A Direct sensitivity approach to predict hourly ozone resulting from compliance with the National Ambient Air Quality Standard

Heather Simon[1,*], Kirk Baker[1], Farhan Akhtar[1], Sergey L. Napelenok[2], Norm Possiel[1], Benjamin Wells[1], Brian Timin[1]

[1]Office of Air Quality Planning and Standards, US EPA, RTP, NC 27711

[2]National Exposure Research Laboratory, US EPA, RTP, NC 27711

*Corresponding author

For submission to ES&T

In setting primary ambient air quality standards, the EPA's responsibility under the law is to establish standards that protect public health. As part of the current review of the Ozone National Ambient Air Quality Standards (NAAQS) standard, the US EPA evaluated the health exposure and risks associated with ambient ozone pollution using a statistical approach to adjust recent air quality to simulate just meeting the current standard level, without specifying emission control strategies. One drawback of this purely statistical concentration "rollback" approach is that it does not take into account spatial and temporal heterogeneity of ozone response to emissions changes. The application of the Higher-order Decoupled Direct Method (HDDM) in the Community Multiscale Air Quality (CMAQ) model is discussed here to provide an example of a methodology that could incorporate this variability into the risk assessment analyses. Because this approach includes a full representation of the chemical production and physical transport of ozone in the atmosphere, it does not require assumed "background" concentrations which have been applied to constrain estimates from past statistical techniques. The CMAQ-HDDM adjustment approach is extended to measured ozone concentrations by determining typical sensitivities at each monitor location and hour of the day based on a linear relationship between first order sensitivities and hourly ozone values. This approach is demonstrated by modeling ozone responses for monitor locations in Detroit and Charlotte to domain-wide reductions in anthropogenic NOx and VOCs emissions. As seen in previous studies, ozone response calculated using HDDM compared well to brute-force emissions changes up to approximately a 50% reduction in emissions. A new step-wise approach is developed here to apply this method to emissions reductions beyond 50%, allowing for the simulation of more stringent reductions in ozone concentrations. Compared to previous rollback methods, this application of modeled sensitivities to ambient ozone concentrations provides a more realistic spatial response of ozone concentrations at monitors inside and outside the urban core and at hours of low ozone concentrations.

1. Introduction

The US EPA sets health based air quality standards (National Ambient Air Quality Standards: NAAQS) for six criteria pollutants including ozone. The ozone standard is based on the 3-year average of the fourth highest measured maximum daily 8-hr average (MDA8). If this quantity, called the design value, exceeds 75 ppb, then a monitor is in violation of the ozone NAAQS. However, many epidemiology studies have used alternate metrics when quantifying the health effects of ozone. For instance, various studies have determined a relationship between premature mortality and ozone based on 1-hr daily maximum ozone [1], 24-hr daily average concentration[2, 3], 8-hr average (10am to 6pm) ozone[4, 5], and 8-hr daily maximum ozone[6]. Respiratory and asthma related hospital and ER visits have been correlated with 24-hr average ozone[7-12] and 5-hr daily average concentrations[13, 14]. In addition, health effects of ozone determined from exposure analyses based on clinical tests rely on hourly ozone time-series[15]. Previous work has shown that quantified health benefits of reductions in ozone concentrations depend strongly on the averaging time used in the analysis[16].

As a part of the 5-year NAAQS review cycle mandated by the Clean Air Act, the EPA estimates how achieving the current ozone standard and various alternative standards will reduce ozone-related exposures and health risks. Since the standard is determined based on the highest daily ozone values, yet risk is affected by overall exposure to the full range of ozone concentrations, three key questions are: 1) How would meeting the standard affect ozone concentrations on mid to lower ozone days or during non-peak hours? 2) How would lowering concentrations at a violating monitor affect ozone concentrations throughout an urban area? 3) What is the total health risk to the population that would occur if an area were to meet various levels of the NAAQS? To answer these questions, the modeled change in design values must be translated into changes in time-series of measured hourly ozone concentrations. These adjusted hourly values can then be re-aggregated to match the metric (e.g. seasonal average of daily maximum 1-hour average, seasonal average MDA8 etc.) used in an epidemiological study to assess public health impacts at these levels of the standard.

Past efforts have used two generalized statistical techniques to decrease hourly concentrations in a given area to meet the design value of the standard being evaluated. These include proportional rollback, where all hourly concentrations are adjusted by the same percentage[19], and quadratic rollback, where linear and quadratic parameters are estimated from the historical ozone measurement record to reduce higher concentrations at a greater rate than lower concentrations[17, 19]. While these techniques have the advantage of being straightforward to implement and quick to compute, they rely on several simplifying assumptions and may not represent the air quality changes which would occur under actual reductions in precursor emissions since the proportional and quadratic rollback techniques assume that all monitors in an urban area respond identically to theoretical emissions reductions. In reality, it is well known that the specific mix of volatile organic compounds (VOCs) and nitrogen oxides (NOx) in an urban area influences the effectiveness of various emissions control strategies[20]. Specifically, higher NOx levels in urban core areas and close to emissions sources, such as vehicle traffic, may make NOx controls less

effective in urban centers than in rural and suburban areas[21-24]. In these oxidant limited conditions, NOx reductions can lead to increases in ozone with decreasing NOx emissions.

Furthermore, some emissions sectors, like mobile sources, have distinct diurnal patterns in emissions[25, 26] which is not resolved in the concentration reductions under either statistical rollback method. Finally, the statistical rollback techniques implement a backstop value below which ozone concentrations are not decreased. This floor is used to limit the statistical reduction in ozone concentrations to account for the "background" portion of ozone, formed from international emissions and from natural sources of ozone precursors. Since these techniques do not explicitly simulate the physical and chemical processes leading to ozone formation and transport, this backstop level is a constant value or a location-specific monthly average background level based on separate studies[17-19].

Each of the limiting assumptions described above can be explicitly addressed using chemical transport models which simulate the effects of pollutant emissions, chemistry, transport and deposition to estimate spatially and temporally varying pollutant concentrations. Moreover, chemical transport models have been instrumented with additional tools to track the sources of pollutants and the transportation of pollutants to receptors. The higher-order decoupled direct method (HDDM) is an extension which uses the governing differential equations within the host model to calculate how a perturbation in the model inputs affects pollutant concentrations[27]. HDDM calculates spatially and temporally varying partial derivatives, or sensitivities, of the pollutant concentration with respect to emissions or another input. These modeled sensitivities can be used in a higher order polynomial expression to describe nonlinear response of ozone to emissions changes. Additional background on HDDM is available in the literature[27-31] and is briefly summarized in the supplemental information. Similar sensitivity information could be achieved by directly perturbing model inputs and re-running the simulation (brute-force method). However, HDDM has the advantage of allowing the user to more efficiently estimate outcomes for a range of input perturbations. HDDM calculations accurately recreate ozone concentration responses results over large emissions perturbations and have been shown to give good approximations of ozone changes for emissions reductions up to 50%[29]. This range of capabilities makes HDDM an ideal approach for estimating ozone concentrations after attainment of current or proposed standards[32].

Here we present work that significantly expands on an initial CMAQ-HDDM technique presented in EPA's 2013 review of the ozone NAAQS [33]. Here, we explore the use of HDDM coefficients to adjust modeled and measured ozone concentrations in a manner that accounts for spatially and temporally varying response within an urban area to broad precursor emission reductions, nonlinearities in ozone chemistry, and explicit sources of background ozone. The intent of this application is not to optimize control strategies but instead to characterize how ozone will respond in different cities to changes in NOx and VOC concentrations.

2. Modeling methodology

We modeled a two month episode (July-August 2005) using the Community Multiscale Air Quality model (CMAQ) version 4.7.1[34, 35] which was instrumented with HDDM[36]. June 28-30 was used as a 3-day spin-up period and not included in the analysis. The modeling domain covered the eastern half of the United States at a 12 km resolution (see Figure S1) and contained 24 vertical layers with the lowest layer extending 38 meters. Temporally varying boundary conditions were derived from a 36 km resolution continental US CMAQ simulation. Meteorological inputs were derived using the MM5 model [37] and are described in detail elsewhere [38]. Emissions of CO, NH_3, NO_x, PM_{10}, $PM_{2.5}$, SO_2 and VOCs are based on the 2005 v4.3 National Emissions Inventory [39] and come from anthropogenic point, area and mobile sources, fires, and biogenic sources. North American emissions from outside the U.S. are based on a 2006 Canadian inventory and a 1999 Mexican inventory[39].

HDDM was configured to calculate first and second order ozone sensitivity coefficients, S and S^2, to emissions of US anthropogenic NOx and VOC within the Eastern US modeling domain. Sensitivities were not tracked for biogenic and fire emissions or for emissions outside of the US. Also, US emissions outside the Eastern US modeling domain were not included in the sensitivities. Of the 20.7 million tons/year of NOx emissions within the modeling domain, 85% came from US anthropogenic sources.

First and second order sensitivities and modeled concentrations were extracted at the location of 7 monitoring sites in the Charlotte area and 8 monitoring sites in the Detroit area (Figures S2 and S3). Charlotte and Detroit were chosen as case studies for this analysis because both cities experienced high ozone concentrations in 2005, the ozone simulation had good agreement between ozone predictions and observations at each location, and the two cities had markedly different ozone formation regimes owing to their geographic locations and source composition. Normalized mean bias/error for MDA8 ozone were 8.6%/14.1% in Charlotte and 4.1%/14.5% in Detroit for the two-month modeled episode. Performance is improved when only high days (above 60 ppb) are evaluated. More details on the model's accuracy at predicting ozone concentrations in Charlotte and Detroit are provided in the supplemental information.

3. Application to modeled data

3.1 Methodology

We apply HDDM to adjust modeled concentrations of ozone in response to generalized reductions in precursor emissions. The analysis here focuses on anthropogenic NOx emissions, though alternative precursors, VOC species, are covered in the supporting information. In each city, sensitivities were used to adjust hourly ozone concentrations based on a single relative emissions perturbation value, $\Delta\varepsilon$, for all sites and all hours using the first 3 terms of Equation S2 (i.e. $\Delta\varepsilon = -0.2$ represents a 20% reduction in NOx emissions). For any given $\Delta\varepsilon$, a new set of hourly ozone concentrations in the urban area can be estimated. From those estimates, the 4th highest MDA8 for the two month modeled period was calculated. For simplicity and due to the 2-month length of the modeling period, we look at the 4th highest modeled value in July and August 2005 rather than the 3-year average for the annual 4th highest MDA8 at each monitor.

Here we find the smallest Δε that predicts all monitors in each urban area to have a 4th highest MDA8 less than or equal to the current NAAQS level of 75 ppb.

As discussed above, previous studies have reported HDDM to be accurate up to 50% NOx emissions changes. In order to cover the entire range of emissions reductions we have devised a multi-step HDDM adjustment approach. For this purpose, the CMAQ-HDDM simulations were rerun with 50% and 75% cuts to the US anthropogenic NOx emissions (referred to hereafter as the 50% NOx cut and 75% NOx cut runs). The sensitivities from these simulations reveal how ozone would respond to emissions changes under these lower NOx conditions. Figure 1 gives a conceptual picture of the multistep adjustment procedure using first-order sensitivities. Sensitivities from the base run are used to adjust ozone concentrations for NOx emissions reductions up to X%. Additional emission reductions beyond X% use sensitivities from the 50% NOx cut run until reductions exceed (X+Y)%. Finally, sensitivities from the 75% NOx cut run are applied for the remaining emission reductions. In order to better approximate the non-linear ozone response to any level of emissions reductions, 2nd order terms are added to the multistep approximation method in Equations 1-4.. Base model simulated ozone is always used as the starting point for the multistep adjustment procedure. This is necessary because it is later applied to ambient ozone concentrations and measurements do not exist for alternative perturbed (i.e. observed ozone where Nox emissions are reduced by 50%) atmospheric conditions. P represents the percentage NOx cut for which the ΔO_3 values are being calculated, S and S^2 are the first and second order ozone sensitivities to US NOx emissions, and X and Y are described above.

$$\Delta O_3 = -a \times S_{NOx\_base} + \frac{a^2}{2} \times S^2_{NOx\_base} - b \times S_{NOx_{50}\%cut} + \frac{b^2}{2} \times S^2_{NOx_{50}\%cut} - c \times S_{NOx_{75}\%cut} + \frac{c^2}{2} \times S^2_{NOx_{75}\%cut}$$

Equation 1

$$a = \begin{cases} \frac{P}{100} & for\ P \le X \\ \frac{X}{100} & for\ P > X \end{cases}$$

Equation 2

$$b = \begin{cases} 0 & for\ P \le X \\ \frac{2\times(P-X)}{100} & for\ X < P \le X+Y \\ \frac{2\times Y}{100} & for\ P > X+Y \end{cases}$$

Equation 3

$$C = \begin{matrix} 0 & for\ P \le X+Y \\ \frac{4\times(P-(X+Y))}{100} & for\ X+Y < P \le 100 \end{matrix}$$

Equation 4

The ideal values for equation transition points, X and Y, are determined by minimizing the least square mean error between the adjusted concentrations using the multistep approach and modeled concentrations from brute force NOx cut runs (see complete methodology in the supplemental information). We first determined the value of X which gave the lowest error compared to brute forces estimates at 50% NOx cuts. Then holding X constant, we determined the value of Y which gave the lowest error compared to brute force estimates at 75% NOx cuts. Mathematical details are provided in the supplemental information. This process was performed independently for

Detroit and Charlotte. For Detroit, X=43 and Y=26 give the lowest overall error in ozone predictions at 50% and 75% NOx cuts. For Charlotte, X=37 and Y=33 give the lowest overall error.

3.2 Results

The multi-step adjustment approach leads to marginal improvements in replication of brute force estimates by HDDM sensitivities in Charlotte and substantial improvements in Detroit. Figure 2 shows this comparison at 75% NOx cuts. Figure S10 in the supplement shows a larger improvement for the extreme 100% NOx cut case.

The multi-step HDDM adjustment approach requires a 48% NOx cut for Charlotte and a 62% NOx cut for Detroit to reduce the 4th highest MDA8 to 75 ppb. Note that the intent of this work is not to determine an optimal control strategy but instead to understand how ozone would respond to changing NOx emissions. Therefore these reductions should not be construed as a reflective of emission controls required to achieve the current ozone standard.

Estimated ozone concentrations from the multi-step HDDM adjustment approach are shown in Table 1 (urban core sites are shaded in gray) and in Figures 3 and S11. These results demonstrate several advantages of using HDDM sensitivities over proportional and quadratic rollback.

First, it is clear that different monitors within an urban area respond differently to the same change in NOx emissions. For instance, the most urban sites in both Charlotte and Detroit appear to be less responsive to NOx emissions reductions that the non-urban sites. The 4th highest value is reduced more at the non-urban sites than at the urban sites even when modeled 4th high MDA8 values are similar. The difference between urban and non-urban sites is greater in Detroit where 4th high MDA8 values at urban sites 260991003 and 161250001 drop by 7 and 5 ppb while 4th high MDA8 values at non-urban sites with similarly high ozone (260990009 and 261470005), 4th high MDA8 values drop by 16 and 18 ppb. This behavior is expected, because urban environments with high concentrations of vehicle NOx emissions tend to be NOx-saturated during high traffic times.

Second, the multistep approach also provides temporal variability in ozone response that better reflects the atmospheric chemistry of ozone formation than the statistical rollback procedures which assume proportional or quadratic fitted hourly responses. Figure 3 shows the diurnal ozone distributions for an urban and rural site in both Charlotte and Detroit. The blue bars show the modeled distribution of ozone at that hour on all days in July and August while the red bars show the adjusted values. In Charlotte, the non-urban site shows decreases at all hours of the day and throughout all portions of the distribution. The urban site, in contrast, shows increases during morning rush-hour times when NOx saturation is especially pronounced. During evening rush-hour times, ozone concentrations do not increase but are also not particularly sensitive to the NOx reductions. Similar, but more pronounced, trends are shown at the Detroit urban site where increases in the median ozone concentration are predicted for NOx emission cuts during most hours of the day. This NOx “disbenefit” trend is not seen on high ozone days.

4. Application to observed data

4.1 Methodology

The previous section demonstrated how HDDM results could be used to adjust modeled concentrations to show how ozone concentrations will respond both temporally and spatially when the 4th highest MDA8 in an urban area is reduced to 75 ppb. However, since regulatory standards are set based on measured values, regulatory assessments generally tie modeling results to ambient data. This is accomplished by applying relative changes in modeled concentrations to measured data. In order to use the HDDM adjustment approach with measured data from July and August 2005, we could simply apply the sensitivities predicted by the model on a grid cell and day specific basis. However, this technique has several drawbacks. First, although model performance was good during this episode, overestimates and underestimates of ozone concentrations still occur on specific days. If, for instance, the modeled precipitation were too high on a particular day, the model might estimate low ozone concentrations when high ozone values were observed. In that case, it would be inappropriate to apply the modeled sensitivity to the observed data. Second, design values are based on 3 years of ambient data and regulatory assessments often cover multiple design value periods. It is therefore desirable to create generalized sensitivities that could be applied to timeframes outside of the modeled episode, similar to the approach typically used for modeled attainment demonstrations.

To address both of these concerns, we devised a technique to provide typical sensitivities for each site based on time-of-day and ozone concentration. We found that first order sensitivities were correlated with hourly ozone values and that second order sensitivities were correlated with first order sensitivities. Therefore, for each grid cell containing a monitor at each hour of the day, a separate linear regression of S_{NOx} and S_{VOC} as functions of hourly ozone was determined (i.e. $S_{NOx} = m \times O_3 + b$). Therefore, for 8am at Detroit Site 260990009, S_{NOx} and O_3 values from all 8am hours in July and August are used to fit this relationship. Similarly, S^2_{NOx} and S^2_{VOC} were calculated as a function of S_{NOx} and S_{VOC} respectively. Tables S4 through S24 give the fitted slopes, intercepts, and correlation coefficients for each sensitivity coefficient at each site and hour. In addition, these tables provide the standard errors for the slope and intercept terms which quantify the uncertainty in these fitted parameters. This regression scheme attempts to depict a "typical" response at each site and hour at all ozone concentrations and inherently will not capture the full range of ozone concentration variability. The regression technique was performed for the first and second order NOx and VOC sensitivities from the base run and the 50% NOx cut and 75% NOx cut simulations. The sensitivities from the NOx cut runs were fitted to hourly ozone concentrations in the base simulation. It was found that correlation coefficients using base case ozone concentrations were similar to those with ozone concentrations from the NOx cut runs.

To apply the HDDM adjustments to observed data, sensitivities must be determined for each hour at each site based on the linear relationship from the modeled data and the observed ozone concentration. The linear regression model also allows us to quantify the standard error of each predicted sensitivity value at each hour and site. Observed ozone from July-August 2005 in

Charlotte and Detroit was adjusted by applying incrementally increasing NOx reductions (equations 1-4) and recalculating MDA8 values at each step until all monitors in an urban area achieved 4th highest values at or below 75 ppb. The standard error associated with each predicted sensitivity from the linear model can be propagated through Equation 1 to quantify the standard error in the final predicted ozone concentration. This gives a measure of variability in the sensitivities at any given ozone concentration and allows us to quantify how much our predicted ozone could change given that variability.

4.2 Results

When applying sensitivities derived from linear regressions to observed data, the multi-step HDDM adjustment approach requires a 41% NOx cut for Charlotte and a 55% NOx cut for Detroit to reduce the observed 4th highest MDA8 to 75 ppb. It is important to keep in mind these values are based on broad emissions reductions and not reflective of area specific control strategies.

We find that overall standard errors in predicted ozone were small with median and maximum values for all hourly adjusted ozone concentrations in Detroit equal to 0.7 and 3.2 ppb respectively. In Charlotte, median and maximum standard error values were 0.5 ppb and 2.2 ppb. Figures S15-S17 show hourly adjusted ozone with standard error bars for all sites on 3 days with different ozone levels.

Figure 4 demonstrates the 3-step HDDM adjustment methodology with the linear regression sensitivities for a daytime hour (2pm) at an urban Detroit site (260991003) and for a downwind Detroit site (260990009). Similar plots are provided in the supplemental information for nighttime and rush-hour times (Figures S18 and S19). The solid lines represent the 3-step adjustment trajectory while the dotted lines show the trajectory that would be taken if the base or 50% NOx cut sensitivities were applied up to 100% NOx cuts. Orange dots represent brute force predictions for this site and hour on days with ozone concentrations within 3 ppb of the values evaluated in this figure. Several features of these plots are of particular interest. First, variability occurs in the brute force estimates, which cannot be captured when using an average profile. However, in most cases, the 3-step trajectory falls closer to the middle of the brute force estimates than the base sensitivity trajectory. This demonstrates that the 3-step application of HDDM sensitivities does well at predicting typical changes in ozone for these ozone concentrations, sites, and hours. Second, it is clear that base sensitivities often underestimate the response of ozone to higher percentages of NOx changes and sometimes predict disbenefits when reductions actually occur. Third, the magnitude of the ozone response to NOx reductions is different at different concentrations. Both the brute force points and the HDDM trajectories show greater ozone reductions at higher concentrations (disbenefits are seen at low concentrations during nighttime and rush-hour periods). This agreement in trends between the brute force and the HDDM sensitivities derived from linear regression supports the use of this technique.

Results from the observation-based HDDM adjustments are shown in Table 1 and in Figure 5 and Figure S12. The observation-based HDDM adjustments behave similarly to the model-based

adjustments. The 4th highest MDA8 value at the urban Charlotte monitors is slightly less responsive than that value at the non-urban Charlotte values. In Detroit, urban monitors 260991003 and 261250001 are especially insensitive to NOx reductions, while the two monitors furthest from urban areas (260910007 and 261470005) are extremely responsive to NOx reductions. Again, Figure 5 shows NOx disbenefits during rush-hour times especially at the urban sites. In general the adjusted ozone looks similar when applied to modeled and observed data (Figure 3 versus 5) especially during daytime hours.

5. Implications

To fully assess the impacts of air pollution policy on human health and wellbeing, policy makers must estimate how pollutant concentrations will vary after policies are implemented. In this work we have explored the use of HDDM to provide estimates of how spatially and temporally varying ozone concentrations might look after changes to precursor emissions. Our modeling allows for more explicit treatment of physical and chemical processes that affect ozone levels and therefore avoids many of the simplifying assumptions made in previously used statistical techniques. However, models pose new challenges including the requirements of additional time and resources to perform the analysis and uncertainties associated with imperfect model performance. This technique might be expected to affect predicted health risk reductions of a new standard in several ways.

First, previous work used a floor "background" ozone value of 40 ppb[19]. From Figures 3 and 5 in this work, it is clear that measured and modeled ozone often occurs at concentrations below this value. The use of a floor is unnecessary with the HDDM adjustments since background sources are explicitly accounted for in the photochemical model simulations. The elimination of this floor value in our method leads to lower ozone concentrations and could result in larger predicted health risk reductions than would be estimated when a 40 ppb floor is applied.

A second improvement under this technique is that ozone concentrations can either increase or decrease, reflecting the local chemical conditions. Since the statistical techniques only decrease ozone concentrations, this new ability may lead to higher predicted ozone concentrations at some times and thus decrease the predicted health risk reductions of meeting the NAAQS. However, most instances for which ozone is predicted to increase with decreasing NOx emissions occur at low ozone concentrations, many of which might be below previously-assumed background levels. Thus, depending on the level of the background ozone assumed in statistical rollback techniques this may have limited impact on predicted health risk reductions from meeting the ozone standard. Some studies have showed adverse health effects even at low ozone levels[40].

Additionally, our analysis captures the generally less-responsive nature of urban areas than non-urban areas to NOx decreases. Statistical rollback techniques force response at all sites to be equivalent to response at the monitor with the highest measured design value. In cases where the highest measured ozone concentration is in an urban area, statistical techniques may underestimate the ozone reductions at suburban and rural monitors since all lower monitors are reduced according to the measured ozone distribution at the highest monitor. Conversely, the highest measured ozone concentrations often occur at downwind non-urban monitors. In that

case, the ozone response at the urban monitors would be overestimated using statistical techniques compared to HDDM. Since the highest population densities occur in urban areas, this behavior could lead to lower estimates of health risk reductions than would be calculated with a statistical rollback technique. Since competing effects may lead to both increased and decreased predicted health risks from ozone, future studies could extend this work by analyzing the health implications of ozone concentrations at multiple standard levels.

Disclaimer

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

Acknowledgements

The authors would like to recognize the contribution of Allan Beidler, Chris Allen, Rich Mason, Alison Eyth, Alexis Zubrow, Karen Wesson, Bryan Hubbell, Tyler Fox, Rob Pinder, Rohit Mathur, Kristen Foley, Greg Yarwood, Chris Emery, Uarporn Nopmongcol and the anonymous reviewers.

Supporting Information Available

This information is available free of charge via the Internet at http://pubs.acs.org/.

References

1. Ito, K.; Thurston, G. D., Daily PM(10)/mortality associations: An investigation of at-risk subpopulations. *J. Expo. Anal. Environ. Epidemiol.* **1996,** *6* (1), 79-95.
2. Moolgavkar, S. H., Air pollution and daily mortality in three US counties. *Environ. Health Perspect.* **2000,** *108* (8), 777-784.
3. Samet, J. M.; Zeger, S. L.; Kelsall, J. E.; Xu, J.; Kalkstein, L. S. *Air Pollution Weather and Mortality in Philadelphia 1973-1988*; Health Effects Institute: Cambridge, MA, 1997.
4. WHO *Health Aspects of Air Pollution with Particulate Matter, Ozone and Nitrogen Dioxide: Report on a WHO working Group*; World Health Organization: Bonn, Germany, 2003.
5. Zanobetti, A.; Schwartz, J., Mortality displacement in the association of ozone with mortality - An analysis of 48 cities in the United States. *Am. J. Respir. Crit. Care Med.* **2008,** *177* (2), 184-189.
6. Bell, M. L.; McDermott, A.; Zeger, S. L.; Samet, J. M.; Dominici, F., Ozone and short-term mortality in 95 US urban communities, 1987-2000. *JAMA-J. Am. Med. Assoc.* **2004,** *292* (19), 2372-2378.
7. Burnett, R. T.; Smith-Doiron, M.; Stieb, D.; Raizenne, M. E.; Brook, J. R.; Dales, R. E.; Leech, J. A.; Cakmak, S.; Krewski, D., Association between ozone and hospitalization for acute respiratory diseases in children less than 2 years of age. *Am. J. Epidemiol.* **2001,** *153* (5), 444-452.
8. Moolgavkar, S. H.; Luebeck, E. G.; Anderson, E. L., Air pollution and hospital admissions for respiratory causes in Minneapolis St. Paul and Birmingham. *Epidemiology* **1997,** *8* (4), 364-370.
9. Schwartz, J., PM(10) ozone, and hospital admissions for the elderly in Minneapolis St.-Paul, Minnesota. *Arch. Environ. Health* **1994,** *49* (5), 366-374.
10. Schwartz, J., Air-pollution and hospital admissions for the elderly in Detroit, Michigan. *Am. J. Respir. Crit. Care Med.* **1994,** *150* (3), 648-655.
11. Schwartz, J., Short-term fluctuations in air-pollution and hosptial admissions of the elderly for respiratory-disease. *Thorax* **1995,** *50* (5), 531-538.

12. Stieb, D. M.; Burnett, R. T.; Beveridge, R. C.; Brook, J. R., Association between ozone and asthma emergency department visits in Saint John, New Brunswick, Canada. *Environ. Health Perspect.* **1996,** *104* (12), 1354-1360.
13. Cody, R. P.; Weisel, C. P.; Birnbaum, G.; Lioy, P. J., The effect of ozone associated with summertime photochemical smog on the freqency of asthma visits to hospital emergency departments. *Environ. Res.* **1992,** *58* (2), 184-194.
14. Weisel, C. P.; Cody, R. P.; Lioy, P. J., Relationship between summertime ambient ozone levels and emergency department visits for asthma in central New-Jersey. *Environ. Health Perspect.* **1995,** *103*, 97-102.
15. USEPA, Heath Risk and Exposure Assessment for Ozone, first external review draft. EPA 452/P-12-001 ed.; United States Environmental Protection Agency: Research Triangle Park, NC, 2012; Vol. EPA 452/P-12-001.
16. Digar, A.; Cohan, D. S.; Bell, M. L., Uncertainties Influencing Health-Based Prioritization of Ozone Abatement Options. *Environ. Sci. Technol.* **2011,** *45* (18), 7761-7767.
17. USEPA *Ozone population exposure analysis for selected urban areas*; United States Environmental Protection Agency: Research Triangle Park, NC, 2007.
18. USEPA *Ozone health risk assessment for selected urban areas*; United States Environmental Protection Agency: Research Triangle Park, NC, 2007.
19. Hubbell, B. J.; Hallberg, A.; McCubbin, D. R.; Post, E., Health-related benefits of attaining the 8-hr ozone standard. *Environ. Health Perspect.* **2005,** *113* (1), 73-82.
20. Seinfeld, J. H.; Pandis, S. N., *Atmospheric chemistry and physics from air pollution to climate change*. John Wiley & Sons, Inc: New York, 1998; p 1326.
21. Marr, L. C.; Harley, R. A., Spectral analysis of weekday-weekend differences in ambient ozone, nitrogen oxide, and non-methane hydrocarbon time series in California. *Atmos. Environ.* **2002,** *36* (14), 2327-2335.
22. Marr, L. C.; Noblet, G. S.; Harley, R. A., Formation of photochemical air pollution in central California - 2. Impact of revised emissions on Eulerian model predictions. *J. Geophys. Res.-Atmos.* **2002,** *107* (D5-6).
23. Murphy, J. G.; Day, D. A.; Cleary, P. A.; Wooldridge, P. J.; Millet, D. B.; Goldstein, A. H.; Cohen, R. C., The weekend effect within and downwind of Sacramento - Part 1: Observations of ozone, nitrogen oxides, and VOC reactivity. *Atmos. Chem. Phys.* **2007,** *7* (20), 5327-5339.
24. Thielmann, A.; Prevot, A. S. H.; Gruebler, F. C.; Staehelin, J., Empirical ozone isopleths as a tool to identify ozone production regimes. *Geophys. Res. Lett.* **2001,** *28* (12), 2369-2372.
25. Harley, R. A.; Marr, L. C.; Lehner, J. K.; Giddings, S. N., Changes in motor vehicle emissions on diurnal to decadal time scales and effects on atmospheric composition. *Environ. Sci. Technol.* **2005,** *39* (14), 5356-5362.
26. Marr, L. C.; Black, D. R.; Harley, R. A., Formation of photochemical air pollution in central California - 1. Development of a revised motor vehicle emission inventory. *J. Geophys. Res.-Atmos.* **2002,** *107* (D5-6).
27. Cohan, D. S.; Napelenok, S. L., Air quality response modeling for deciscion support. *Atmosphere* **2011,** *2* (3), 407-425.
28. Dunker, A. M., The Decoupled Direct Method for calculating sensitivity coefficients in chemical-kinetics. *J. Chem. Phys.* **1984,** *81* (5), 2385-2393.
29. Hakami, A.; Odman, M. T.; Russell, A. G., High-order, direct sensitivity analysis of multidimensional air quality models. *Environ. Sci. Technol.* **2003,** *37* (11), 2442-2452.
30. Hakami, A.; Odman, M. T.; Russell, A. G., Nonlinearity in atmospheric response: A direct sensitivity analysis approach. *J. Geophys. Res.-Atmos.* **2004,** *109* (D15).

31. Yang, Y. J.; Wilkinson, J. G.; Russell, A. G., Fast, direct sensitivity analysis of multidimensional photochemical models. *Environ. Sci. Technol.* **1997,** *31* (10), 2859-2868.
32. Emery, C.; Yarwood, G.; Jung, J., Using CAMx/HDDM to estimate ozone levels across the US at various levels of anthropogenic NOx and VOC. In *Community Modeling and Analysis System Annual Conference*, Chapel Hill NC, 2012.
33. Simon, H.; Baker, K.; Possiel, N.; Akhtakr, F.; Napelenok, S. L.; Timin, B.; Wells, B. *Model-based rollback using the higher order direct decoupled method (HDDM)*; memo to EPA Docket # EPA-HQ-OAR-2008-0669: Research Triangle Park, NC, 2012.
34. Byun, D.; Schere, K. L., Review of the governing equations, computational algorithms, and other components of the models-3 Community Multiscale Air Quality (CMAQ) modeling system. *Appl. Mech. Rev.* **2006,** *59* (1-6), 51-77.
35. 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., et al., Incremental testing of the Community Multiscale Air Quality (CMAQ) modeling system version 4.7. *Geosci. Model Dev.* **2010,** *3* (1), 205-226.
36. Napelenok, S. L.; Cohan, D. S.; Odman, M. T.; Tonse, S., Extension and evaluation of sensitivity analysis capabilities in a photochemical model. *Environ. Modell. Softw.* **2008,** *23* (8), 994-999.
37. Grell, G.; Dudhia, J.; Stauffer, D. *A descripton of the Fifth-Generation Penn State/NCAR Mesoscale Model (MM5)*; National Center for Atmospheric Research: Boulder, CO, 1994; p 138.
38. USEPA *Air quality modeling technical support document: final EGU NESHAP*; United States Environmental Protection Agency: Research Triangle Park, NC, 2011.
39. USEPA *Emissions modeling for the final mercury and air toxics standards technical support document*; United States Environmental Protection Agency: Research Triangle Park, NC, 2011.
40. Bell, M. L.; Peng, R. D.; Dominici, F., The exposure-response curve for ozone and risk of mortality and the adequacy of current ozone regulations. *Environ. Health Perspect.* **2006,** *114* (4), 532-536.

Table 1: Modeled and observed fourth highest 8-hr daily maximum ozone values for Charlotte and Detroit area monitoring sites during July-August 2005. Urban sites are shaded in gray.

Area	Monitor	Modeled 4th high 8-hr daily max ozone (ppb)	HDDM adjustment of modeled data: 4th high 8-hr daily max ozone (ppb)	Observed 4th high 8-hr daily max ozone (ppb)	HDDM adjustment of observed data: 4th high 8-hr daily max ozone (ppb)
Charlotte	371090004	76	60	75	61
Charlotte	371190041	**91**	**75**	87	**75**
Charlotte	371191005	88	71	82	68
Charlotte	371191009	88	70	**90**	74
Charlotte	371590021	81	63	84	67
Charlotte	371590022	87	68	86	71
Charlotte	371790003	77	58	76	61
Detroit	260910007	73	57	74	60

Detroit	260990009	83	67	82	70
Detroit	260991003	80	73	**83**	**75**
Detroit	261250001	80	**75**	75	69
Detroit	261470005	81	63	78	65
Detroit	261610008	77	66	70	61
Detroit	261630001	77	71	76	67
Detroit	261630019	**85**	72	80	70

Figure 1. Conceptual picture of 3-step HDDM adjustment approach. The gray line shows a hypothetical ozone concentration response from an infinite number of brute force runs at every possible NOx emission level (P). The red, blue, and green lines represent the first-order approximations of the ozone response curve from the base, 50% NOx cut, and 75% NOx cut DDM sensitivities. Black dots mark the points at which first order sensitivities were derived from base, 50% NOx and 75% NOx cuts. X and Y are used to define the switch points between when sensitivities are used from the 3 DDM simulations as defined in Equations 1-4. The procedure for finding X and Y is described in Section 3.1. The 3-step concentration response estimation procedure begins at current concentrations levels, and incrementally increases the precursor emission reductions until the estimated concentration response meets the desired design value for the entire modeling or measurement period.

Figure 2. Density scatter plots comparing ozone predictions using DDM sensitivites to 75% NOx cuts to model predictions from runs with brute force emissions cuts at Charlotte (top) and Detroit (bottom) sites. These density plots are a variation on the traditional scatterplot with colors representing the percentage of points falling at each location on the plot. Perfect replication of the brute force runs would be represented by all points falling on the 1:1 line. One step DDM adjustment results are shown in left-hand plots and three step DDM adjustment results are shown in right-hand plots.

Figure 3. Hourly modeled ozone distributions for an urban (left) and a non-urban (right) site in Charlotte (top) and Detroit (bottom) for July and August 2005. Centerline shows the median values, boxes show the 25^{th} and 75^{th} percentiles and whiskers extent to 1.5 times the interquartile range. Values from the base model run are shown in blue while values adjusted using HDDM sensitivities to reach 75 ppb for the 4^{th} highest 8-hr daily maximum at the highest site in the area are shown in red/pink.

Figure 4. Depiction of 3-step DDM adjustment approach using sensitivities derived from the linear regression method at 3 different hourly ozone levels. Each panel shows the change in ozone over the entire range of NO_x reductions. The solid line shows the path followed for the 3-step DDM adjustment, while the dotted lines show changes in ozone that would be predicted if the base or step 2 sensitivities were used down to 0 NO_x emissions. Orange dots show change in ozone from model runs employing brute force NO_x emissions cuts on the days that had hourly ozone concentrations at 2 pm within +/- 3ppb

of the hourly ozone concentration being examined (i.e days with hourly ozone between 77 and 83 ppb at 2pm at site 260991003 for the bottom-left panel). Right panels ozone response on 40, 60, and 80 ppb days for urban Detroit site 260991003 at 2pm. Left panels ozone response on 40, 60, and 80 ppb days for downwind Detroit site 260990009 at 2pm.

Figure 5. Hourly observed ozone distributions for an urban (left) and a non-urban (right) site in Charlotte (top) and Detroit (bottom) for July and August 2005. Centerline shows the median values, boxes show the 25th and 75th percentiles and whiskers extent to 1.5 times the interquartile range. Observed values are shown in gray/black while values adjusted using HDDM sensitivities to reach 75 ppb for the 4th highest 8-hr daily maximum at the highest site in the area are shown in red/pink.

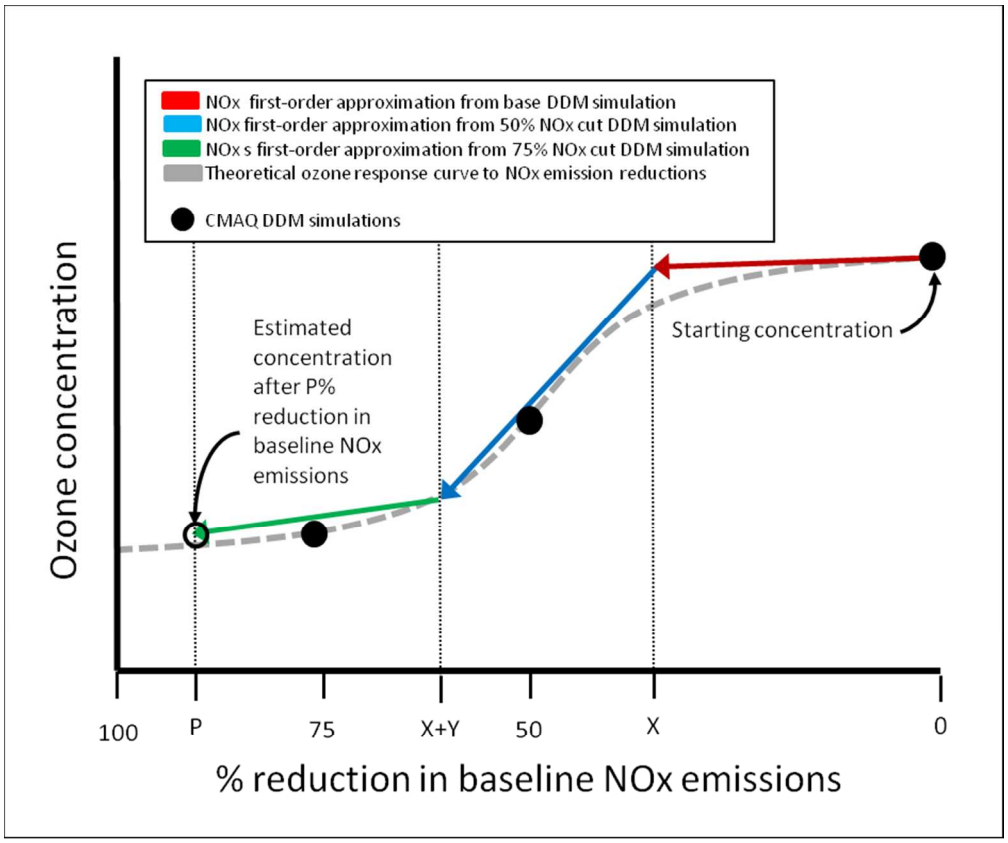


Figure 1. Conceptual picture of 3-step HDDM adjustment approach. The gray line shows a hypothetical ozone concentration response from an infinite number of brute force runs at every possible NOx emission level (P). The red, blue, and green lines represent the first-order approximations of the ozone response curve from the base, 50% NOx cut, and 75% NOx cut DDM sensitivities. Black dots mark the points at which first order sensitivities were derived from base, 50% NOx and 75% NOx cuts. X and Y are used to define the switch points between when sensitivities are used from the 3 DDM simulations as defined in Equations 1-4. The procedure for finding X and Y is described in Section 3.1. The 3-step concentration response estimation procedure begins at current concentrations levels, and incrementally increases the precursor emission reductions until the estimated concentration response meets the desired design value for the entire modeling or measurement period.
158x132mm (150 x 150 DPI)

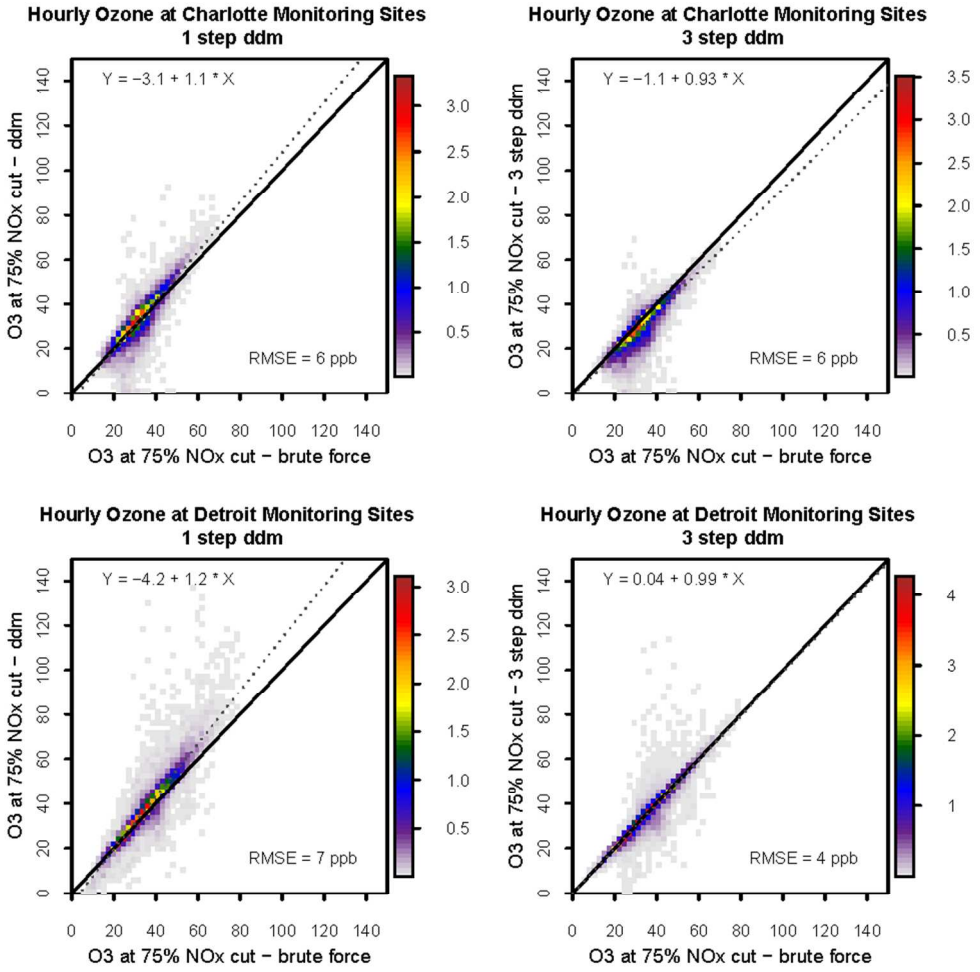


Figure 2. Density scatter plots comparing ozone predictions using DDM sensitivites to 75% NOx cuts to model predictions from runs with brute force emissions cuts at Charlotte (top) and Detroit (bottom) sites. These density plots are a variation on the traditional scatterplot with colors representing the percentage of points falling at each location on the plot. Perfect replication of the brute force runs would be represented by all points falling on the 1:1 line. One step DDM adjustment results are shown in left-hand plots and three step DDM adjustment results are shown in right-hand plots.
127x127mm (200 x 200 DPI)

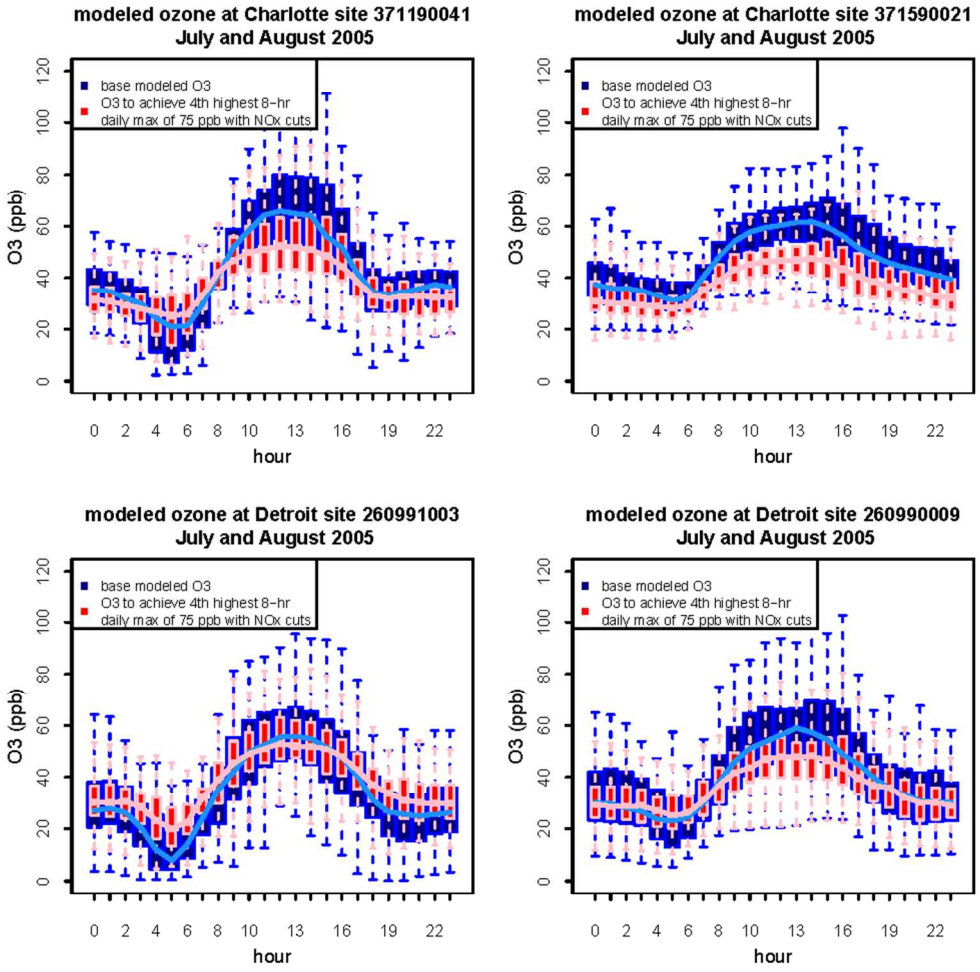


Figure 3. Hourly modeled ozone distributions for an urban (left) and a non-urban (right) site in Charlotte (top) and Detroit (bottom) for July and August 2005. Centerline shows the median values, boxes show the 25th and 75th percentiles and whiskers extent to 1.5 times the interquartile range. Values from the base model run are shown in blue while values adjusted using HDDM sensitivities to reach 75 ppb for the 4th highest 8-hr daily maximum at the highest site in the area are shown in red/pink.
127x127mm (200 x 200 DPI)

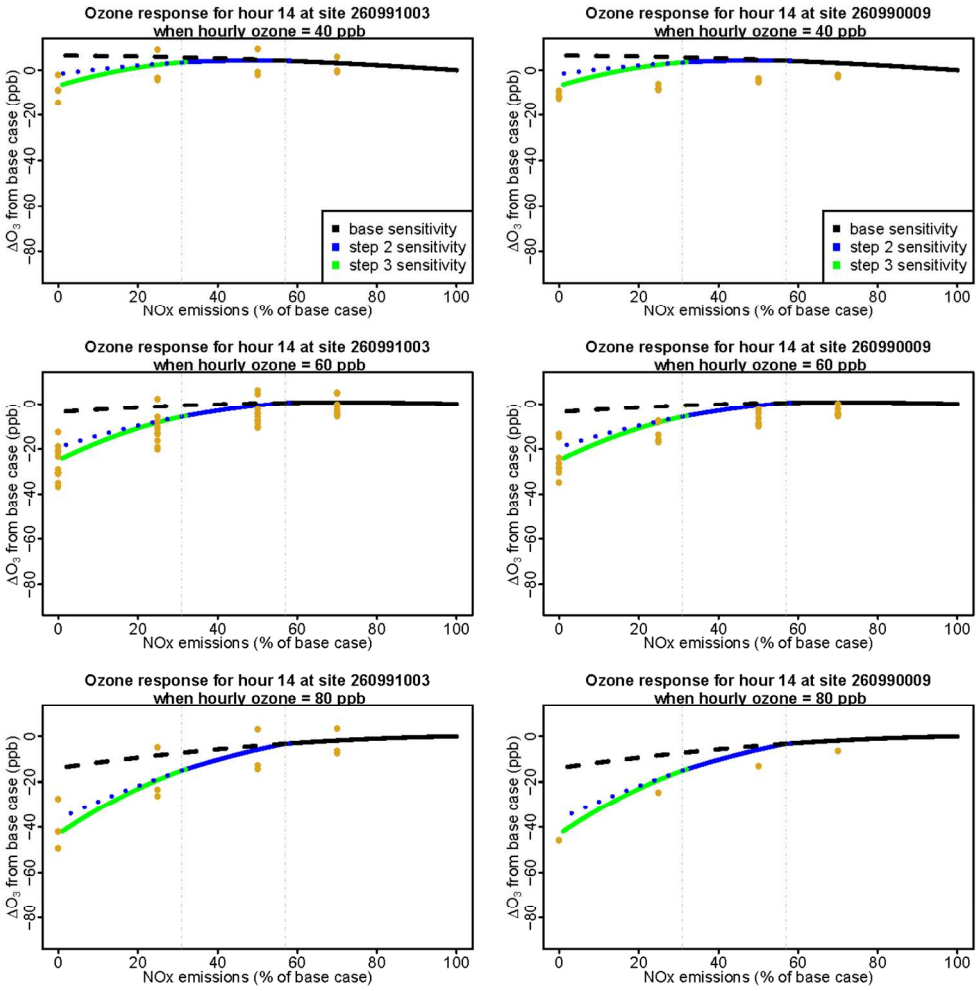


Figure 4. Depiction of 3-step DDM adjustment approach using sensitivities derived from the linear regression method at 3 different hourly ozone levels. Each panel shows the change in ozone over the entire range of NOx reductions. The solid line shows the path followed for the 3-step DDM adjustment, while the dotted lines show changes in ozone that would be predicted if the base or step 2 sensitivities were used down to 0 NOx emissions. Orange dots show change in ozone from model runs employing brute force NOx emissions cuts on the days that had hourly ozone concentrations at 2 pm within +/- 3ppb of the hourly ozone concentration being examined (i.e days with hourly ozone between 77 and 83 ppb at 2pm at site 260991003 for the bottom-left panel). Right panels ozone response on 40, 60, and 80 ppb days for urban Detroit site 260991003 at 2pm. Left panels ozone response on 40, 60, and 80 ppb days for downwind Detroit site 260990009 at 2pm.
177x177mm (200 x 200 DPI)

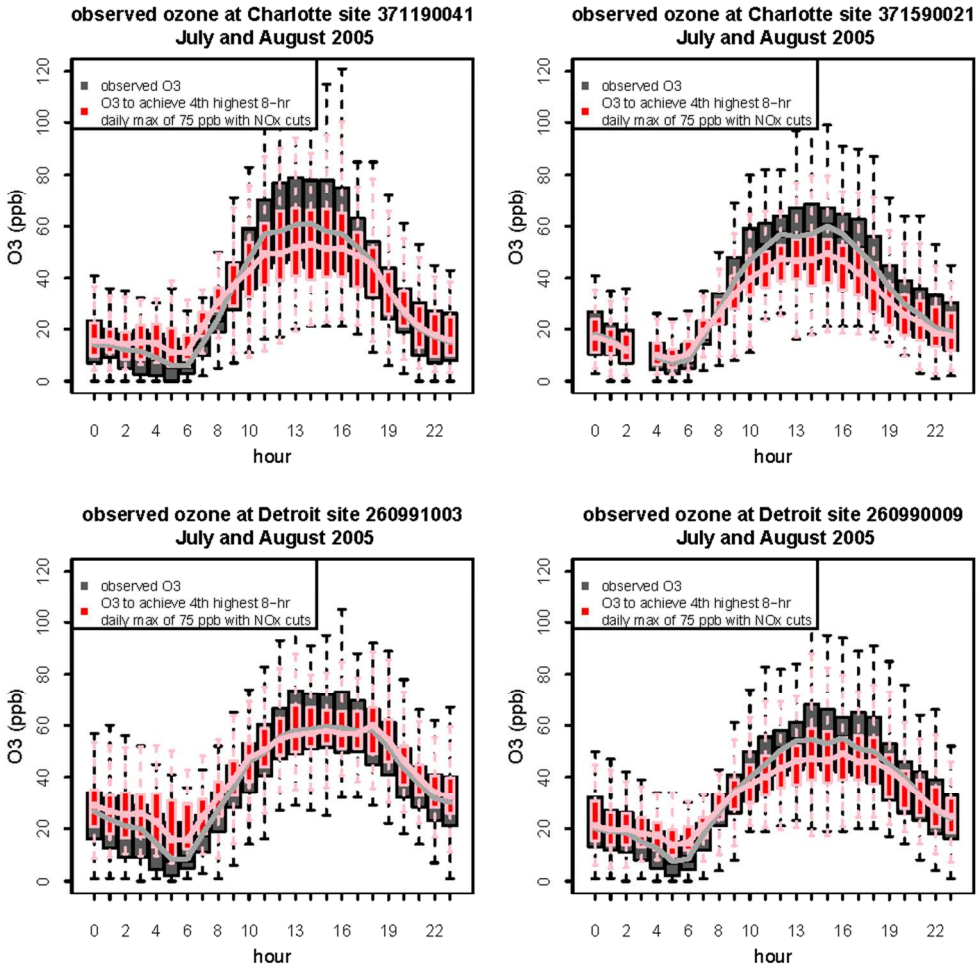
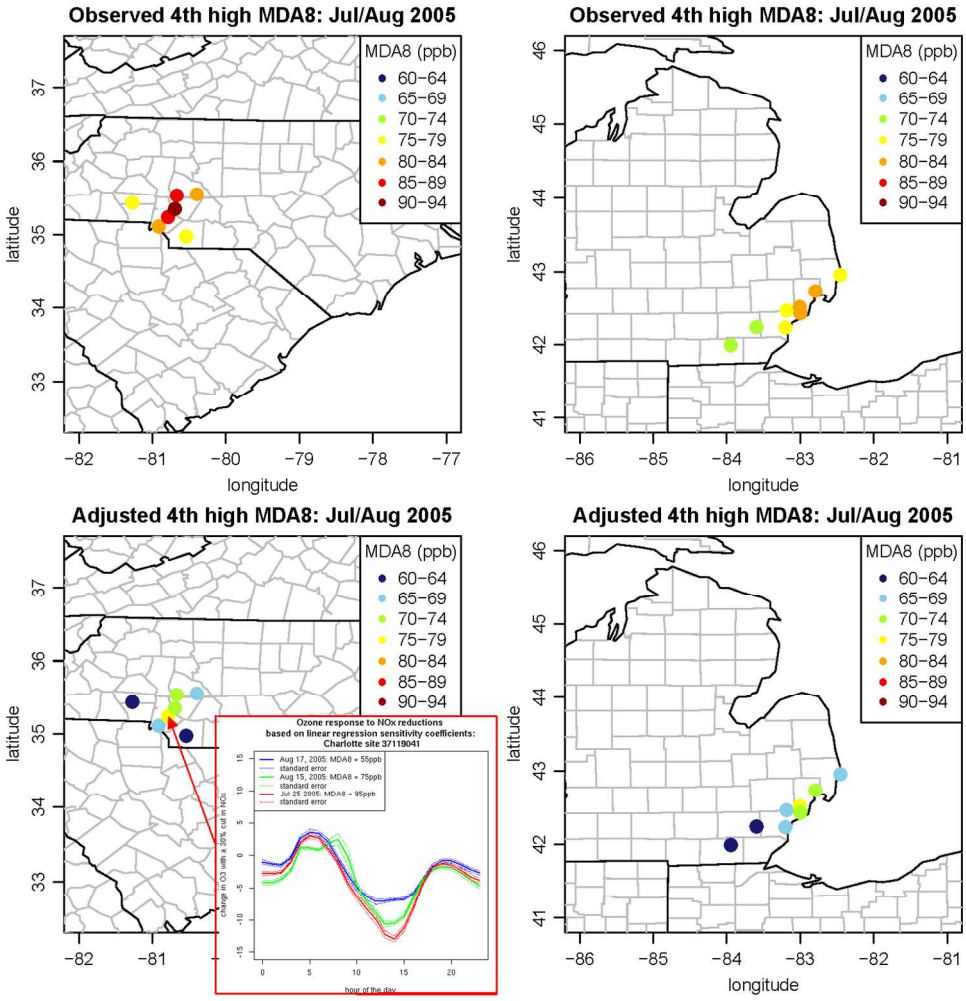


Figure 5. Hourly observed ozone distributions for an urban (left) and a non-urban (right) site in Charlotte (top) and Detroit (bottom) for July and August 2005. Centerline shows the median values, boxes show the 25th and 75th percentiles and whiskers extent to 1.5 times the interquartile range. Observed values are shown in gray/black while values adjusted using HDDM sensitivities to reach 75 ppb for the 4th highest 8-hr daily maximum at the highest site in the area are shown in red/pink.
127x127mm (200 x 200 DPI)



203x203mm (200 x 200 DPI)