SENSITIVITY ANALYSIS OF OZONE IN THE SOUTHEAST

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1. INTRODUCTION

With the onset of more stringent federal standards, dozens of additional counties in the Southeast will likely become non-attainment areas for ground-level ozone. Effective formulation of emission control strategies for ozone attainment requires knowledge of the sensitivity of ozone to its precursor gases, nitrogen oxides (NO_x = $NO+NO_2$) and volatile organic compounds (VOCs).

Traditionally, sensitivity analysis in air quality modeling is conducted by the "brute force method." Ozone concentrations are modeled under "base case" conditions, and differenced from a perturbed run in which one or more emissions rates are altered. However, the brute force method faces key shortcomings: (1) numerical noise for small perturbations, (2) unclear applicability to perturbations other than the size modeled, and (3) burdensome computations when a large number of sensitivity parameters is desired.

The Decoupled Direct Method in 3D (DDM-3D) provides an accurate, computationally efficient alternative to the brute force method [e.g., Yang *et al*., 1997]. DDM-3D operates simultaneously with a base case run to compute the local sensitivity of pollutant concentrations to perturbations in input parameters (initial conditions, boundary conditions, or emission rates).

Earlier, we presented an initial implementation of gas-phase DDM-3D into the Community Multiscale Air Quality (CMAQ) model [Cohan *et al*., 2002]. Here, we present the extension of CMAQ-DDM to compute second-order sensitivity coefficients. We apply CMAQ-DDM to assess the sensitivity of ozone to NO_x and VOC emissions during an air pollution episode in the Southeast.

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2. METHODOLOGY

We have upgraded CMAQ-DDM to reflect the September 2003 release of CMAQ (version 4.3). Though calculations of concentrations reflect the CMAQ aero3 aerosol module, the current implementation of DDM-3D ignores all aerosol and aqueous chemistry processes except heterogeneous hydrolysis of N_2O_5, as this process significantly impacts ozone- NO_x chemistry.

We have extended CMAQ-DDM to compute second-order sensitivity coefficients by the method of Hakami *et al*. (2003). First-order sensitivity coefficients, $s_{ij}^{(1)} = \partial C_i/\partial P_j$, represent the local sensitivity or "slope" of species *i* with respect to input parameter *j*. Second-order sensitivities, $s_{i,j1,j2}^{(2)} = \partial^2 C_i/(\partial P_{j1}\partial P_{j2})$, represent the second-derivative or local "curvature" of the species-parameter relationship. In this paper we present sensitivity coefficients S_{ij} semi-normalized to the size of the unperturbed input field. Thus, for example, if the sensitivity of ozone to domain-wide NO_x emissions is +0.010 ppmV at a given time, then a 10% reduction in NO_x would be expected to reduce ozone concentrations by 0.001 ppmV.

We apply CMAQ-DDM to the Fall-Line Air Quality Study domain for August 11-18, 2000. The base-case modeling of this domain and air pollution episode, along with modifications to eddy diffusivity thresholds in CMAQ, are described by Hu *et al*. (2003). Here, we assess the sensitivity of ozone concentrations within the 12-km domain (5-state region centered on Georgia) to perturbations in anthropogenic NO_x and VOC emissions throughout the 36-km domain (eastern USA).

3.0 RESULTS

3.1 Performance of CMAQ-DDM

We assess the accuracy of CMAQ-DDM sensitivity coefficients by comparing them to finite difference calculations from brute force model runs with NO_x emissions perturbed by +/- 10%. The

statistical agreement between brute-force and CMAQ-DDM calculations of first- and second-order sensitivities is shown in Figure 1. After the initial ramp-up day, r^2 values are consistently greater than 0.98 for first-order sensitivities, and in the range 0.86-0.96 for second-order sensitivities.

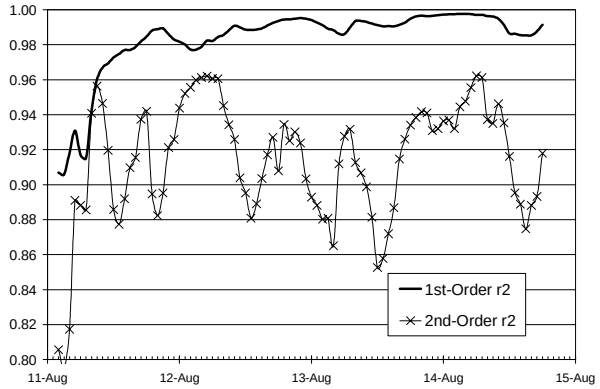

Fig. 1 Time series plot of r^2 values comparing first- and second-order DDM sensitivities to brute force sensitivities, for +/-10% perturbations in domain-wide NO_x emissions.

These r^2 values, along with consistently low levels of bias and error in CMAQ-DDM relative to brute force, indicate that DDM-3D sensitivities are reliable for ozone sensitivity analysis. The lower values for second-order sensitivities reflect the amplification of error in computing what is essentially a "sensitivity of a sensitivity," and a truncation error in the brute force method. The r^2 values for both first- and second-order sensitivities are lower than those reported by Hakami *et al*. (2003) in the Multiscale Air Quality Simulation Platform (MAQSIP), likely because (1) MAQSIP uses shorter timesteps, (2) Hakami *et al*. turned off aerosol and aqueous chemistry processes (CMAQ-DDM, as currently implemented, applies these processes to concentrations but not to sensitivities), and (3) Hakami *et al*. used double precision for brute force outputs.

3.2 Sensitivity of ozone to emissions

Ozone concentrations and their first- and second-order DDM-3D sensitivities with respect to domain-wide NO_x and VOC emissions were calculated throughout the episode. Figure 2 shows time series of modeled and observed ozone concentrations, and first-order semi-normalized sensitivities of concentrations to NO_x and VOC emissions, in Augusta, Macon, and Atlanta, GA. As explained earlier, the sensitivity values can be interpreted by scaling to a perturbation of interest. Negative sensitivity indicates that ozone increases with a reduction in emissions.

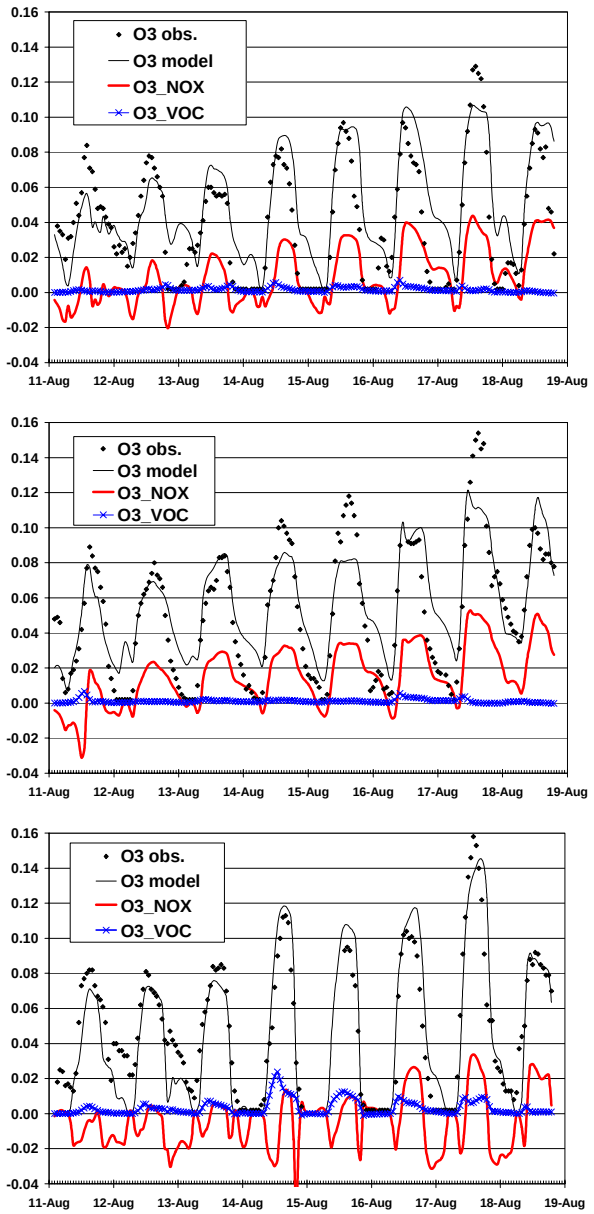

Fig. 2 Time series plot of observed (diamonds) and modeled (thin black line) ozone concentrations, and the first-order sensitivity of ozone to NO_x emissions (red line) and VOC emissions (blue line with x's) at (a) Augusta, (b) Macon, and (c) Atlanta, Georgia, on Aug. 11-18, 2000. Concentrations are in ppmV and sensitivities are scaled to a 100% perturbation.

In Augusta and Macon, daytime sensitivities of ozone to NO_x are positive and track the total concentration. Sensitivity to anthropogenic VOC emissions is very small in these cities, reflecting

NO_x-limited chemistry. In Atlanta, a city with a much larger population and correspondingly greater NO_x emissions, ozone oscillates between positive and negative sensitivity to NO_x emissions. All three cities typically exhibit negative sensitivity to NO_x emissions during the night, when photochemistry is inactive and NO titrates ozone.

Figure 3 shows the ozone concentrations at 5pm on August 17, the peak hour of the episode at many locations. Atlanta and Birmingham exhibit ozone concentrations above 140 ppbv at this hour, and elevated concentrations are also modeled in smaller cities such as Augusta and Macon.

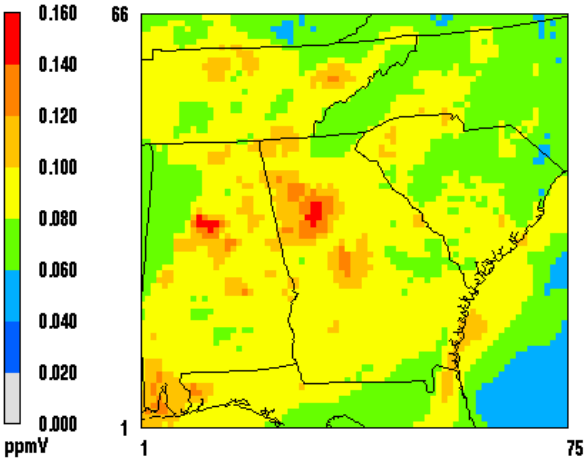

Fig. 3 Modeled ozone concentrations at 5pm EDT, August 17, 2000.

The semi-normalized sensitivity of ozone to anthropogenic NO_x and VOC emissions are shown in Figures 4a and b, respectively. Note that although the scale of Figure 4b is reduced by a factor of 5 relative to Figure 4a, only the cores of major urban areas such as Atlanta, Knoxville, and Charlotte demonstrate significant sensitivity to VOC emissions. The remainder of the Southeast exhibits sensitivity only to NO_x emissions. This NO_x-limited regime reflects the abundant biogenic VOC emissions in the Southeast.

The second-order sensitivity of ozone to NO_x emissions is shown in Figure 4c. Note that values are negative throughout the domain, reflecting an "inverted-U" curvature to the relationship of ozone to NO_x. This indicates that as NO_x emissions reductions increase, ozone concentrations would decrease more rapidly than predicted by the first-order relationship. This is intuitively logical because as NO_x concentrations decrease, the regime becomes more NO_x-limited. The magnitudes of the second-order sensitivities in Figure 4c are spatially correlated with the ozone concentrations in Figure 3, reflecting the more non-linear photochemistry near peak ozone.

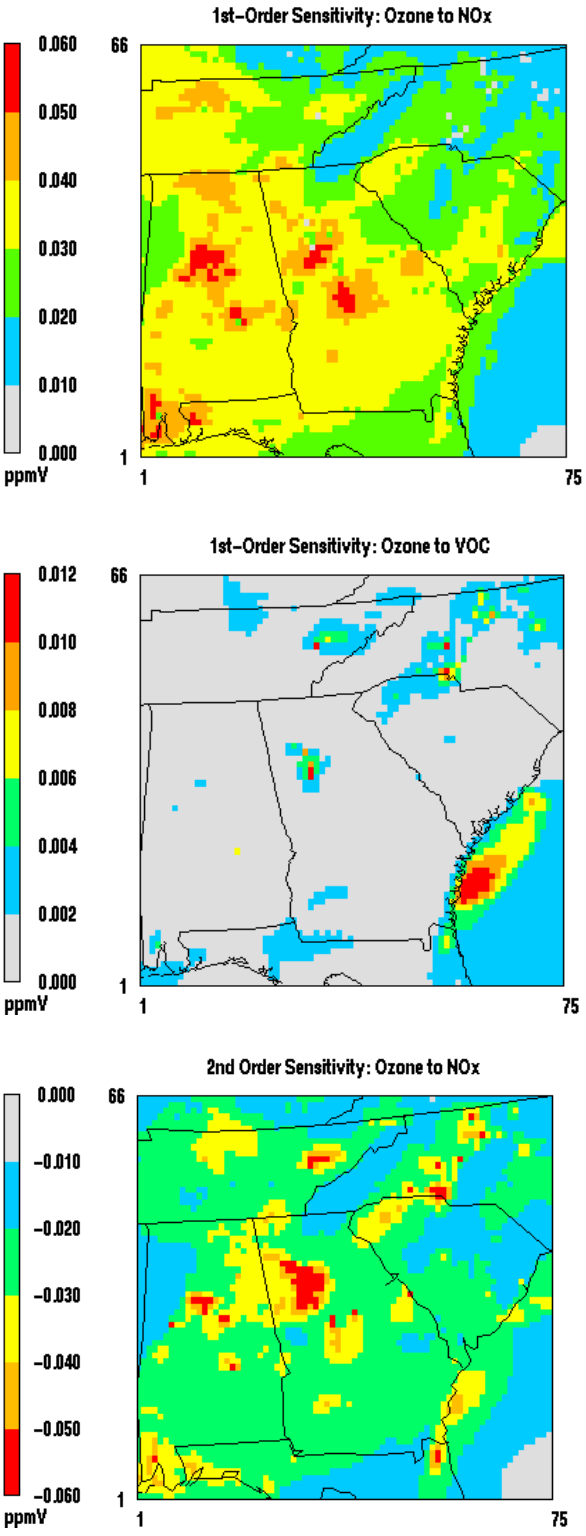

Fig. 4 First-order sensitivity of ozone to (a) NO_x and (b) VOC emissions, and (c) second-order sensitivity to NO_x emissions, at 5pm EDT, August 17, 2000.

The second-order sensitivities of ozone to VOCs ($\partial^2 O_3/(\partial EVOC^2)$)and to NO_x and VOCs ($\partial^2 O_3/(\partial ENO_x \partial EVOC)$) (not shown), when semi-normalized, are typically much smaller in magnitude than the second-order sensitivity of ozone to NO_x. The 3 second-order sensitivities and 2 first-order sensitivities can be inserted into a Taylor expansion to estimate ozone for any combination of NO_x and VOC emissions perturbations with respect to a base case.

$$C(E_{base} + \Delta E_{NOx} + \Delta E_{VOC}) = C(E_{base}) + \Delta E_{NOx} \cdot S_{O3,NOx} + \Delta E_{VOC} \cdot S_{O3,VOC} + \frac{\Delta E_{NOx}^{\ 2}}{2} \cdot S_{O3,NOx,NOx} + \frac{\Delta E_{VOC}^{\ 2}}{2} \cdot S_{O3,VOC,VOC} + \Delta E_{NOx} \Delta E_{VOC} \cdot S_{O3,NOx,VOC}$$

Here, ΔE represents the fractional change in the parameter, and $S_{i,j}$ is the semi-normalized sensitivity of concentration i to parameter j.

The Taylor expansion approximations enable the creation of ozone isopleths as functions of NO_x and VOC emissions at a given location and time [Hakami et al., in preparation]. Figure 5 shows ozone isopleths for Macon and Atlanta at their respective hour of peak modeled concentration on August 17, 2000. Macon is strongly NO_x-limited at this time as reflected in the nearly horizontal isopleths. Similarly horizontal isopleths are also found at Augusta (not shown). The isopleths for Atlanta reflect the more non-linear chemistry associated with its higher base case concentration. Atlanta is still NO_x-limited at this time, but some ozone reduction could be attained by VOC emission reductions.

4. CONCLUSIONS

The applicability of CMAQ-DDM has been demonstrated for sensitivity analysis of ozone to its precursor emissions. CMAQ-DDM, as enhanced with higher-order sensitivities, represents a powerful and computationally efficient tool for addressing key issues in the science and policy of air pollution.

Ozone in the Southeast is shown to be predominately NO_x-limited during the August 11-18, 2000 episode. Anthropogenic VOC emissions become important only in the largest cities, which are also the locations of the most non-linear ozone-NO_x photochemistry.

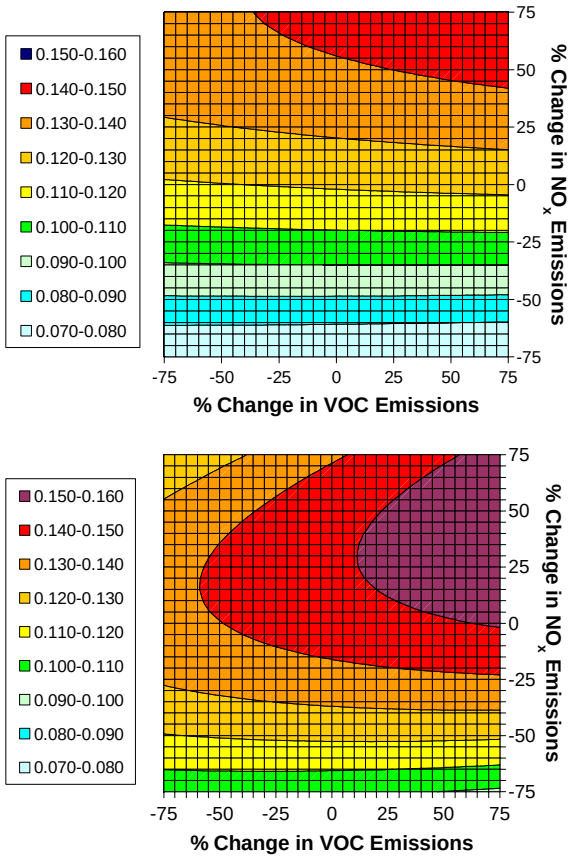

Fig. 5 Isopleths of ozone (in ppmV) at (a) Macon and (b) Atlanta at their hour of peak modeled concentration on Aug. 17, 2000. Axes reflect percentage changes from base case emissions.

5. REFERENCES

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