and ozone responses to EGU emissions are dominated by NO_x changes (Nunnermacker et al., 2000), we choose to focus only on NO_x emissions from these 80 facilities.

We quantified the impact of these 80 EGUs on predicted high ozone using DDM and HDDM. We also conducted a brute-force (BF) simulation where emissions from all 80 facilities were removed, or zeroed out ($ZOC_{BF} = C_{E=E_0} - C_{E=0}$), which represents the total impact of the NO_x emission perturbation including all nonlinearities. Although useful in assessing maximum sensitivity, it is not practical to use multiple BF simulations to forecast sensitivities for

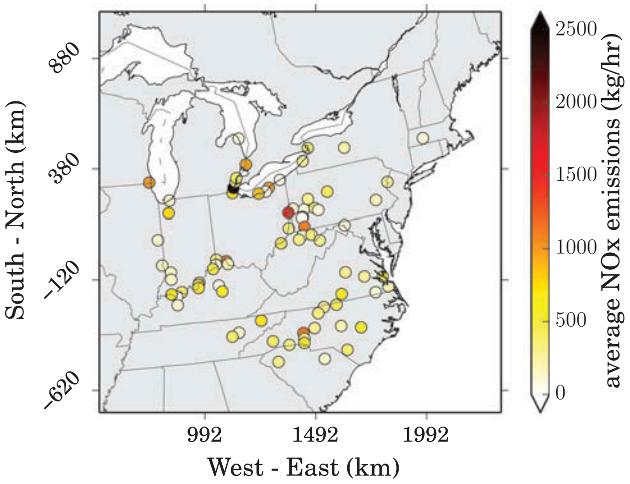

Figure 3. Location and average hourly NO_x emissions for the 80 tracked power plant facilities on August 4. These points show the 80 facilities closest to Pittsburgh, PA, with average hourly emissions rate of at least 1000 mol/hr.

individual EGUs, because of the computing resources required. $\mathrm{ZOC_{DDM}}$ and $\mathrm{ZOC_{HDDM}}$ were compared to $\mathrm{ZOC_{BF}}$ for removing all 80 EGUs, to evaluate their effectiveness in predicting ozone sensitivity to EGU NO_x emissions.

Results

The results are organized according to the four topics described in the Introduction. We use BF simulations to bound the maximum effectiveness of dynamic management, including time scales over which power plant emissions might contribute to an ozone exceedance. We then present the DDM results to quantify the contributions of individual power plants and evaluate the accuracy of DDM.

Influence of EGUs on ozone

We first estimate the total influence of EGU NO_x on ozone exceedances through a BF simulation. Using model restarts from the full unperturbed 2005 summer simulation, we zeroed all NO_x emissions from the 80 modeled EGU facilities from 12:00 p.m. EST on August 2 through 7:00 p.m. EST on August 4, which is when the experimental portion of the simulation ended. This scenario is referred to as the "36-hr case" in Figure 4 because NO_x emissions were reduced to zero 36 hours prior to 12:00 a.m. EST August 4. The 36-hr case led to a total emissions reduction of 1,841.5 tonnes of NO_x over 55 hours.

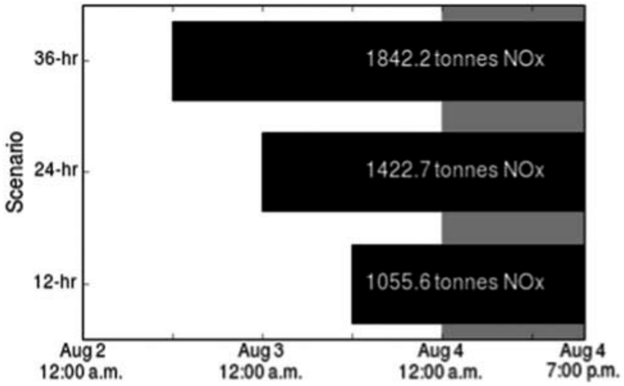

Figure 4. The time during which NO_x emissions were zeroed out for each scenario. Each bar spans the hours during which power plant emissions were reduced. The scenarios are identified by the number of hours before 12:00 a.m. August 4. For example, the 24-hr scenario is so named because emissions were reduced at 12:00 a.m. August 3, or 24 hr before 12:00 a.m. August 4. Total NO_x reductions for each scenario are given in each bar. Note that the simulation ended at 7:00 p.m. August 4.

Figure 5c shows the maximum changes to 1-hr ozone that resulted from this NO_x reduction. The maximum $\mathrm{ZOC_{BF}}$, 19.4 ppb, occurred over a rural area of southern Virginia. The effects of the 36-hr case reduction in EGU NO_x extend into several widespread plumes that show maximum 1-hr ozone impacts more than 2 ppb, with the

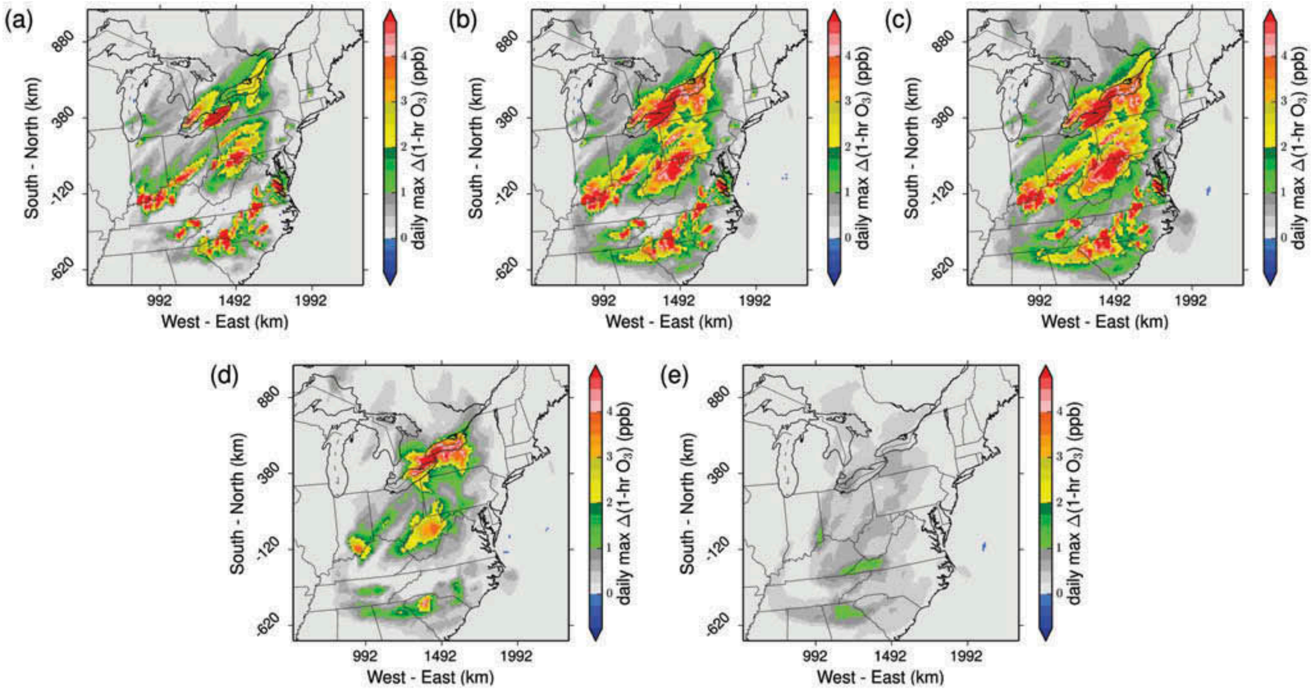

Figure 5. Maximum 1-hr ozone $\mathrm{ZOC_{BF}}$ for each scenario on August 4: (a) 12 hr, (b) 24 hr, and (c) 36 hr. Maximum 1-hr ozone $\mathrm{ZOC_{BF}}$ differences between the 12- and 24-hr cases (d) and the 24- and 36-hr cases (e). For subplots (d) and (e), the shorter scenario is subtracted from the longer scenario (e.g., 24-hr minus 12-hr). Positive values indicate the amount by which daily maximum 1-hr ozone is reduced when the NO_x emissions are removed, relative to the base case. Values are not necessarily time paired; that is, they could have occurred during different hours on August 4.

largest changes in the plume centers. Overall, 14.8% of all grid cells had a ZOC_{BF} of at least 2 ppb, and 2.4% of all cells had ZOC_{BF} greater than 5 ppb or less than -1 ppb. The fact that Figure 5c shows plumes of individual EGUs or clusters of EGUs suggests that ozone in a particular location may be strongly influenced by a small number of EGUs.

Seven analysis regions were chosen near Pittsburgh, PA, based on their simulated maximum 8-hr ozone concentration on August 4, as well as on their proximity to plumes of ozone sensitivity (Figure 6). Each analysis region consists of a 3 × 3 square of 12 km grid cells (36 km × 36 km), reported as an average to avoid large local sensitivities (positive and negative) in a single grid cell, following the EPA's model guidance (EPA, 2007).

Base case daily maximum 8-hr ozone concentrations (Table 2) ranged from 72.8 ppb in Altoona, PA, to 91.5 ppb in Friendsville, MD. With the exception of Altoona, PA, all locations exceeded the 75 ppb standard. Measured and simulated concentrations are in good agreement at all sites (NME < 20%), and particularly Pittsburgh, where peak 8-hr ozone concentrations differ by less than one ppb (Table 1). However, the model incorrectly predicted whether 8-hr ozone exceeded 75 ppb at several sites, highlighting an important limitation of current forecast models for dynamic management. The sensitivity of maximum 8-hr ozone to EGU NO_x was determined by averaging the 1-hr ZOC_{BF} values during the 8-hr window of maximum ozone for each region. The 8-hr sensitivities ranged from 1.13 ppb in Pittsburgh, PA, to 5.40 ppb in Clarksburg, WV. Table 2 also shows daily maximum 1-hr ozone concentrations and the ZOC_{BF} during the hour of maximum 1-hr ozone, though not necessarily the maximum sensitivity. While zeroing out NO_x from 80 EGUs was not sufficient to bring any analysis region below the standard, these sensitivities are large enough to suggest that generally there is potential for dynamic management of EGU emissions to be used beneficially to avoid high ozone episodes.

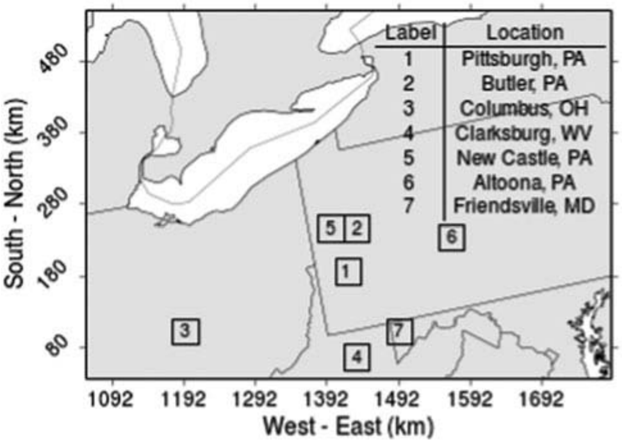

Figure 6. The locations of the seven urban regions. Each region consists of nine 12-km grid cells that are spatially averaged to a single 36-km grid cell.

Table 2. Maximum 8-hr ozone concentrations for each urban region and the ZOC_{BF} during each region's maximum 8-hr ozone window on August 4, and peak 1-hr ozone concentrations and the ZOC_{BF} during the hour of maximum 1-hr ozone.

Region	max 8-hr O_3	ZOC_{BF} during max 8-hr O_3	max 1-hr O_3	ZOC_{BF} during max 1-hr O_3
Pittsburgh, PA	80.8	1.13	85.9	1.09
Butler, PA	81.5	3.01	85.5	2.04
Columbus, OH	78.9	1.43	88.7	2.36
Clarksburg, WV	87.8	5.40	94.7	7.30
New Castle, PA	78.2	1.65	82.7	1.96
Altoona, PA	72.8	2.23	78.9	2.56
Friendsville, MD	91.5	2.08	94.5	2.72

Note: ZOC_{BF} are from the 36-hr case. All values are in ppb.

Time of emission reduction

To inform decisions on how long to shut down EGUs in a dynamic management system, we also simulated the 24-hr and 12-hr cases (Figure 4), zeroing-out emissions from all 80 facilities in BF simulations (Figure 5). Again, we used restart files from the full 2005 summer simulation so the unperturbed spin-up period is identical to the base case. The shortest case of 12 hr prior to 12:00 a.m. EST on August 4 shows fairly compact plumes of high ozone sensitivity to EGU NO_x extending from clear points of origin, which align with clusters of facilities shown in Figure 3. As older emissions are incorporated into the sensitivity, these plumes become less defined, and the effect spreads over a larger region and with a greater effect on ozone across the domain.

Figures 5d and 5e show the added benefit (i.e., ozone reductions) obtained by reducing EGU NO_x emissions earlier. Moving from the 12-hr to the 24-hr case increased (time-paired) ZOC_{BF} by up to 8.09 ppb. Extending emissions reductions by an additional 12 hours eliminates the morning (12:00 a.m.–12:00 p.m. EST) NO_x emissions of August 3. These emissions would have reacted throughout the day to form additional ozone, which may contribute to ozone concentrations on August 4. The differences between the 36-hr and 24-hr cases (Figure 5e) are much smaller than in Figure 5d, as the 36-hr case sensitivities were only up to 1.34 ppb greater (time-paired) than the 24-hr case. This smaller value suggests that the older NO_x emissions from 1 day earlier may be removed before having a large influence on ozone. Including the additional 12 hr in the 36-hr case incorporates an additional evening

Table 3. ZOC_{BF} during each region's maximum 8-hr ozone window for each scenario on August 4 and the 24-hr case on August 13, with the percent increase in ZOC_{BF} (August 4 only) when moving from the 12- to the 24-hr case and moving from the 24- to 36-hr case.

	8-hr ZOC_{BF} (ppb)				% change	
Region	12-hr case	24-hr case	36-hr case	8/13, 24-hr case	12-hr to 24-hr	24-hr to 36-hr
Pittsburgh, PA	0.39	0.78	1.13	2.33	100.00	44.87
Butler, PA	2.17	2.78	3.01		28.11	8.27
Columbus, OH	0.62	1.21	1.43		95.16	18.18
Clarksburg, WV	3.31	4.97	5.40		50.15	8.65
New Castle, PA	0.76	1.46	1.65	0.68	92.11	13.01
Altoona, PA	1.67	1.85	2.23		10.78	20.54
Friendsville, MD	0.27	1.82	2.08		574.07	14.29

and nighttime hours during which NO_x could convert to less reactive NO_z species like HNO_3 or N_2O_5, without forming ozone, due to the lack of sunlight. On other days or in other locations, the influence of different timing of emission reductions may differ, depending on meteorological conditions and the distance between the source and receptor.

The differences between the three emission timing scenarios within the seven urban regions follow this domain-wide trend (Table 3). Nearly all regions see a larger relative increase in ozone sensitivity from the 12- to 24-hr case than from the 24- to 36-hr case. The exception was Altoona, PA, where ozone reduction due to EGU NO_x emissions increased 20.5% between the 24- and 36-hr cases, but only 10.8% between the 12- and 24-hr cases. Altoona is further east than the other locations and is at a greater distance from major EGUs. The longer time to transport both precursor NO_x emissions from these facilities and produce ozone may account for this difference.

The average maximum 8-hr ozone reduction across these seven regions (Table 3) for a 12-hr EGU NO_x reduction was 1.31 ppb, while a 24-hr and 36-hr reduction resulted in an average maximum 8-hr ozone reduction of 2.12 ppb and 2.42 ppb. These results indicate diminishing returns as EGU NO_x emissions are shut down for longer, under the conditions of our modeling episode. Shutting down a facility 36 hr before an anticipated high ozone event may incur greater economic costs while minimally reducing ozone concentrations as compared to a 24-hr case. Substantial ozone benefits were seen in the 24-hr case over the 12-hr case, however, and subsequent analysis for August 13 focuses on the 24-hr case.

Of the 80 EGUs identified and zeroed out for the August 13 simulation, all but one are also included in the analysis for August 4 (because day-specific CAMx point source files differ not only in emissions rates, but also in the number and location of individual point sources). The zeroing out of 80 EGUs began at 12:00 a.m. on August 12 and ended at 7:00 p.m. EST on August 13, removing a total of 1,350.6 tonnes of NO_x. Figure 7 shows the maximum 1-hr ZOC_{BF} on August 13. As in Figure 5, the greatest sensitivities occur in plumes downwind of the 80 EGUs. The maximum 1-hr ZOC_{BF} was 20.0 ppb and occurred in eastern Tennessee. The magnitudes of the 8-hr ZOC_{BF} (Table 3) on August 13 were comparable to those on August 4.

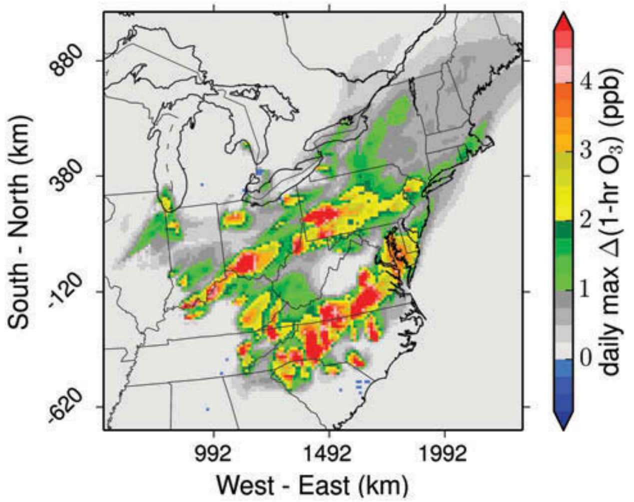

Figure 7. Maximum 1-hr ozone ZOC_{BF} for the 24-hr case on August 13. Values are not necessarily time paired; that is, they could have occurred during different hours on August 13.

Sensitivity to individual EGUs

The influences of the 80 EGU facilities were tracked individually and simultaneously using DDM within CAMx. Emissions from these facilities were tagged in the DDM input to simulate NO_x reductions in the same three temporal scenarios (12-hr, 24-hr, and 36-hr) on August 4, and the 24-hr scenario on August 13. The model restarts used to initialize the DDM simulations are the same files used to initialize the BF simulations, and EGU facility emissions were tagged during the same temporal windows (Figure 4). The ZOC_{DDM} results summed over all 80 EGUs are compared with the ZOC_{BF} results to test for error, particularly to evaluate whether the local sensitivities calculated by DDM are applicable to 100% removal from 80 EGUs. Since EGU emissions account for ~16% of total anthropogenic NO_x in 2005 (EPA, 2011c), even large reductions in EGU emissions over a given area may have only a small effect on nonlinear ozone chemical regimes.

By pairing sensitivities in time and space over the analysis domain, we find that ZOC_{DDM} summed over 80 EGUs compare favorably (normalized mean bias and error ~20%) with ZOC_{BF} on both days (Figures 8 and 9). Each emissions reduction scenario in Figure 8 performs similarly with slopes between 0.79 and 0.85, indicating that DDM underestimates sensitivities compared to BF. On August 4, more than 96% of all grid cells had ZOC_{DDM} within 0.5 ppb of ZOC_{BF} for each NO_x emissions scenario, and 83% were within 0.1 ppb (although, given that the absolute ZOC for BF and DDM are on the order of 5 ppb or less, the percent differences between the two methods could be large).

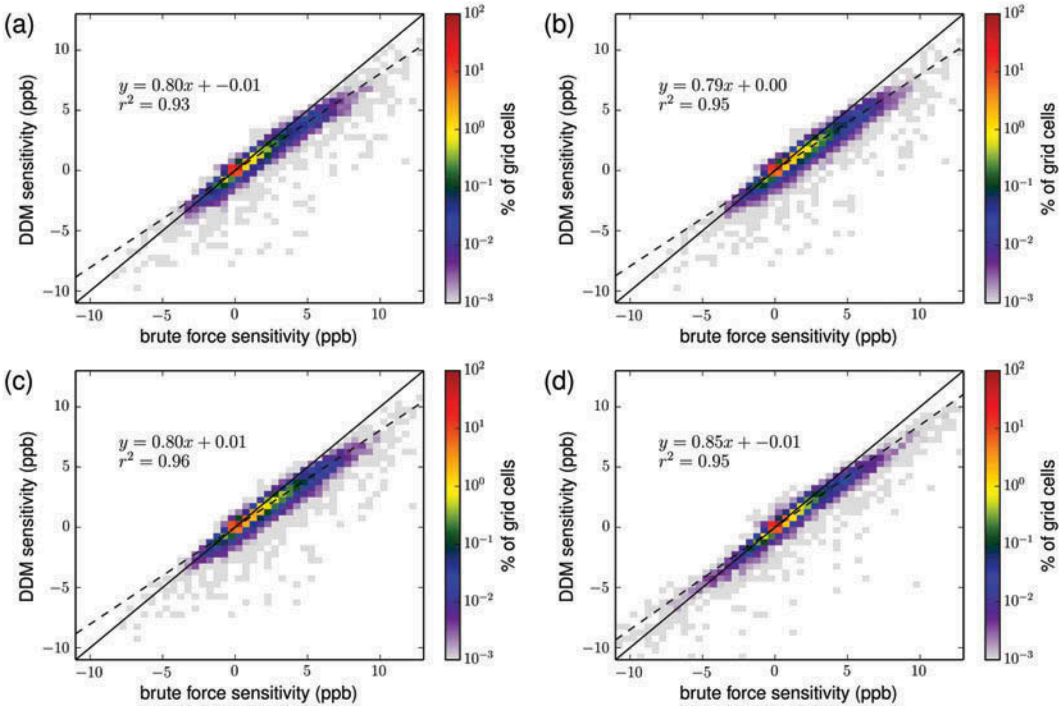

Figure 8. ZOC_{DDM} versus ZOC_{BF} for all grid cells in each scenario on August 4, (a) 12 hr, (b) 24 hr, and (c) 36-hr, and on August 13, (d) 24 hr only. All values are time and space paired. The colors show the density of points as a fraction of all points ($n = 433{,}219$; 151 rows, 151 columns, 19 hours). The solid line represents complete agreement between DDM and BF sensitivities; the dotted line gives the line of best fit.

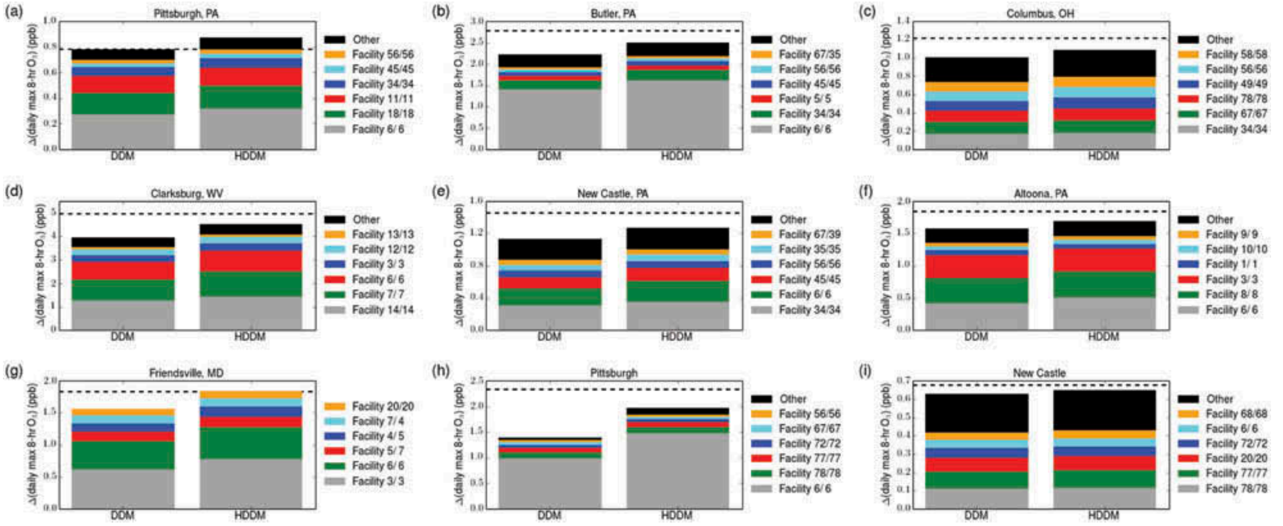

Figure 9. ZOC_{BF} (dotted line), ZOC_{DDM}, and ZOC_{HDDM} during each region's maximum 8-hr ozone window on (a)–(g) August 4 and (h), (i) August 13 (Pittsburgh and New Castle only) for the 24-hr scenarios. For DDM and HDDM simulations, the top six contributing sources are shown explicitly while the remaining sources are combined into "Others." The first facility number in the legend corresponds to DDM (left) case, and the second facility number corresponds to HDDM (right). These numbers are often but not always identical. There is no "other" category for Friendsville, MD, because the total contribution of the other facilities is negative (see Table 5).

Table 4. Performance statistics comparing ZOC_{DDM} and ZOC_{HDDM} to ZOC_{BF} on August 4 and August 13.

	ZOC	NMB	NME	r^2
Aug. 4 12-hr	DDM	−0.249	0.304	0.931
	HDDM	−0.117	0.202	0.971
24-hr	DDM	−0.195	0.219	0.951
	HDDM	−0.102	0.142	0.979
Aug. 13 24-hr	DDM	−0.195	0.237	0.947
	HDDM	−0.100	0.157	0.974

Discrepancies are likely due to nonlinearity introduced by modeled processes such as diffusion, ozone titration, and NO_x regime shifts.

Including second-order sensitivities, ZOC_{HDDM} was calculated for the 12-hr and 24-hr cases on August 4, and for the 24-hr case on August 13. Including second-order sensitivities showed an improvement with respect to ZOC_{BF} compared to just the first-order sensitivities (Figure 9). For example, slopes of ZOC_{HDDM} versus ZOC_{BF} improved from 0.80 to 0.90 for the 12-hr case and from 0.79 to 0.89 for the 24-hr case. HDDM also provided a notable reduction in both normalized mean error (NME) and normalized mean bias (NMB) (Table 4), where NME and NMB were calculated as

$$NMB = \Sigma\left(ZOC_{(H)DDM} - ZOC_{BF}\right)/\Sigma ZOC_{BF} \qquad (6)$$

$$NME = \Sigma\left|ZOC_{(H)DDM} - ZOC_{BF}\right|/\Sigma ZOC_{BF} \qquad (7)$$

For both the 12-hr and 24-hr cases, HDDM reduces NMB by about half and NME by about one-third, compared to DDM. Second-order sensitivities affected overall ZOC_{HDDM} nearest the emissions source (Figure 10). A comparison of the 12-hr case and 24-hr case on August 4 shows the nonlinear effect that older emissions have on ozone concentrations. In both cases, the effect of second-order sensitivities resulted in maximum ozone sensitivity increases of less than 0.1 ppb over 99% of all grid cells.

The DDM and HDDM simulations were also used to quantify the sensitivity of ozone to emissions from individual EGUs (Figure 9). Within each of the seven analysis regions, the number of EGUs with an individual ZOC_{DDM} of at least ±1 ppt for the 24-hr case on August 4 ranged from 15 at Friendsville, MD, to 27 at Altoona, PA, during the maximum 8-hr ozone window. On August 13, both New Castle and Pittsburgh had 26 EGUs with individual ZOC_{DDM} of at least ±1 ppt. The majority of this ozone sensitivity was contributed by significantly fewer sources. Table 5 shows the combined contribution of the six facilities with the greatest individual ZOC_{DDM} and compares this to the total ZOC_{DDM} of all 80 facilities. For the 24-hr case, the top six facilities contributed at least 66% of the total ZOC_{DDM} for each region. As the duration of NO_x emissions reductions

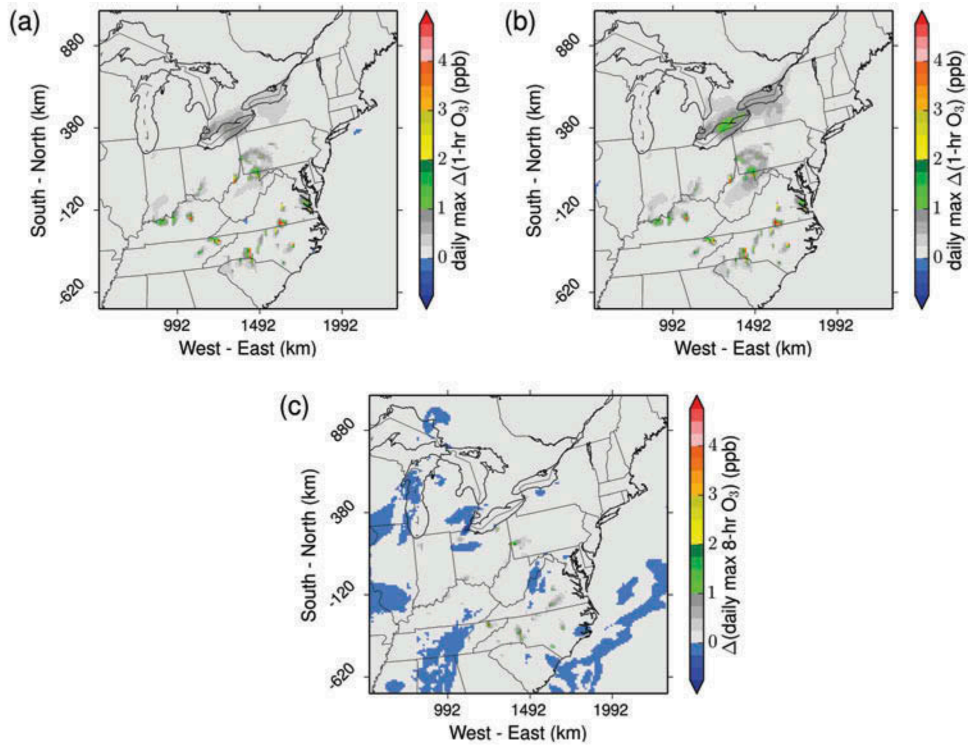

Figure 10. Maximum 1-hr differences between ZOC_{HDDM} and ZOC_{DDM} for the (a) 12-hr and (b) 24-hr scenarios on August 4 and (c) the 24-hr scenario on August 13. ZOC_{HDDM} and ZOC_{DDM} are time paired, which means these plots show the maximum 1-hr contributions from just the second-order effects.

Table 5. ZOC_{DDM} during each region's maximum 8-hr ozone for each scenario on August 4, and the 24-hr scenario for August 13 (Pittsburgh and New Castle only), showing the contributions from the top six facilities (ppb), contributions from all 80 facilities (ppb), the percent of the total comprised by just the top six facilities.

	12-hr case			24-hr case			36-hr case		
Region	Top six facilities	All facilities	Top 6(%)	Top six facilities	All facilities	Top 6(%)	Top six facilities	All facilities	Top 6(%)
Pittsburgh, PA	0.51	0.45	113.3	0.70	0.78	89.7	0.81	1.07	75.7
Butler, PA	1.65	1.71	96.5	1.92	2.22	86.5	2.04	2.44	83.6
Columbus, OH	0.39	0.51	76.5	0.74	1.01	73.3	0.88	1.21	72.7
Clarksburg, WV	2.49	2.63	94.7	3.53	3.94	89.6	3.60	4.28	84.1
New Castle, PA	0.49	0.54	90.7	0.87	1.13	77.0	0.95	1.31	72.5
Altoona, PA	1.32	1.43	92.3	1.36	1.58	86.1	1.39	1.88	73.9
Friendsville, MD	0.46	-0.17	–	1.57	1.05	149.5	1.63	1.26	129.4
				August 13					
Pittsburgh, PA	—	—	—	1.34	1.40	96.2	—	—	—
New Castle, PA	—	—	—	0.42	0.63	66.4	—	—	—

Note: Some facility contributions are negative (a reduction of NO_x at some facilities actually increases ozone); consequently, it is possible for the contribution of the top six facilities to be more than the sum of all the facility contributions.

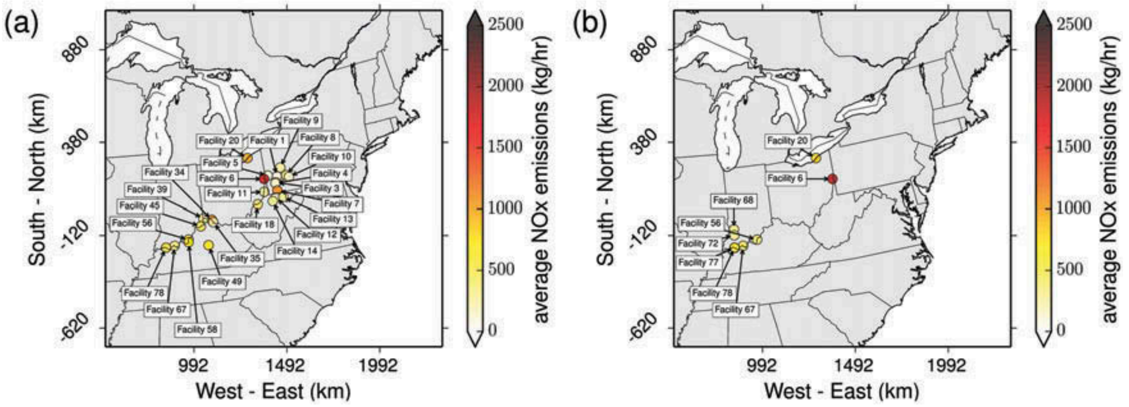

Figure 11. The locations and average hourly NO_x emissions of the urban regions' top six facilities on (a) August 4 and (b) August 13 identified in Figure 9.

increases, EGUs farther away from each region have larger impacts on ozone; that is, the top six facilities make up a smaller percentage of the total ZOC_{DDM}.

In the case of Butler on August 4 (Figure 9b) and Pittsburgh on August 13 (Figure 9h) the majority of the ozone sensitivity came from a single EGU (Facility 6, near the intersection of Ohio, Pennsylvania, and West Virginia; Figure 11), and it was a top six facility in each region on both days except for Columbus, OH, which is upwind of Facility 6. In this case, eliminating NO_x emissions at Facility 6 alone was simulated to reduce regional maximum 8-hr ozone concentrations by an amount ranging from 0.04 ppb at New Castle (August 13) to 1.40 ppb at Butler (August 4).

Conclusions

We investigated the sensitivity of two single-day high ozone episodes to emissions of NO_x from individual EGUs, with the purpose of informing the design of a dynamic management system that aims to avoid daily violations of the ozone standard by adjusting electricity generation among EGUs.

First, ozone was shown to be affected by EGU NO_x emissions. Using a brute force simulation in which emissions of 80 EGUs were removed simultaneously, the daily maximum 1-hr ozone impact was between –1 and 5 ppb in the majority of grid cells, with large areas of ozone reduction greater than 2 ppb downwind of individual EGUs or clusters of EGUs. This contribution is large enough that efforts to reduce EGU emissions through a dynamic management scheme could be effective at avoiding some high ozone episodes that contribute to a violation of the standard in cases where the standard is exceeded by a few ppb. While we modeled 2005 conditions, however, NO_x emissions from U.S. EGUs in 2014 have decreased by 53% relative to the 2005 inventory used here (EPA, 2015). With lower emissions from EGUs, we would expect that the sensitivities of peak ozone to EGU emissions would generally be smaller, suggesting a smaller potential benefit from dynamic management. On the other hand, the EPA has recently adopted a tighter standard for 8-hr ozone. Consequently, air quality managers may find it more difficult to meet the standard with current tools, and dynamic management may provide a cost-effective and attractive alternative.

Second, reducing EGU emissions roughly 1.5 days in advance of the high ozone episode (the 24-hr case) was significantly more effective (2.12 ppb reduction in 8-hr ozone averaged over 7 analysis regions) than reducing roughly 1 day in advance (the 12-hr case, 1.31 ppb). Our analysis of two high ozone days showed that reducing 2 full days in advance (the 36-hr case) brings a smaller additional ozone reduction (2.42 ppb) in the analysis regions, as the additional reductions in NO_x during nighttime hours contribute less to the ozone sensitivity. These ozone reduction benefits should be evaluated with respect to the costs of reducing electricity generation at particular facilities over different time windows.

Third, DDM and HDDM were shown to perform well with respect to the BF simulations for the simultaneous zero-out of 80 EGUs. DDM tends to underestimate ozone sensitivities by about 20%. HDDM reduces this normalized mean bias to about 10%, but does so with a significant increase in computational burden (~90% increase in total run time and double the required storage capacity). These findings suggest that DDM could be incorporated within air quality forecasting models to forecast sensitivities to emissions from individual EGUs, while high ozone episodes are also being forecast. Future work should further evaluate the use of online sensitivity techniques, including DDM, and the computational demands for including sensitivities in real-time air quality forecasts.

Fourth, in the seven analysis regions, a small number of EGUs dominate the total ozone sensitivity from all EGUs. At some locations, just one EGU causes most of the sensitivity, while over all locations considered, six EGUs comprised more than two-thirds of the overall sensitivity. Consequently, to avoid an episode of high ozone in a particular location, it may be necessary to temporarily shut down or reduce production at a small number of EGUs. Notably, while our seven test cities are all within the same administrative footprint of the power grid (run by the PJM Interconnection, LLC), the locations of the high-sensitivity EGUs span two or three administrative boundaries. This suggests that while dynamic ozone management may be able to improve air quality locally, doing so may requires regional coordination that spans beyond current decision-making boundaries for the power grid.

Future work should consider testing these conclusions over a wider range of meteorological conditions and locations, which may allow our specific findings to be generalized. In particular, future work should test the effectiveness of using first-order DDM sensitivities further, to evaluate its use for forecasting EGU effects on ozone. Other similar sensitivity techniques, including adjoint models, should also be evaluated with respect to DDM, for possible inclusion in air quality forecasting. Future work should also evaluate these conclusions for new model versions and applications (e.g., improved vertical resolution) and for new emission inventories. The dynamic management proposed here may be limited by current forecasting inaccuracies, especially when using model predictions in an absolute—rather than relative—sense. Future improvements in air quality forecasting, including the development of more robust techniques for dealing with inherent model uncertainty (e.g. bias correction described by Djalalova et al. [2015]), could improve dynamic management systems.

Together these findings suggest that dynamic management of EGUs to avoid ozone episodes may be a viable strategy, as EGUs have a notable impact during high ozone episodes, the number of EGUs that would need to be controlled is rather small, and the duration during which EGU production would be altered is within the scope of current air quality forecast models. A dynamic management system could use the DDM sensitivities of ozone to emissions from EGUs as input to an electrical grid dispatch model, to allow those models to adjust electricity generation in a way that is most cost-effective, while meeting air quality goals. Scaling back production at individual EGUs will require additional generation where ozone is not expected to be high. The costs and effects of these changes in generation on air quality should be fully evaluated to determine the viability or benefits of dynamic management with respect to alternatives for managing ozone. In addition, high ozone episodes often occur at multiple locations simultaneously and are often associated with hot weather and high electricity demand. The design of a system to provide the best benefits from reductions in peak ozone, over many locations simultaneously and at low cost, should continue to be investigated.

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About the authors

Evan Couzo is an assistant professor in the Department of Education at the University of North Carolina at Asheville.

James McCann contributed to this work while completing an MSEE in the Department of Environmental Sciences & Engineering at the University of North Carolina at Chapel Hill, and is presently an associate with Ramboll Environ in Arlington, VA

William Vizuete is an associate professor in the Department of Environmental Sciences & Engineering at the University of North Carolina at Chapel Hill.

Seth Blumsack is an associate professor in the Department of Energy and Mineral Engineering at Penn State University.

J. Jason West is an associate professor in the Department of Environmental Sciences & Engineering at the University of North Carolina at Chapel Hill.

References

Baker, K.R., and J.T. Kelly. 2014. Single source impacts estimated with photochemical model source sensitivity and apportionment approaches. *Atmos. Environ*. 96:266–74. doi:10.1016/j.atmosenv.2014.07.042

Bergin, M.S., A.G. Russell, M.T. Odman, D.S. Cohan, and W.L. Chameides. 2008. Single-source impact analysis using three-dimensional air quality models. *J. Air Waste Manage. Assoc*. 58:1351–59. doi:10.3155/1047-3289.58.10.1351

Cohan, D.S., A. Hakami, Y. Hu, and A.G. Russell. 2005. Nonlinear response of ozone to emissions: Source apportionment and sensitivity analysis. *Environmental Science & Technology* 39:6739–48. doi:10.1021/es048664m

Cohan, D.S., Y. Hu, and A.G. Russell. 2006. Dependence of ozone sensitivity analysis on grid resolution. *Atmos. Environ*. 40:126–35. doi:10.1016/j.atmosenv.2005.09.031

Djalalova, I., L. Delle Monache, and J. Wilczak. 2015. $PM_{2.5}$ analog forecast and Kalman filter post-processing for the Community Multiscale Air Quality (CMAQ) model. *Atmos. Environ*. 108:76–87. doi:10.1016/j.atmosenv.2015.02.021

Dunker, A.M. 1984. The decoupled direct method for calculating sensitivity coefficients in chemical kinetics. *J. Chem. Phys*. 81:2385–93. doi:10.1063/1.447938

Dunker, A.M., G. Yarwood, J.P. Ortmann, and G.M. Wilson. 2002. The decoupled direct method for sensitivity analysis in a three-dimensional air quality model—Implementation, accuracy, and efficiency. *Environ. Sci. Technol*. 36(13): 2965–76. doi:10.1021/es0112691

Eder, B., D. Kang, S.T. Rao, R. Mathur, S. Yu, T. Otte, K. Schere, R. Wayland, S. Jackson, P. Davidson, J. McQueen, and G. Bridgers. 2010. Using national air quality forecast guidance to develop local air quality index forecasts. *Bull. Am. Meteorol. Soc*. 91:313–26. doi:10.1175/2009BAMS2734.1

Energy Information Administration. 2012. Annual energy review 2011. http://www.eia.gov/totalenergy/data/annual/index.cfm (accessed July 14, 2015).

Energy Information Administration. 2013. Annual energy outlook 2013. www.eia.gov/forecasts/aeo (accessed July 14, 2015).

Environ. 2011. Comprehensive Air Quality Model with Extensions (CAMx), version 5.30. Environ International Arlington, VA..

Gego, E., A. Gilliland, J. Godowitch, S.T. Rao, P.S. Porter, and C. Hogrefe. 2008. Modeling analyses of the effects of changes in nitrogen oxides emissions from the electric power sector on ozone levels in the Eastern United States. *J. Air Waste Manage. Assoc*. 58:580–88. doi:10.3155/1047-3289.58.4.580

Hakami, A., M.T. Odman, and A.G. Russell. 2003. High-order, direct sensitivity analysis of multidimensional air quality models. *Environ. Sci. Technol*., 37(11): 2442–52. doi:10.1021/es020677h

Hakami, A., M.T. Odman, and A.G. Russell. 2004. Nonlinearity in atmospheric response: A direct sensitivity analysis approach. *J. Geophys. Res*. 109(D15303): 1–12. doi:10.1029/2003JD004502

Kelly, J.T., K.R. Baker, S.L. Napelenok, and S.J. Roselle. 2015. Examining single-source secondary impacts estimated from brute-force, decoupled direct method, and advanced plume treatment approaches. *Atmos. Environ*. 111:10–19. doi:10.1016/j.atmosenv.2015.04.004

Koo, B., G. Yarwood, and D.S. Cohan. 2008. Higher-order decoupled direct method (HDDM) for ozone modeling sensitivity analyses and code refinements. Prepared for the Texas Commission on Environmental Quality, 582-07-84005-FY08-07. http://www.tceq.state.tx.us/assets/public/implementation/air/am/contracts/reports/pm/5820784005FY0807-20080831-environ-camx_hddm_final_report.pdf (accessed July 14, 2015).

National Association of Clean Air Agencies. 2015. Implementing EPA's Clean Power Plan: A menu of options. http://www.4cleanair.org/NACAA_Menu_of_Options (accessed July 14, 2015).

National Oceanic and Atmospheric Administration. 2013. AQM model description. http://nomads.ncep.noaa.gov/txt_descriptions/AQM_doc.shtml (accessed July 14, 2015).

National Research Council. 2004. *Air Quality Management in the United States*. Washington, DC: National Academies Press. http://www.nap.edu/catalog/10728/air-quality-management-in-the-united-states (accessed July 14, 2015).

Nunnermacker, LJ, L.I. Kleinman, D. Imre, H. Daum, Y.-N. Lee, J.H. Lee, S.R. Springston, L. Newman, and N. Gillani. 2000. NO_y lifetimes and O_3 production efficiencies in urban and power plant plumes: Analysis of field data. *J. Geophys. Res*. 105(D7): 9165–76. doi:10.1029/1999JD900753

Simon, H., K.R. Baker, F. Akhtar, S.L. Napelenok, N. Possiel, B. Wells, and B. Timin. 2013. A direct sensitivity approach to predict hourly ozone resulting from compliance with the National Ambient Air Quality Standard. *Environ. Sci. Technol*. 47(5): 2304–13. doi:10.1021/es303674e

U.S. Environmental Protection Agency. 2007. Guidance on the use of models and other analyses for demonstrating attainment of air quality goals for ozone, $PM_{2.5}$, and regional haze. Research Triangle Park, NC. EPA-454/B-07-002. http://www3.epa.gov/ttn/scram/guidance/guide/final-03-pm-rh-guidance.pdf(accessed November 16, 2015).

U.S. Environmental Protection Agency. 2009. Clean air transport rule. Washington, DC. EPA-HQ-OAR-2009-0491. http://www.epa.gov/airtransport/pdfs/TR_070611_WEB.pdf (accessed July 14, 2015).

U.S. Environmental Protection Agency. 2011b. Air quality modeling final rule technical support document. Research Triangle Park, NC. http://epa.gov/airtransport/pdfs/AQModeling.pdf (accessed July 14, 2015).

U.S. Environmental Protection Agency. 2011c. Emissions inventory final rule technical support document. Washington, DC. EPA-HQ-OAR-2009-0491. ftp://ftp.epa.gov/EmisInventory/2005v4_2/transportrulefinal_eitsd_28jun2011.pdf (accessed July 14, 2015).

U.S. Environmental Protection Agency. 2014 . 2011National Emissions Inventory, version 1, Technical support document, June 2014 Draft, Office of Air Quality Planning and Standards. http://www.epa.gov/ttn/chief/net/2011nei/2011_nei_tsdv1_draft2_june2014.pdf (accessed August 12, 2015).

U.S. Environmental Protection Agency. 2015. 1970–2014 Average annual emissions, all criteria pollutants in MS Excel (March 2015). http://www3.epa.gov/ttn/chief/trends/index.html(accessed November 16, 2015).

Yang, Y.-J., J.G. Wilkinson, and A.G. Russell. 1997. Fast, direct sensitivity analysis of multidimensional photochemical models. *Environ. Sci. Technol.* 31(10): 2859–68. doi:10.1021/es970117w

Yarwood, G., S. Rao, M. Yocke, and G. Whitten. 2005. Updates to the carbon bond chemical mechanism: CB05. Final report to the US EPA. RT-04-00675. http://www.camx.com/publ/pdfs/cb05_final_report_120805.pdf (accessed July 14, 2015).

Zhang, Y., K. Vijayaraghavan, and C. Seigneur. 2005. Evaluation of three probing techniques in a three-dimensional air quality model. *J. Geophys. Res.* 110(D2): 1–21. doi:10.1029/2004JD005248

Zhou, W., D.S. Cohan, R.W. Pinder, J.A. Neuman, J.S. Holloway, J. Peischl, T.B. Ryerson, J.B. Nowak, F. Flocke, and W.G. Zheng, 2012. Observation and modeling of the evolution of Texas power plant plumes. *Atmos. Chem. Phys*. 12:455–68. doi:10.5194/acp-12-455-2012.