SENSITIVITY ANALYSIS IN AIR QUALITY MODELS FOR
PARTICULATE MATTER

A Dissertation
Presented to
The Academic Faculty

by

Sergey L. Napelenok

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy in Environmental Engineering
School of Civil and Environmental Engineering

Georgia Institute of Technology
December 2006

COPYRIGHT © 2006 SERGEY L. NAPELENOK
SENSITIVITY ANALYSIS IN AIR QUALITY MODELS FOR
PARTICULATE MATTER

Approved by:

Dr. Armistead G. Russell, Advisor
Department of Civil and Environmental Engineering
Georgia Institute of Technology

Dr. Michael H. Bergin
Department of Civil and Environmental Engineering
Georgia Institute of Technology

Dr. Michael E. Chang
School of Earth and Atmospheric Sciences
Georgia Institute of Technology

Dr. Gary W. Miller
Rollins School of Public Health
Emory University

Dr. M. Talat Odman
Department of Civil and Environmental Engineering
Georgia Institute of Technology

Date Approved: October 9, 2006
To my wife and family
ACKNOWLEDGEMENTS

I would like to thank the many people who have provided their support during my studies. I sincerely appreciate the guidance of my advisor, Professor Armistead (Ted) Russell. He has created and maintained a productive and enjoyable working environment, and I feel honored to have been a part of his research group. I would like to thank my committee members – Dr. Michael H. Bergin, Dr. Michael E. Chang, Dr. Gary Wise, and Dr. M. Talat Odman – for their time and input on my work. I would also like to recognize the members of the Laboratory for Atmospheric Modeling, Diagnostics and Analysis (LAMDA) at Georgia Institute of Technology who have been excellent friends and helpful colleagues. Foremost, I would like to recognize the extent of both knowledge and patience of Dr. Yongtao Hu, who has been tremendously helpful in all matters relating to atmospheric modeling. I have had the pleasure of working with other LAMDA members including my officemates Di Tian, Jaemeen Baek, and Sun-Kyoung (Helena) Park, and also Daniel Cohan, Sangil Lee, Kasemsan Manomaiphiboon, Amit Marmur, Efthimios Tagaris, Amir Hakami, Alper Unal, Michelle Bergin, Burcak Kaynak, Evan Cobb, K.J. Liao, and so many others. Furthermore, I would like to thank the faculty and staff of the School of Civil and Environmental Engineering at Georgia Tech.

Outside of Atlanta, I would like express my gratitude to Professor Brian Lamb of Washington State University who helped me start in this field. Of course, I would be lost without the support and encouragement of my family, and the unbelievable patience and love of my wife Kathy. I also appreciate the suggestions and editing efforts on some chapters by Professor Ronald L. Kincaid.
Finally, I would like to recognize the sources of financial support for this dissertation which have included grants from the U.S. Environmental Protection Agency (RD82897602, RD83107601, RD83096001), Georgia Power, the State of Georgia, as well as the Georgia Tech Presidential Fellowship and the American Meteorological Society Fellowship.
## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>LIST OF SYMBOLS AND ABBREVIATIONS</td>
<td>xvii</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>xviii</td>
</tr>
<tr>
<td><strong>CHAPTER</strong></td>
<td></td>
</tr>
<tr>
<td>1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Overview</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Health Effects of Particulate Matter</td>
<td>3</td>
</tr>
<tr>
<td>1.2.1 Epidemiological Studies</td>
<td>4</td>
</tr>
<tr>
<td>1.2.2 Exposure Studies</td>
<td>10</td>
</tr>
<tr>
<td>1.2.3 Health Effects Summary</td>
<td>12</td>
</tr>
<tr>
<td>1.3 Scope of This Work</td>
<td>13</td>
</tr>
<tr>
<td>2 Decoupled Direct 3D Sensitivity Analysis for Particulate Matter (DDM-3D/PM)</td>
<td>18</td>
</tr>
<tr>
<td>Abstract</td>
<td>18</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>19</td>
</tr>
<tr>
<td>2.2 Method</td>
<td>20</td>
</tr>
<tr>
<td>2.2.1 CMAQ Model</td>
<td>20</td>
</tr>
<tr>
<td>2.2.2 DDM-3D/PM</td>
<td>20</td>
</tr>
<tr>
<td>2.3 Application</td>
<td>25</td>
</tr>
<tr>
<td>2.4 Summary</td>
<td>34</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>34</td>
</tr>
<tr>
<td>----------------</td>
<td>----</td>
</tr>
<tr>
<td>References</td>
<td>35</td>
</tr>
<tr>
<td>3 Regional Source Apportionment of PM$_{2.5}$ in Georgia Using Direct Sensitivities</td>
<td>37</td>
</tr>
<tr>
<td>Abstract</td>
<td>37</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>38</td>
</tr>
<tr>
<td>3.2 Method</td>
<td>39</td>
</tr>
<tr>
<td>3.3 Results and Discussion</td>
<td>43</td>
</tr>
<tr>
<td>3.4 Summary</td>
<td>52</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>53</td>
</tr>
<tr>
<td>References</td>
<td>54</td>
</tr>
<tr>
<td>4 Regional Source Apportionment of PM$_{2.5}$ in Georgia Using Direct Sensitivities Forecasted to 2007</td>
<td>55</td>
</tr>
<tr>
<td>Abstract</td>
<td>55</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>57</td>
</tr>
<tr>
<td>4.2 Method</td>
<td>57</td>
</tr>
<tr>
<td>4.3 Results</td>
<td>61</td>
</tr>
<tr>
<td>4.3.1 Atlanta</td>
<td>64</td>
</tr>
<tr>
<td>4.3.2 Macon</td>
<td>66</td>
</tr>
<tr>
<td>4.3.3 Columbus</td>
<td>67</td>
</tr>
<tr>
<td>4.3.4 Augusta</td>
<td>68</td>
</tr>
<tr>
<td>4.4 Discussion</td>
<td>71</td>
</tr>
<tr>
<td>4.5 Summary</td>
<td>72</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>73</td>
</tr>
<tr>
<td>References</td>
<td>73</td>
</tr>
</tbody>
</table>
5 Area of Influence (AOI) Development: Fast Generation of Receptor-oriented Sensitivity Fields Based on Inversion of Source-oriented Sensitivities 75

Abstract 75
5.1 Introduction 77
5.2 Method 79
  5.2.1 Generation of Forward Sensitivity Fields from AQMs 79
  5.2.2 Receptor-oriented, or Reverse, Sensitivity Fields 81
  5.2.3 Generation of Reverse Sensitivity Fields by Interpolation and Inversion of Forward Sensitivities 82
5.3 Results 90
  5.3.1 Evaluation 91
  5.3.2 Area of Influence Calculation for Atlanta and Columbus, GA 82
5.4 Discussion 97
Acknowledgements 99
References 99

6 Area of Influence (AOI) Sensitivity Analysis: Application to Atlanta, Georgia 102

Abstract 102
6.1 Introduction 104
6.2 Method 105
  6.2.1 Area of Influence (AOI) 105
  6.2.2 Application 106
6.3 Results and Discussion 110
  6.3.1 Ozone Area of Influence 112
  6.3.2 Particulate Matter Area of Influence 116
  6.3.3 Upper Level Emissions 117
LIST OF TABLES

Table 2-1 Statistical Comparison of Brute Force and DDM 3D/PM.a Sensitivities are shown to domain-wide emissions of SO$_2$, NO$_x$, NH$_3$, Xylene, and Terpene. Averages and standard deviations for concentrations and sensitivities are followed by the results of a regression analysis between BF and DDM. Higher correlation coefficients exist for modeled specie – emitted specie pairs for which there are clearly defined direct relationships in the model. 27

Table 3-1 Sensitivity of secondary components of fine particulate matter to emissions of their gaseous precursors in Atlanta, GA. The values presented here are averages over all days in the three episodes and the emissions represent total domain-wide amounts. 51

Table 6-1 Particulate Matter modeling performance for the 1-10 August, 1999 episode. 111

Table 6-2 AOI performance evaluation for sulfate sensitivity in Atlanta to domain-wide emissions of SO$_2$ at the ground level. AOI predicts a higher fraction of the expected sensitivity with four additional points some of which are located upwind and in areas of high SO$_2$ emissions. 121
LIST OF FIGURES

Figure 1-1 PM$_{2.5}$ Non-attainment Areas in Georgia. From 2004 GA EPD Ambient Air Surveillance Report. 2

Figure 1-2 Hypothesized pathways/mechanisms of potential cardiovascular effects of particulate matter. From Air Quality Criteria for Particulate Matter (US-EPA, 2004). 4

Figure 1-3 Adjusted Mortality Rate Ratios in the six cities. P – Portage; T – Topeka; W – Watertown, L – St. Louis; H – Harriman; S – Steubenville. From Dockery et al., 1993, with permission from the Massachusetts Medical Society Copyright © 1993. All rights reserved. 6

Figure 1-4 Risk Ratio and 95% confidence intervals for various pollutants and multi-pollutant models for the association of emergency room visits for cardiovascular disease. With permission from Metzer et al., 2004. 8

Figure 2-1 Fall line Air Quality Study (FAQS) domains used for modeling with three grid-size resolution regions indicated. Dark areas denote urban regions. 26

Figure 2-2 Spatial comparison between DDM and brute force (24-hour average) for the sensitivity of sulfate to domain-wide emissions of SO$_2$ (accumulation mode). 28

Figure 2-3 Numerical Noise in brute force method. Areas of high negative sensitivities exist in cells adjacent with near maximum positives in the brute-force method for the sensitivity of ammonium to domain-wide emissions of SO$_2$. 29

Figure 2-4 Sensitivity of nitrate to domain-wide emissions of SO$_2$ (24-hour average). The brute-force method shows different results depending on the magnitude of the difference used to calculate the sensitivity. At a small difference (upper left), the result is mostly due to numerical noise. 30

Figure 2-5 Sensitivity of sulfate to domain-wide emissions of NH$_3$ (24-hour average). 31

Figure 2-6 Run-time comparison between DDM and brute force. 33

Figure 2-7 CPU time comparison for a five parameter DDM 3D simulation. “CHEM” includes only gas-phase chemistry. “CLD” includes aqueous chemistry, wet deposition, and below cloud mixing. “AERO” includes all physical and chemical aerosol processes except transport. “VHDIFF” and “XYZADV” includes the transport for all species. 33
Figure 3-1  a) The modeling domain (12 km grid nested within the 36 km grid). b) Regional designations within the state of Georgia. Metropolitan areas of Atlanta, Augusta, Columbus, and Macon were treated separately and the rest of the state was divided into central, northern, and southern regions. Emissions in each of these regions, as well as in other individual states in the 12km domain, were considered for the purpose of regional source apportionment.

Figure 3-2  Frequency of CART bins. Analysis was performed for the period of Jan. 1, 2000 – Dec. 31, 2003. Filled circles represent modeled days. (Bin 1 occurred 621 times and was also modeled)

Figure 3-3  Model performance. Total PM$_{2.5}$ during each episode as well as the majority of individual components fall within acceptable limits.

Figure 3-5  Species sensitivities to Tennessee VOC emissions. VOCs use up the OH radical during daylight hours (a). As a result, less sulfuric acid is produced (b). This leads to less Aitken mode sulfate (c) and ultimately less accumulation mode sulfate (d). In the dark, there is little OH (e) and sulfuric acid (f) activity, but the sulfate sensitivities, in both Aitken (g) and Accumulation (h) modes, are advected towards GA. Thus, in Atlanta, TN VOC emissions have a negative impact on PM, while locally in TN more SOA is produced.

Figure 3-4  Episode average source contributions to sensitivities. Emissions from each state and boundary conditions are shown as they contribute to primary and secondary fine particulates. (“other” denotes the sum of contributions from the remaining simulated sources that individually were significant)

Figure 3-6  Daily variations in source contribution for August 2000. Varying emissions and meteorology can lead to difference in total magnitude and composition of the sensitivity at a receptor. (“other” denotes the sum of contributions from the remaining simulated sources that individually were significant)

Figure 3-7  Sources of gaseous precursors emitted in Georgia that lead to the formation of secondary particulate matter in the four cities – a) Atlanta, b) Augusta, c) Columbus, d) Macon. For each city, the total sensitivity that is attributed to GA emissions is shown followed by the total primary and secondary sensitivity sensitivity from all sources in the domain. (“OTHER ” represents the sum of contributions from all other modeled regions)

Figure 3-8  Correlation between sulfate and nitrate sensitivities to domain-wide emissions of SO$_2$ – August 2000. Each point on the chart represents the average of all 24-hour PM concentrations during the 2000 episode in each 12-km resolution grid cell. While the correlation between the two variables is poor, there appears to be a minor “replacement” effect where reducing sulfate through SO$_2$ controls would increase nitrate concentrations slightly.
Figure 4-1  a) The modeling domain (12 km grid nested within the 36 km grid). b) Regional Designations within the state of Georgia. Metropolitan areas of Atlanta, Augusta, Columbus, and Macon were identified and the rest of the state was divided into central, northern, and southern regions. Emissions in each of these region, as well as in other individual states in the 12km domain, were considered for the purpose of regional source apportionment.

Figure 4-2 Daily Emissions of a) SO$_2$, b) NO$_x$, c) NH$_3$, and d) VOC. ATL, MAC, AUG, and COL categories show emissions in counties belonging to the metropolitan areas of Atlanta, Macon, Augusta, and Columbus respectively. N.GA, S.GA, and C.GA are categories of emissions from North, South, and Central Georgia excluding the above metropolitan areas. SCH and BRA are coal-fire power plants Scherer and Branch. SO$_2$ emissions are mostly point sources; NO$_x$ is split between point and mobile sources; NH$_3$ and VOC are primarily from area sources. The two power plants contribute a significant portion of the regions SO$_2$ emissions.

Figure 4-3 Model Performance of Particulate Matter. Poorer performance of organic carbon is likely caused by the under prediction of the formation of secondary organic aerosols by current air quality models.

Figure 4-4 Modeled PM$_{2.5}$ composition in A) Atlanta, B) Macon, C) Columbus, and D) Augusta. Sulfate is the primary component in each city followed by ammonium and biogenic SOA.

Figure 4-5 Contributions to Atlanta PM$_{2.5}$ (“Other Secondary” represents the sum of the rest of the modeled sources that individually did not amount to over 3% of the total contribution.) *Primary categories are contributions from emissions in the entire domain.

Figure 4-6 Contributions to Macon PM$_{2.5}$ (“Other Secondary” represents the sum of the rest of the modeled sources that individually did not amount to over 3% of the total contribution.) *Primary categories are contributions from emissions in the entire domain.

Figure 4-7 Contributions to Columbus PM$_{2.5}$ (“Other Secondary” represents the sum of the rest of the modeled sources that individually did not amount to over 3% of the total contribution.) *Primary categories are contributions from emissions in the entire domain.

Figure 4-8 Contributions to Augusta PM$_{2.5}$ (“Other Secondary” represents the sum of the rest of the modeled sources that individually did not amount to over 3% of the total contribution.) *Primary categories are contributions from emissions in the entire domain.
Figure 4-9 Spatial “foot-print” of different sensitivities. A) shows the sensitivity of sulfate to emissions of SO$_2$ in only Georgia. B) shows the sensitivity of EC to emissions of EC in only Georgia. Sulfate has impacts much further away from the sources of SO$_2$, while primary EC impacts are much more local.

Figure 5-1 (left) Nested 36 and 12-km grid domain and (right) distribution of the 25 sources in the 12-km Georgia domain.

Figure 5-2 Superpositions of a regular grid of 25 directly modeled sensitivity fields for concentrations of aerosol nitrate (a) and ozone (d) to emissions of NO$_x$ for August 2, 1999. Directions of the plumes vary significantly even within short distances. (b) and (e) show superpositions of the same fields interpolated using data withholding (see Eq. 5-18). Besides minor differences, the interpolated fields look the same as the original fields. (c) and (f) show superpositions of the inverted, receptor-oriented, AOI sensitivity fields calculated d for the same positions for the receptors as the sources’ positions of the forward fields.

Figure 5-3 (a) Calculated sensitivity fields for two virtual sources located at $\bar{x}_1$ and $\bar{x}_2$. $dx$ and $dy$ are the cartesian distances from the source locations in the x and y directions, respectively. (b) Sensitivity field for source location $\bar{x}_0$ derived from interpolation of the original sensitivity fields corresponding to $\bar{x}_1$ and $\bar{x}_2$ using Eq. 5-10, i.e. without angular interpolation. (c) Similar to (a), but $dr$ is the distance in the radial direction along the axis of the plume, and $dp$ is the distance perpendicular to the radial direction. (d) Sensitivity field interpolated for $\bar{x}_0$ using angular interpolation (Eqs. 11-13). Note the artificial diffusion of the plume in (b) vs. (d).

Figure 5-4 Correlation between the 25 original fields and interpolated fields using a withholding technique for sensitivity of (a) ozone and (b) NO$_2$ to NO$_x$ emissions. A log-log scale is used.

Figure 5-5 Comparison of known and interpolated sensitivities found after inversion using data withholding for ozone sensitivity to NO$_x$ emissions.

Figure 5-6 Maximum 8-hour average ozone concentrations over Georgia on August 6$^{th}$, 1999. A represents the location of Atlanta, and C the location of Columbus, GA.

Figure 5-7 Forward sensitivity (FS) and AOI pairs for Atlanta: Ozone to NO$_x$ on August 3$^{rd}$ (FS: a; AOI: b) and August 8$^{th}$ (FS: c; AOI: d), and sulfate to SO$_2$ emissions on August 3$^{rd}$ (FS: e; AOI: f) and August 8$^{th}$ (FS: g; AOI: h).
Figure 5-8 Receptor-oriented AOI showing ozone sensitivity in Columbus to NO\textsubscript{x} emissions (ppb per mole/sec) on (a) August 3\textsuperscript{rd} and (b) 8\textsuperscript{th} 1999 and also sulfate sensitivity in Columbus to SO\textsubscript{2} emissions (ug m\textsuperscript{-3} per mole/sec) on (c) August 3\textsuperscript{rd} and (d) 8\textsuperscript{th} 1999. Strong variation between the different fields is apparent, suggesting that decision making based on AOI fields requires data from many different days.

Figure 6-1 Domain used for AOI analysis. a) The larger course grid is 78x66 with 36km resolution and the smaller nested grid is 57x60 with 12km resolution. Urban areas are distinguished by the blue areas. b) Distribution of the preselected sources of forward sensitivities is show as black dots. Sensitivities to emissions of various pollutants were calculated as point sources at these 25 locations and later interpolated for the rest of the grid cells in the domain. Red dots denote the four additional locations used for the refined analysis.

Figure 6-2 Simulated maximum daily 8-hour ozone concentrations for a) 3 August, b) 5 August, c) 7 August, d) 9 August, 1999. Observed and simulated concentrations exceeded the 8-hour NAAQS of 0.8 for ozone each day.

Figure 6-3 Simulated 24-hour averaged PM\textsubscript{2.5} concentrations for a) 3 August, b) 5 August, c) 7 August, d) 9 August, 1999. PM\textsubscript{2.5} is the sum of Aitken and accumulation modes of sulfate, nitrate, ammonium, elemental carbon, primary and secondary organic carbon, and “unspecified” aerosol. Simulated concentrations exceeded the daily averaged NAAQS of 65 ug/m\textsuperscript{3} on the 7\textsuperscript{th} and were well above the annual standard of 15 µg/m\textsuperscript{3} each day.

Figure 6-4 Forward fields of ozone sensitivity to NO\textsubscript{x} emissions on 5 August, 1999 at a) 01:00 b) 06:00 c) 11:00 d) 16:00 and e) 21:00 (8-hour average). Sensitivities are computed to a 1.0 mole/sec increase in NO\textsubscript{x} emissions at each location. The 25 fields were computed independently, but are presented as a summation. Blue areas indicate ozone titration by NO\textsubscript{x} during night-time, while the red areas represent the formation of ozone in the presence of sunlight.

Figure 6-5 Ozone Area of Influence from emissions of NO\textsubscript{x} on a) 3 August, b) 5 August, c) 7 August, d) 9 August, 1999. Results are shown for the 8-hour average at 18:00 on each day.

Figure 6-6 Reverse wind trajectories as computed by the HYSPLIT model ((Draxler and Hess, 1998)) on a) 3 August, b) 5 August, c) 7 August, d) 9 August, 1999. The 100 meter, 24 hour trajectories are shown arriving in Atlanta at 18:00 (red), 16:00 (dark blue), 14:00 (green), 12:00 (light blue). While a) and d) show fairly constant winds, the other two days evidently experienced frequent changes in wind direction which is reflected in the AOI results.
Figure 6-7 Area of Influence on 7 August, 1999 of a) sulfate to SO$_2$ emissions, b) sulfate to NO$_x$ emissions, c) SOA to anthropogenic VOC emissions, d) ammonium to NH$_3$ emissions, e) total PM$_{2.5}$ to NH$_3$ emissions, and f) elemental carbon to elemental carbon emissions. All results are 24-hour averaged.

Figure 6-8 Area of Influence on a) 5 August and c) 7 August, 1999 of sulfate to SO$_2$ emissions at 500 meters and the corresponding day’s – b), d) – contribution of the same sensitivity (calculated as the product of emissions at 500 meters and the AOI). All results are 24-hour averaged.

Figure A-1 Sulfate sensitivity to domain-wide emissions of SO$_2$ for brute force (left side) and DDM (right side)

Figure A-2 Sulfate sensitivity to domain-wide emissions of NO$_x$ for brute force (right side) and DDM (left side)

Figure A-3 Sulfate sensitivity to domain-wide emissions of NH$_3$ for brute force (left side) and DDM (right side)

Figure A-4 Nitrate sensitivity to domain-wide emissions of SO$_2$ for brute force (left side) and DDM (right side)

Figure A-5 Nitrate sensitivity to domain-wide emissions of NO$_x$ for brute force (left side) and DDM (right side)

Figure A-6 Nitrate sensitivity to domain-wide emissions of NH$_3$ for brute force (left side) and DDM (right side)

Figure A-7 Ammonium sensitivity to domain-wide emissions of SO$_2$ for brute force (left side) and DDM (right side)

Figure A-8 Ammonium sensitivity to domain-wide emissions of NO$_x$ for brute force (left side) and DDM (right side)

Figure A-9 Ammonium sensitivity to domain-wide emissions of NH$_3$ for brute force (left side) and DDM (right side)

Figure A-10 Anthropogenic SOA sensitivity to domain-wide emissions of xylene for brute force (left side) and DDM (right side)

Figure A-11 Biogenic SOA sensitivity to domain-wide emissions of terpenes for brute force (left side) and DDM (right side)
LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOI</td>
<td>Area of Influence</td>
</tr>
<tr>
<td>AQM</td>
<td>Air Quality Model</td>
</tr>
<tr>
<td>CMAQ</td>
<td>Community Multiscale Air Quality Model</td>
</tr>
<tr>
<td>DDM-3D/PM</td>
<td>Decoupled Direct Method in Three Dimensions for Particulate Matter</td>
</tr>
<tr>
<td>EC</td>
<td>Elemental Carbon</td>
</tr>
<tr>
<td>MM5</td>
<td>Mesoscale Meteorological Model version 5</td>
</tr>
<tr>
<td>NAAQS</td>
<td>National Ambient Air Quality Standards</td>
</tr>
<tr>
<td>OC</td>
<td>Organic Carbon</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>Particulate Matter with aerodynamic diameter less than 2.5 $\mu$m</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>Particulate Matter with aerodynamic diameter less than 10.0 $\mu$m</td>
</tr>
<tr>
<td>SMOKE</td>
<td>Sparse Matrix Operator Kernel Emissions</td>
</tr>
<tr>
<td>SOA</td>
<td>Secondary Organic Aerosol</td>
</tr>
<tr>
<td>US-EPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
</tr>
</tbody>
</table>
SUMMARY

Fine particulate matter (PM$_{2.5}$) has been associated with a variety of problems that include adverse health effects, reduction in visibility, damage to buildings and crops, and possible interactions with climate. Although stringent air quality regulations are in place, policy makers need efficient tools to test a wide range of control strategies. Sensitivity analysis provides predictions on how the interdependent concentrations of various PM$_{2.5}$ components and also gaseous pollutant species will respond to specific combinations of precursor emission reductions. The Community Multiscale Air Quality Model (CMAQ) was outfitted with the Decoupled Direct Method in 3D for calculating sensitivities of particulate matter (DDM-3D/PM). This method was evaluated and applied to high PM$_{2.5}$ episodes in the Southeast United States. Sensitivities of directly emitted particles as well as those formed in the atmosphere through chemical and physical processing of emissions of gaseous precursors such as SO$_2$, NO$_x$, VOCs, and NH$_3$ were calculated. DDM-3D/PM was further extended to calculate receptor oriented sensitivities or the Area of Influence (AOI). AOI analysis determines the geographical extent of relative air pollutant precursor contributions to pollutant levels at a specific receptor of interest. This method was applied to Atlanta and other major cities in Georgia. The tools developed here (DDM-3D/PM and AOI) provide valuable information to those charged with air quality management.
CHAPTER 1

INTRODUCTION

1.1 Overview

Particulate Matter (PM) control is perhaps the most complex piece of the current air quality puzzle. PM is a mixture of liquid and solid particles of varying size, chemical composition, and origin. Suspended particles in the air have been linked to adverse health effects in people (Dockery et al., 1993; Peel et al., 2005; Sarnat et al., 2006), visibility reduction (Latha and Badarinath, 2005), damage to buildings and crops (Baptista-Neto et al., 2006), and may impact the climate (IPCC, 2001). The potential of PM to do harm to the human body is dependent on its ability to penetrate into the lungs after inhalation. Thus, PM is regulated in most countries on the basis of size. “Super-coarse” particles range in size between 10 and 40 micrometers and sometimes larger. They settle quickly out of the atmosphere, and do not penetrate into the lungs efficiently if inhaled. While “super-coarse” particle pollution is still important to consider, it is the finer particles that have been linked to adverse health effects after penetrating into the tracheobronchial and alveolar regions of the respiratory tract. “Fine” particulate matter is distinguished by having an aerodynamic diameter smaller than 2.5 micrometers and is designated as PM$_{2.5}$. “Coarse” particles that fall in the range between 2.5 and 10 micrometers are inhalable, but settle in the upper regions of the respiratory system. “Ultrafine” particles, smaller than 0.1 micrometers, are generally exhaled. The United States Environmental Protection Agency (US EPA) has several regulations concerning particulate matter under the National Ambient Air Quality Standards (NAAQS). The
long-term standard for PM$_{2.5}$ is 15 $\mu$g/m$^3$ averaged over one year (calculated as the average of three latest annual averages) and the short-term standard is 65 $\mu$g/m$^3$ averaged over 24 hours (calculated as the three year average of the 98th percentile concentrations). PM$_{10}$ standards are set at 50 $\mu$g/m$^3$ averaged annually and 150 $\mu$g/m$^3$ averaged over 24 hours. Lower standards are currently under consideration.

The state of Georgia has several areas that are in non-attainment of the PM$_{2.5}$ standards, particularly the counties including and surrounding the Atlanta metropolitan area (Figure 1-1). Several millions of people reside in these designated areas and are potentially exposed to unhealthy levels of particulate pollutants.

Figure 1-1 PM$_{2.5}$ Non-attainment Areas in Georgia. From 2004 GA EPD Ambient Air Surveillance Report.
1.2 Health Effects of Particulate Matter

Perhaps the major concern with elevated particulate matter levels is their effects on the general health of the population. The more sensitive segment of the population, such as children, elderly, those with preexisting heart or lung conditions, is most at risk. However, general loss of productivity, decreased lung function, symptomatic effects associated with bronchitis, asthma, and emphysema, enhancement of allergic response to allergens, and premature death are possible health related endpoints for all people exposed to PM$_{2.5}$. The most important exposure mechanism for particulate matter is through inhalation. Fine particles enter the thoracic region of the respiratory tract where they are potentially deposited. Accumulation mode particles generally deposit in greater quantity in the tracheobronchial and alveolar regions of the respiratory tract, because both larger and ultrafine sized aerosols are more efficiently removed higher. Deposition is greater in the regions of airway bifurcations. The removal of the particles is dependent on the region of deposition. In the alveoli, removal through endocytosis and by macrophages is most common. In the trachea and bronchioles, removal is more common through mucociliary transport and coughing. Soluble particles in both regions can also be absorbed into the bloodstream (US-EPA, 2005). Many mechanisms have been hypothesized and tested through which particulate matter can effect human health (Figure 1-2).

In order to quantify the relationships between particulate matter and specific health outcomes, several approaches have been developed. These have included epidemiologic studies that seek to link ambient PM$_{2.5}$ concentrations with hospital visits
for cardiovascular distress and also toxicological exposure studies which have used human volunteers, laboratory animals, and in vitro tissue samples.

Figure 1-2 Hypothesized pathways/mechanisms of potential cardiovascular effects of particulate matter. From Air Quality Criteria for Particulate Matter (US-EPA, 2004).

1.2.1 Epidemiological Studies

The classic epidemiological study that is often cited as the strongest evidence of a link between particulate air pollution and increased mortality is the Harvard School of
Public Health Six Cities study (Dockery et al., 1993). This study tracked the health of over 8,000 residents for up to 16 years starting in 1974. Six U.S. cities were sampled randomly to collect the volunteers: Watertown, MA; Harriman, TN; St. Louis, MO; Steubenville, OH; Portage, WI; and Topeka, KS. The subjects were polled annually on their vital status and their death certificates were obtained to confirm the causes of death. During the period of study, air pollution data were collected for total suspended particulate matter, sulfur dioxide, ozone, and particulate sulfate. PM data were further classified by size with size-selective aerosol samplers. Using these data, life-table survival probabilities for each year from the beginning of the study and mortality rates were calculated for each city. The major impact of this study was that the researchers were among the first to correct for many of the confounding risk factors that included age, sex, cigarette smoking, education level, body-mass index, and occupational exposure. The six cities had very different levels of particulate pollution and also mortality rates. After adjusting for confounders, these differences were statistically significant. It was concluded that mortality was more strongly associated with fine particles and specifically sulfate, than with gaseous pollutants and total suspended particulates. The most common causes of death associated with PM were usually lung cancer and cardiopulmonary disease. However, both overall mortality and mortality from cardiopulmonary causes were positively associated with fine particulate matter. Steubenville was found have the highest averaged annual sulfate and PM$_{2.5}$ concentrations and also the highest mortality rates (Figure 1-3).
The Harvard Six Cities study played an important and perhaps controversial role in establishing the current standards for particulate matter in the United States. For this reason, the data from this study have been reanalyzed. While some minor discrepancies in original questionnaires, death certifications, and data processes have been identified, the same results were reproduced after correction (Krewski et al., 2004). Follow-up studies in the U.S. and other parts of the world have also shown positive associations between PM$_{2.5}$ and increased mortality risks (Lee et al., 2000; Medina et al., 2004; Laden et al., 2006).

A more recent epidemiological study was conducted at the Rollins School of Public Health at Emory University (Metzer et al., 2004; Peel et al., 2005). Referred to as the Study of Particles and Health in Atlanta (SOPHIA), this study also tried to establish a relationship between ambient air pollutants and cardiovascular disease. Over four million emergency department visits were reviewed from 31 hospitals in the Atlanta area between the years of 1993 and 2000. Size and chemical composition sampling of particulate matter from a network of sites was collected for the majority of the time.
period. Chemical composition of PM$_{2.5}$ was considered in order to discern possible differences in their health effects. Whereas the majority of previous epidemiological studies were concerned primarily with total mass and sometimes with sulfate concentration, this study also considered organic and elemental carbon, metals, and acidity in addition to gaseous criteria pollutants of O$_3$, NO, CO, and SO$_2$. With the wealth of health outcome and air pollution data, researchers were able to provide correlations for each pollutant independently as well as several combinations (Figure 1-4). The study also accounted for the possibility of lag between exposure and exacerbation of a cardiovascular condition.
Figure 1-4  Risk Ratio and 95% confidence intervals for various pollutants and multi-pollutant models for the association of emergency room visits for cardiovascular disease. With permission from Metzer et al., 2004.

An important consideration of any epidemiological study that aims to link ambient air pollutants with health effects is the issue of exposure. People tend to spend the majority of their time indoors. With different ventilation systems in homes, schools,
offices, etc., the ambient concentrations might not represent true exposure. Furthermore, since air pollutants are not exactly perfectly mixed in the indoor air either, a true representation of an individual’s exposure is the measurement of the personal air they breathe. Various research efforts have tried to investigate the problem of outdoor, indoor, and personal exposure. Recently, the Health Effects Institute (HEI) has published the results of their study – Relationship of Indoor, Outdoor, and Personal Air (RIOPA) (Weisel et al., 2005). This study measured some VOC species, carbonyls, and PM$_{2.5}$ in the ambient atmosphere, inside of subjects’ homes and vehicles, and in their personal space. The study was not designed to represent a greater population, since homes near significant sources were preferentially selected. However, valuable information that is applicable to the population at large was still uncovered. Most importantly, this study tried to quantify the contribution of outdoor concentrations to indoor and personal air. For PM$_{2.5}$, and also for VOC and carbonyls, personal concentrations were consistently higher than both indoor and outdoor levels. Outdoor concentrations were determined to contribute as much as 60% to personal concentrations. However, indoor sources from activities such as cooking and cleaning often dominated personal air. Depending on the air exchange ratios with the outside and the ventilation systems in individual homes, there was considerable correlation between ambient outdoor concentrations and personal concentrations. This suggests that while individual exposure may not be equivalent to what is measured by air quality monitoring stations, outdoor concentrations can still be used as surrogates of exposure in epidemiological studies.
1.2.2 Exposure Studies

Complementary to the epidemiological studies, several toxicological exposure studies have explored the mechanisms through which PM affects the body. As mentioned previously, these effects are mainly respiratory and cardiovascular. Laboratory animals, human volunteers, and also in vitro tissue samples have been issued as hosts for exposure to particulates of various compositions and from various sources.

Respiratory responses of PM exposure are generally manifested through pulmonary inflammation and direct effects on lung tissue. The individual health status, exposure parameters, and chemical characteristics of the particles determine more specific mechanisms. One study exposed laboratory rats to concentrated ambient particles collected in Boston, MA (Clarke et al., 1999). Some rats had SO$_2$-induced bronchitis prior to the exposure to represent a sensitive sub-population. After the experiment, both healthy and bronchitic rats exhibited an increase in tidal volume, significant pulmonary inflammation, increases in neutrophils, lymphocytes, and lavage protein. The bronchitic rats were more significantly affected by PM exposure. The researchers also concluded that two response mechanisms were evident: pulmonary function reaction through increased air flow; and acute pulmonary inflammation.

Particles originating from mobile sources, specifically elemental and organic carbon, have been thoroughly investigated for their effects on the respiratory system. Mobile source particles are important, because individual exposure can be quite high near major roadways, where a surprising number of schools, sporting venues, and other busy locations are found. Diesel engines produce higher concentrations of particles than their gasoline counterparts. When diesel fuel burns in an engine, a large quantity of soot
particles containing polycyclic aromatic hydrocarbons (PAHs) and also various gaseous pollutants like NO\textsubscript{x}, SO\textsubscript{2}, various VOCs, and carbon monoxide are produced. Exposed to high concentrations of this mixture, people can experience irritation of mucous membranes, lightheadedness, headaches, general weakness, wheezing, and vomiting. One study found that exposure to diesel exhaust particle levels such as those found presently in urban environments impairs the regulation of vascular tone and endogenous fibrinolysis (Mills et al., 2005). In an independent study, healthy volunteers were exposed to high concentrations (100 µg/m\textsuperscript{3}) of diesel exhaust particles (Behndig et al., 2006). Mucosal biopsies were taken at 18 hours past exposure to examine the effects. The researchers observed an increase in bronchial mucosa neutrophil, mast cell numbers, interleukin-8, and myeloperoxidase concentrations. These outcomes point to increased antioxidant responses in the airway and alveolar regions. Diesel particles have also been shown to suppress the defenses against bacterial infection in the pulmonary system (Yin et al., 2005). This was determined by exposing laboratory rats to high concentrations of particles (21.2 mg/m\textsuperscript{3}) through inhalation. After the PM exposure, *Listeria monocytogenes* was administered to the rats. The results showed that diesel particle exposure prolonged the growth of bacteria. The researchers suggested that similar impacts on the pulmonary health of humans are possible.

Other combustion source particles, specifically residual oil fly ash, have also been investigated. These particles are characterized by their high water soluble sulfate and metal content. Intratracheal instillation of varying doses of fly ash particles have been shown to trigger severe inflammation. Fly ash may contain metals, such as Fe, Ni, and V, deposition of which leads to lung injury. Furthermore, a study on rats showed that
individual transitional metal sulfates caused less injury than a fly ash mixture suggesting that chemical interactions play a significant role (Kodavanti et al., 1997). Other fly ash studies have also shown that the metal composition is critical in the types of responses it produces.

While studies of the impacts of PM$_{2.5}$ exposure on the cardiovascular system are fewer, there is still evidence that inhalation of particles has cardiovascular endpoints. Generally, effects stem from the uptake of particles in the blood and the subsequent responses of the heart and circulatory system. This mechanism is possible for soluble and ultrafine particles. One study found increased blood fibrinogen levels after exposing volunteers to concentrated ambient PM collected in Chapel Hill, NC (Ghio et al., 2000), but other pathways are also possible (Figure 1-2). For example, pulmonary reflexes stemming from PM inhalation may result in the autonomic nervous responses that could alter heart rhythm.

Long-term air pollution exposure has also been considered. A recent study exposed mice for a period of six months to concentrated ambient particles (Sun et al., 2005). Some mice were fed a more high-fat diet, and others acted as a control group. Composite atherosclerotic plaque and vasomotor tone were measured as outcomes. High-fat diet mice exposed to PM$_{2.5}$ showed significantly higher responses in these outcomes compared to their counterparts. It was concluded that long-term exposure to low concentrations of PM$_{2.5}$ altered vasomotor tone, and induced vascular inflammation.

1.2.3 Health Effects Summary

Risk ratios obtained by epidemiological studies associated with PM$_{2.5}$ exposure and various health outcomes are generally not much greater than 1.0. However, the
correlations are frequently statistically significant and, when coupled with laboratory exposure study results, they are convincing enough to lead the US-EPA and other regulatory bodies to set ambient standards. A broad range of cardiovascular and respiratory health endpoints is possible from exposure to PM$_{2.5}$. Both short-term exposure to high concentrations of particles and long-term exposure to levels consistent with urban ambient concentrations have been shown to cause adverse health effects. Toxicological studies have been key in coupling specific PM characteristics with health endpoints, showing interactive effects of various aerosol and gaseous pollutants, identifying susceptible population subgroups, and determining exposure-response relationships.

1.3 Scope of This Work

Health effects of particulate matter have been found to correlate with PM concentrations. A clear understanding of the sources of PM is necessary in order to effectively reduce concentrations. This dissertation explores how the origins of both primary and secondary components of fine particulate matter can be determined using sensitivity analysis in air quality models (AQMs). While this thesis focuses on cities in Georgia, the tools developed as part of this work can be applied to any other episode or region.

Thesis chapters include the following:

- **Chapter 2: Decoupled Direct 3D Sensitivity Analysis For Particulate Matter (DDM-3D/PM)**. A method for calculating direct sensitivities is integrated into the latest version of the Community Multiscale Air Quality (CMAQ) model (version 4.3). Sensitivities of various PM$_{2.5}$ components are calculated and
compared with the traditional “brute-force” approach both in terms of magnitudes and computational time.

- **Chapter 3: Regional Source Apportionment of PM$_{2.5}$ in Georgia Using Direct Sensitivities.** The sources of PM$_{2.5}$ are examined using DDM-3D sensitivities during three summer-time episodes in four major cities in Georgia – Atlanta, Augusta, Columbus, and Macon. Sensitivities are calculated based on defined geographical areas in order to discern their relative importance. Long range transport into the region is considered. Interactions between different PM$_{2.5}$ components are explored in their response to possible controls.

- **Chapter 4: Regional Source Apportionment of PM$_{2.5}$ in Georgia Using Direct Sensitivities Forecasted to 2007.** A summer episode is projected to the year 2007 and sensitivities are calculated again to pre-defined geographical areas. On-the-books controls and economic growth in the region are considered.

- **Chapter 5: Area of Influence (AOI) Development: Fast Generation of Receptor-oriented Sensitivity Fields Based on Inversion of Source-oriented Sensitivities.** A method for efficiently generating reverse sensitivities from receptors is developed. Forward sensitivities originating at regularly spaced point sources throughout the domain are extrapolated and inverted to obtain AOIs. AOIs map the potential responses that receptor pollutant levels would have to pollutant sources at locations upwind.

- **Chapter 6: Area of influence (AOI) sensitivity analysis: application to Atlanta, Georgia.** AOI analysis is applied with Atlanta, Georgia as the receptor. Reverse sensitivities for various PM$_{2.5}$ components and also ozone are calculated.
The geographic extent of the influence on Atlanta of primary and secondary particulates and ozone is determined.

- **Chapter 7: Conclusions and Future Research.** Major findings of this work are summarized and recommendations for further research directions are presented.

- **Appendix A: Spatial Comparison of Brute Force and DDM-3D/PM Sensitivity Calculations.** Additional comparisons between two methods of sensitivity calculation are provided as an extension to Chapter 2.

**References**


CHAPTER 2

Decoupled Direct 3D Sensitivity Analysis
For Particulate Matter (DDM-3D/PM)∗

Abstract

The Decoupled Direct Method (DDM) and DDM-3D have been implemented in air quality models in order to efficiently compute sensitivities. Initial implementation of DDM/DDM-3D in models was confined only to gas phase species as the treatment of sensitivities in the dynamics of secondary aerosol formation is more complex. Here, it is extended to calculate particulate matter sensitivities. DDM-3D/PM results compare well spatially and temporally with the traditional brute force approach, particularly for species responses to emissions of their “parent” precursor (e.g., sulfate to SO₂ emissions.) Correlations of more indirect relationships between aerosols and gaseous emissions (e.g., nitrate to SO₂ emissions) are worse, but these sensitivities are usually small. DDM-3D/PM appears to work better than the brute force approach in some cases due to numerical noise and other factors, as identified from the application on a southeastern U.S. domain for a summer episode. DDM-3D/PM is also computationally efficient. While CPU usage was found to scale linearly with the number of sensitivity parameters of interest (for a given domain size), it was significantly less than using the brute force approach.

2.1 Introduction

Policy makers are tasked with developing control strategies to lower levels of air pollutants, including particulate matter (PM). In order to simulate various different strategies, the ability to quickly and efficiently calculate the response of ambient concentrations of various gaseous and aerosol pollutants in the atmosphere to changes in emissions is increasingly more important. Due to the non-linear relationship between ozone and secondary particulate matter components with their precursors, several directions might exist to lower final ambient concentrations, and the levels of control required are not immediately known. The Decoupled Direct Method in 3D has proven to be a powerful and efficient approach to identifying how sources impact ozone and particulate matter air quality for use in policy development (Dunker, 1984; Mendoza-Dominguez et al., 2000; Dunker et al., 2002; Odman et al., 2002). DDM-3D operates with an underlying atmospheric model to simulate pollutant concentrations and simultaneously compute local sensitivities of pollutant concentrations to perturbations in input parameters such as emission rates and initial and boundary conditions.

During the Southern Appalachians Mountains Initiative (SAMI), DDM-3D was extended in the urban-to-rural multi-scale (URM) model to treat secondary particulate matter formation in addition to gas phase species (Odman et al., 2002). Later, Dunker and associates extended the CAMx air quality model to include DDM for treatment of gas-phase pollutants (Dunker et al., 2002). Recently, Cohan and associates implemented the higher order DDM-3D for gas phase species in the Community Multiscale Air
Quality (CMAQ) model to develop an optimized air quality strategy in the state of Georgia (Cohan et al., 2005) following the work of Hakami and associates (Hakami et al., 2003). CMAQ is a widely-used air quality model with detailed physical and chemical treatment of gaseous and condensed phase pollutant dynamics (Byun and Ching, 1999). Here we describe the extension of CMAQ (version 4.3) DDM-3D to include PM formation and transformation (DDM-3D/PM), and evaluation of its accuracy and computational performance.

### 2.2 Method

#### 2.2.1 CMAQ Model

CMAQ is an Eulerian photochemical model that simulates the emissions, transport, and chemical transformations of gases and particles in the troposphere. Similar to other photochemical transport models, CMAQ numerically solves the species conservation governing reactive transport as follows:

\[
\frac{\partial C_i}{\partial t} = -\nabla (uC_i) + \nabla (K \nabla C_i) + R_i + E_i
\]  

(2-1)

where \(C_i\) is the concentration of specie \(i\), \(u\) is the fluid velocity, \(K\) is the eddy diffusivity tensor, \(R_i\) is the net rate of chemical generation of specie \(i\), and \(E_i\) is rate of addition of the specie (emissions). A detailed description of CMAQ is available elsewhere (US-EPA, 1999).

#### 2.2.2 DDM-3D/PM.

DDM-3D computes the first-order, semi-normalized sensitivity of \(C_i\) to perturbations in an input field as:
$$S_{i,j}^{(1)}(x,t) = \frac{\partial C_i(x,t)}{\partial \varepsilon_j}$$  \hspace{1cm} (2-2)$$

where $\varepsilon_j$ is the relative perturbation. If, $I_{j,0}(x,t)$ is the base model input parameter field, such as emissions, initial, or boundary conditions, etc., and $p_j(x,t)$ is a parameter field of interest, then the modified field is defined as:

$$I_j(x,t) = I_{j,0}(x,t) + \varepsilon_j \cdot p_j(x,t)$$  \hspace{1cm} (2-3)$$

Both $I$ and $p$ can be “mixed,” i.e. include multiple sources or species. This leads to an analogous equation governing the sensitivity field:

$$\frac{\partial S_{i,j}}{\partial t} = -\nabla (u S_{i,j}) + \nabla (K \nabla S_{i,j}) + J S_{i,j} + E_i'$$  \hspace{1cm} (2-4)$$

where $S_{i,j}$ is the sensitivity of species $i$ to parameter $j$, $J$ is the $i$th row vector in the Jacobian matrix $J$, $(J_{ij} = \partial R_i / \partial C_j)$, which represents the chemical interaction between species, and $E_i'$ is the unperturbed emission rate.

DDM-3D uses the same numerical algorithms for transport related processes (advection, diffusion, deposition, etc.) as for concentrations (Dunker, 1981; Yang et al., 1997). Processes that are not linear, such as aerosol formation and cloud dynamics, are treated slightly differently, as discussed below.

CMAQ uses a modal approach to describe the aerosol size distribution and growth (US-EPA, 1999). It categorizes aerosols as belonging to Aitken, accumulation, or the non-reactive coarse mode. Aerosols in the two smaller modes are inorganic [e.g., sulfate ($SO_4$), nitrate ($NO_3$), ammonium ($NH_4$), and elemental carbon (EC)], organic [e.g., secondary anthropogenic, secondary biogenic, or primary], or “unspecified.” CMAQ also includes other PM species such as coarse mode sea salt, and coarse mode, soil-
derived aerosol. CMAQ assumes that the ionic inorganic components of PM are in equilibrium as described by ISORROPIA (Nenes et al., 1998). Secondary organic aerosols (SOA) are partitioned between the gas and condensed phases based on empirically derived coefficients. Based on the classification of their source, SOA can be either biogenic (SOA-B) or anthropogenic (SOA-A). For example, aerosols that partition from monoterpene products are considered biogenic.

While the majority of the processes in the aerosol phase are linear allowing for direct propagation of DDM-3D sensitivities, thermodynamic interactions between all of the aerosols and their precursor gases in ISORROPIA require a different approach as does SOA partitioning and cloud processing.

Odman and associates addressed how to treat the thermodynamic equilibrium of inorganic PM in URM for implementation of DDM-3D by taking the derivative of each equilibrium expression (Odman et al., 2002). For example, consider the following reaction:

\[ HSO_4^{-} (aq) \leftrightarrow K_1 H^+ (aq) + SO_4^{2-} (aq) \]  

Equation 5 leads to an equilibrium expression for SO$_4^{2-}$ as follows:

\[ [SO_4^{2-}] = \frac{K_1[HSO_4^{-}]}{[H^+]} \]  

First order semi-normalized sensitivity to any parameter $P_j$ would then be:

\[ \frac{\partial [SO_4^{2-}]}{\partial P_j} P_j = \left( -\frac{[SO_4^{2-}]}{[H^+]} \frac{\partial[H^+]}{\partial P_j} + \frac{[SO_4^{2-}]}{[HSO_4^{-}]} \frac{\partial[HSO_4^{-}]}{\partial P_j} + \frac{\partial[K_1]}{\partial P_j} \frac{[HSO_4^{-}]}{[H^+]}} \right) P_j \]  

or,

\[ \frac{S_{SO_4^{2-},j}}{[SO_4^{2-}]} = -\frac{S_{H^+,j}}{[H^+]} + \frac{S_{HSO_4^{-},j}}{[HSO_4^{-}]} + \frac{S_{K_1,j}}{K_1} \]  

22
K₁, to first order, is determined from meteorological parameters (e.g., temperature, relative humidity) and not individual species concentrations. Thus $S_{K_{i,j}} / K_i$ is small, and can be ignored. Such expressions were calculated for each equilibrium reaction of all ionic species. Additionally, mass conservation and charge balance equations were constructed, leading to a complete set of linear equations for each species (gas and PM) involved in the equilibrium. Calculation of the secondary organic aerosol sensitivities parallels the equilibrium process of partitioning semi-volatile species concentrations between gaseous and aerosol phases.

CMAQ includes a more complex description of cloud processes than many other models. These include below cloud mixing, aqueous phase chemistry, scavenging, and wet deposition. A cloud is present when the relative humidity is sufficient to activate aerosol particles and turn them into cloud droplets. These droplets provide the means of removal of pollutants by rain-out and scavenging. Furthermore, these droplets provide the media for aqueous-phase chemical equilibrium reactions (US-EPA, 1999).

Scavenging and wet deposition are linear processes in CMAQ. If $\tau$ is the length of the time step and $\alpha$ is a scavenging coefficient, then the removal of pollutants and in any grid cell, $C_{f(i,j,k,t)}$, is given by:

$$C_{f(i,j,k,t)} = C_{0(i,j,k,t)} \cdot e^{-\alpha \tau} \quad (2-9)$$

From this, the semi-normalized sensitivity follows as:

$$S_{f(i,j,k,t)} = S_{0(i,j,k,t)} \cdot e^{-\alpha \tau} - C_{0(i,j,k,t)} \frac{\partial \alpha}{\partial P_j} P_j \quad (2-10)$$

The scavenging coefficient, $\alpha$, represents the rate of removal for a given precipitation rate. It is a function of water content in the cloud, temperature, and cloud thickness. It is
not sensitive to emissions, chemical rate constants, etc., and for this reason $\partial \alpha / \partial P_j$ is typically zero.

Heterogeneous oxidation of $\text{SO}_2$ and subsequent conversion to sulfate aerosol follows five pathways. Sulfur can be oxidized by hydrogen peroxide, ozone, methyl hydrogen peroxide (MHP), peroxycetic acid (PAA), and catalytically in the presence of metals ($\text{Fe}^{+++}$ and $\text{Mn}^{++}$). Rates of conversion through the majority of these pathways are calculated based on empirical data, which differ with pH and amount of sulfur available. Sensitivities are local derivatives and are computed as such for each of the rate expressions. For example, at a pH above 2.7, the oxidation rate of $\text{SO}_2$ due to ozone as a function of hydrogen ion, ozone, and total dissolved $\text{SO}_2$ is described by the following empirical expression:

$$\frac{d[C]}{dt}_{\text{H}_2\text{O}} = -4.19e^{5.0}\left(1.0 + \frac{2.39e^{-4.0}}{[H^+]}ight)\cdot[O_{\text{g(liq)}}]\cdot[S(IV)]$$

(2-11)

The derivative of this expression is:

$$\frac{d[S_j]}{dt}_{\text{H}_2\text{O}} = -4.19e^{5.0}\left(\frac{-2.39e^{-4.0}}{[H^+]}\cdot[O_{\text{g(liq)}}]\cdot[S(IV)]\cdot S_{H^+,j} + \left(1.0 + \frac{2.39e^{-4.0}}{[H^+]}\right)\cdot[S(IV)]\cdot S_{O_{\text{g(liq)}}}\right)$$

(2-12)

pH in the CMAQ cloud module is calculated using the method of reiterative bisection through a charge balance of all ions. Sensitivity of the hydrogen ion is important in accurately calculating such expressions, but $\text{H}^+$ (and hence $S_{\text{H}^+}$) is not treated explicitly, so $S_{\text{H}^+}$ is calculated using a charge balance.

Aqueous phase conversion rates are used to determine the time step over which aqueous chemistry calculations are performed. This is based on the minimum amount of
time required to convert a set amount of sulfur through any one of the five pathways. Sensitivity calculations use the same time step.

CMAQ clouds are divided into two categories – resolved and unresolved. Resolved clouds occupy the entire grid cell. Thus, the effects of aqueous chemistry on concentrations and sensitivities include the entire cell. Unresolved clouds fill the grid cell only partly. The effects of aqueous chemistry in these clouds are “diluted” by the air outside the cloud. Furthermore, there is a cloud driven movement and mixing of gases and aerosols in the column below the cloud. At this time, calculation of sensitivities follows exactly the routines defined for concentrations in regard to below cloud mixing and entrainment.

2.2.3 Application

CMAQ was set up to simulate a summer episode; July 6 – July 18, 2001, using a 36 km resolution grid covering the eastern United States (Figure 2-1) with a 12 km nest over part of the southeast and a 4 km nest over northern Georgia. This domain is the same as that was used previously for the Fall Line Air Quality Study (Hu et al., 2004). July 5 was used as a ramp-up day. Meteorology for the period was developed using MM5 version 3.6 (PSU/NCAR, 2003) and emissions were processed using SMOKE version 1.5 (US-EPA, 2004). SAPRC99 was used as the chemical mechanism (Carter, 2000).

Comparison is made between DDM-3D/PM sensitivities and those developed by the difference method (i.e. “brute force”):

\[
S_{yj}^{bf} = \frac{C^{+10\%} - C^{-10\%}}{0.2} \quad (2-13)
\]
where $C^{+10\%}$ is the simulated concentration at an emissions level 10% higher than the base, $C^{-10\%}$ is the concentration at emissions 10% lower, and $S_y^{bf}$ is the approximate first-order, brute force sensitivity. The twenty percent difference was chosen to be large enough to prevent numerical noise, while being small enough to capture the local derivative at the base level of emissions. This method still led to numerical noise at times. Both DDM-3D/PM and brute force sensitivities to domain-wide emissions of NO$_x$, SO$_2$, NH$_3$, monoterpenes (as a representative biogenic VOC), and xylene (as a representative anthropogenic, SOA-producing VOC) were computed as 100% change in emissions assuming linearity.

Figure 2-1 Fall line Air Quality Study (FAQS) domains used for modeling with three grid-size resolution regions indicated. Dark areas denote urban regions.
Table 2-1 Statistical Comparison of Brute Force and DDM 3D/PM. a Sensitivities are shown to domain-wide emissions of SO$_2$, NO$_x$, NH$_3$, Xylene, and Terpene. Averages and standard deviations for concentrations and sensitivities are followed by the results of a regression analysis between BF and DDM. Higher correlation coefficients exist for modeled specie – emitted specie pairs for which there are clearly defined direct relationships in the model.

<table>
<thead>
<tr>
<th>(ug/m$^3$)</th>
<th>Concentration</th>
<th>Sensitivity to E(SO$_2$)</th>
<th>Sensitivity to E(NO$_x$)</th>
<th>Sensitivity to E(NH$_3$)</th>
<th>Sensitivity to E(Xyl)</th>
<th>Sensitivity to E(Terp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X, σ</td>
<td>X, σ</td>
<td>X, σ</td>
<td>X, σ</td>
<td>X, σ</td>
<td>X, σ</td>
<td>X, σ</td>
</tr>
</tbody>
</table>

| Sulfate   | 3.04, 0.72    | 1.93, 0.58              | 0.29, 0.14               | 0.05, 0.02               |                       |                       |
| R$^2$     | 0.97, 0.01    | 0.84, 0.16              | 0.55, 0.10               |                         | b                     |                       |
| Slope     | 1.00, 0.05    | 0.87, 0.11              | 0.77, 0.12               |                         |                       |                       |
| Intercept | 0.08, 0.04    | 0.01, 0.01              | 0.02, 0.01               |                         |                       |                       |

| Nitrate   | 0.20, 0.06    | -0.12, 0.05             | 0.20, 0.06               | 0.19, 0.06               |                       |                       |
| R$^2$     | 0.44, 0.14    | 0.81, 0.06              | 0.72, 0.05               |                         | b                     |                       |
| Slope     | 0.42, 0.12    | 1.06, 0.17              | 1.00, 0.23               |                         |                       |                       |
| Intercept | 0.02, 0.01    | 0.03, 0.01              | 0.02, 0.01               |                         |                       |                       |

| Ammonium  | 0.87, 0.19    | 0.29, 0.08              | 0.12, 0.04               | 0.32, 0.09               |                       |                       |
| R$^2$     | 0.90, 0.05    | 0.81, 0.07              | 0.91, 0.02               |                         | b                     |                       |
| Slope     | 1.05, 0.05    | 0.97, 0.15              | 1.10, 0.08               |                         |                       |                       |
| Intercept | 0.01, 0.01    | 0.00, 0.01              | 0.01, 0.01               |                         |                       |                       |

| Anth.Org. | 0.02, 0.01    |                       |                         | 0.01, 0.00               |                       |                       |
| R$^2$     |                         | b                     | b                       | 0.82, 0.08               | b                     |                       |
| Slope     |                         |                       |                         | 1.05, 0.11               |                       |                       |
| Intercept |                         |                       |                         | 0.00, 0.00               |                       |                       |

| Bio.Org.  | 0.32, 0.07    |                       |                         |                         |                       | 0.25, 0.05 |
| R$^2$     |                         | b                     | b                       | b                       | b                     | 0.96, 0.01 |
| Slope     |                         |                       |                         |                         |                       | 0.84, 0.03 |
| Intercept |                         |                       |                         |                         |                       | 0.00, 0.00 |

a For the slope and intercept statistics, BF results are regressed against DDM. Sensitivity values are shown for the DDM-3D results.

b Indicates sensitivities that are less than 5% of concentrations in magnitude.
To evaluate DDM-3D/PM, 24-hour brute force and DDM-3D sensitivities were computed in each cell for each day. Linear regression analysis and spatial mapping were used to assess the agreement between brute force and DDM-3D (Table 2-1). Statistical comparison is performed for all cells for the entire episode.

Overall, the two methods show similar results. The agreement is better when there is a more direct relationship between the aerosol and the gaseous emissions, and large responses are found. For example, sensitivities of sulfate to SO$_2$ emissions are highly correlated between the two methods, with a near unity slope. Further, they compare well spatially with the “brute-force” method (Figure 2-2). There is high sensitivity off the coast of Virginia and North Carolina (note that the positive sensitivities shown are a response to an increase in emissions). These areas had significant cloud cover during this period leading to aqueous phase SO$_2$ oxidation and high sensitivities. This indicates that heterogeneous conversion of SO$_2$ to sulfate is captured.

![Figure 2-2 Spatial comparison between DDM and brute force (24-hour average) for the sensitivity of sulfate to domain-wide emissions of SO$_2$ (accumulation mode).](image)
When the relationship is less direct, more nonlinearity exists, and lower correlations are found. However, the reasons for non-agreement are not initially apparent. For example, the brute force method can be susceptible to numerical noise that skews the correlation. In the case of the sensitivity of ammonium to emissions of SO$_2$, brute force shows some cells with high negative values that are adjacent to cells with high positive values (Figure 2-3). This is due to numerical diffusion affecting the two fields, as has been seen by others (Cohan et al., 2005), (Hakami et al., 2004).

![DDM and Brute Force Maps](image)

**Figure 2-3** Numerical Noise in brute force method. Areas of high negative sensitivities exist in cells adjacent with near maximum positives in the brute-force method for the sensitivity of ammonium to domain-wide emissions of SO$_2$.

Sensitivity of nitrate to emissions of SO$_2$ is of interest to policy makers who are concerned about increasing nitrate levels as SO$_2$ controls are implemented. While the correlation between DDM-3D/PM results and brute force is low (0.455), the DDM field is more sensible (Figure 2-4). Levels of nitrate are expected to rise when there is less sulfate-producing SO$_2$ in the domain, as is found using DDM-3D/PM. On the other hand,
The brute force method is producing results that are erratic (Figure 2-4). This is evident as sensitivity strongly depends on the amount of SO\textsubscript{2} removed. Note that the extreme values in the 10% brute force calculation (computed using \((C^{+10} - C^{\text{base}})/0.1\)) are most likely due to numerical errors, as they are very different from the central difference calculation.

Figure 2-4 Sensitivity of nitrate to domain-wide emissions of SO\textsubscript{2} (24-hour average). The brute-force method shows different results depending on the magnitude of the difference used to calculate the sensitivity. At a small difference (upper left), the result is mostly due to numerical noise.
It is not clear, at this time, why the correlation for the sensitivity of sulfate to domain-wide emissions of NH$_3$ is low. However, some days have a significantly better agreement (July 6, $R^2 = 0.6$) than others (July 7, $R^2 = 0.3$) (Figure 2-5). In both cases, the sensitivities are low and susceptible to numerical noise.

Figure 2-5 Sensitivity of sulfate to domain-wide emissions of NH$_3$ (24-hour average).

While the ability to more accurately capture small sensitivities is a driving reason for using DDM-3D, the computational efficiency of this method also makes it an attractive tool. To test the efficiency, DDM-3D was applied to calculate varying numbers of sensitivity coefficients while noting CPU usage. Comparing this result with the time needed to calculate a similar number of sensitivities using brute force shows that DDM-
3D/PM was more efficient for calculating more than one coefficient (Figure 2-6). Effect of domain size was also considered. The comparison was also done on a smaller domain to consider the effect of domain size. Domain size had a negligible impact on the efficiency comparison. Memory limits the number of sensitivities that can be efficiently calculated in a single simulation.

CPU usage was also calculated for various CMAQ modules to identify where efficiency improvements might have the most benefit. Results for a five parameter DDM-3D simulation, as compared to the base case simulation (Figure 2-7), show that the chemistry and horizontal advection require the most time (note: six fields are being advected, five for sensitivities and one for base concentrations.) Required CPU time for advection increases proportionally with the number of sensitivity parameters, for chemistry, sub-proportionally, while for cloud processes, on the other hand, super-proportionally.
Figure 2-6 Run-time comparison between DDM and brute force.

Figure 2-7 CPU time comparison for a five parameter DDM 3D simulation. “CHEM” includes only gas-phase chemistry. “CLD” includes aqueous chemistry, wet deposition, and below cloud mixing. “AERO” includes all physical and chemical aerosol processes except transport. “VHDIFF” and “XYZADV” includes the transport for all species.
2.3 Summary

DDM-3D/PM was integrated into the current CMAQ code and is a promising tool to aid policy makers in developing control strategies for particulate matter. Results compare well spatially with the traditionally used brute-force approach for most sensitivity parameters. In some cases, DDM-3D/PM provides more reasonable results than brute-force. For example, DDM-3D/PM finds that sensitivities of nitrate to emissions of SO$_2$ are negative, meaning that reducing SO$_2$ would actually increase the nitrate portion of PM. However, brute-force finds erratic results, suggesting limitations in such an approach. Reasons for such results are not entirely evident, but include numerical diffusion. DDM-3D/PM is also computationally efficient, with most of the CPU savings coming from a less than proportional increase in the calculation of chemical processes and aerosol dynamics.

DDM-3D/PM would also easily translate into other versions of CMAQ, for example CMAQ-MADRID, which uses the sectional treatment of aerosols. It is also capable of incorporating any improvements to the ISORROPIA code with only slight modification of the thermodynamic equilibrium matrix for sensitivities.

Acknowledgements

The authors would like to thank U.S. Environmental Protection Agency for providing funding for this project under Agreements RD82897602, RD83107601, RD83096001 as well as the State of Georgia, through the Fall-line Air Quality Study (FAQS).
References


CHAPTER 3

Regional Source Apportionment of PM$_{2.5}$ in Georgia Using Direct Sensitivities*

Abstract

Sources of primary and secondary fine particulate matter in Georgia were quantified through the use of a regional air quality model CMAQ with the Decoupled Direct Method in 3D (DDM-3D). DDM-3D provides sensitivities of the different components of total particulate mass. Four Georgia cities were examined; Atlanta, Augusta, Columbus, and Macon during three separate summertime episodes. Stagnant meteorological conditions during each episode and high emissions in the region led to simulated particulate concentration levels that in some cases were above the standard. In each city, both primary and secondary sources of particles were considered and found to be significant. Sulfate, produced from SO$_2$ oxidation, was the dominant component of fine particulate matter. VOC emissions from mostly biogenic sources in the region led to the formation of secondary organic aerosols near the emission locations, but also to a reduction in sulfate formation downwind. Sources of particulate species varied with the meteorology, but were a mixture of local emissions as well as long-range transport. Daily variability in source locations was also observed. A small negative sensitivity of nitrate aerosol to emissions of SO$_2$ was found suggesting a replacement of secondary sulfate by nitrate through SO$_2$ controls, but the effect was minor for the summer periods examined.

* This chapter was submitted to Journal of Air and Waste Management with Daniel S. Cohan, Yongtao Hu, M. Talat Odman, and Armistead G. Russell as coauthors.
**Key Words**

Atmospheric Modeling, Sensitivity Analysis, Decoupled Direct Method, Source Apportionment

### 3.1 Introduction

As policy makers draft strategies for decreasing particulate matter (PM) concentrations, it is becoming increasingly important to quantitatively understand the sources of this pollution. Several areas within the state of Georgia are in non-attainment of the National Ambient Air Quality Standards (NAAQS) for PM$_{2.5}$ (particles with aerodynamic diameter of less than 2.5 micrometers). The U.S. EPA has set the NAAQS for PM$_{2.5}$ at 15 ug/m$^3$ for an annual average and 65 ug/m$^3$ for a 24 hour average, although the 24 hour standard is proposed to be tightened to 35 ug/m$^3$. While many highly populated counties in the state of Georgia are already in non-attainment, more would be with the proposed lower value. In either case, Georgia, and other states, need to develop State Implementation Plans (SIPs) to demonstrate now controls will lead to future attainment. This process typically involves air quality modeling and sensitivity analysis.

Four Georgia cities – Atlanta, Augusta, Columbus, and Macon – were selected as receptors in this study. While located in different regions of the state, each of these cities is near or above the current NAAQS, showing the pervasiveness of PM$_{2.5}$ in the area. Contributions to PM$_{2.5}$ in different regions in the Southeast from emissions of primary particulates and gaseous precursors to secondary particulates were calculated in each city using direct sensitivities.
3.2 Method

CMAQ was used to simulate the air quality. Described in more detail elsewhere (Byun and Ching, 1999), it is a regional, multiphase model that operates by solving the atmospheric diffusion equation:

\[
\frac{\partial C_i}{\partial t} = -\nabla (uC_i) + \nabla (KC_i) + R_i + E_i
\]

where \( C_i \) is the concentration of species \( i \), \( u \) is the fluid velocity, \( K \) is the molecular diffusivity tensor, \( R_i \) is rate of chemical generation of species \( i \), and \( E_i \) is rate addition of the species (emissions). CMAQ has been used extensively in the regulatory and research communities. More recently, the model’s capabilities have been extended to include the direct computation of sensitivities (Cohan et al., 2005; Napelenok et al., 2006). This is done through the implementation of the Decoupled Direct Method in 3D (DDM-3D) in the model (based on CMAQ release version 4.3). DDM-3D computes first-order sensitivities by solving the following equation (Dunker, 1984):

\[
\frac{\partial S_{i,j}}{\partial t} = -\nabla (uS_{i,j}) + \nabla (KS_{i,j}) + JS_{i,j} + E_i'
\]

where \( S_{i,j} \) is the sensitivity of species \( i \) to parameter \( j \), \( J \) is the \( i \)th row vector in the Jacobian matrix \( J \), \( (J_{ij} = \partial R_i / \partial C_j) \), which represents the chemical interaction between species, and \( E_i' \) is the unperturbed emission rate of the sensitivity parameter.

Sensitivities of secondary fine particulates to emissions of their gaseous precursors are nearly linear for sulfate and secondary organic aerosols (SOA), two of the largest components of total mass in this region during the summer months (Hu et al, 2005). Thus, computation of sensitivities of fine PM components on a regional level provides an approximation of regional source apportionment. At individual receptors,
such as non-attainment counties, this kind of information is valuable for determining control strategies. Furthermore, sensitivities can be used in conjunction with the receptor-based source apportionment methods such as the Chemical Mass Balance (CMB) model to better understand the sources of air pollution regionally.

The domain chosen for this study was a 75 by 66 grid with 12km resolution covering the southeastern United States nested within a 36km grid (Figure 3-1a) as used previously for the Fall Line Air Quality Study (FAQS) (Hu et al., 2004). The fine grid includes the states of Georgia, Alabama, and South Carolina, and portions of Tennessee and North Carolina and northern Florida. Sensitivities of secondary particulates to emissions of SO\textsubscript{2}, NO\textsubscript{x}, NH\textsubscript{3}, and VOC from individual states were calculated using DDM-3D/PM. Georgia was further divided into the regions representing the Atlanta, Augusta, Columbus, and Macon metropolitan areas as well as central, northern, and southern Georgia. These divisions follow county lines (Figure 3-1b) and are similar to non-attainment areas.
Classification and Regression Tree (CART) analysis was used to initially select the episodes for FAQs. CART selects days as candidates for modeling based on their meteorological and air quality characteristics. This is done by specifying a classification variable, such as 24-hour average PM$_{2.5}$ concentration, and partitioning all days in the year based on influential variables (wind speed, temperature, etc.) to segregate the days. The result is a collection of bins of days each representing similar meteorological and air quality conditions. This is useful because it is possible to determine the frequency of occurrence of certain days that might be of interest as well as the assurance that a particular modeling episode has a range of types of days that might be used as representatives for conditions of poor air quality in a region for longer temporal scales than are convenient to model.

Three summer episodes were chosen for detailed study: August 1 – 12, 1999; August 13 – 19, 2000; July 5 – 19, 2001. While for fine particulate matter, CART
analysis was available for years 2000-2003, there were not enough PM measurement data available for analysis of 1999 and that episode was selected mainly on the distribution of PM$_{2.5}$ exceedances in Georgia and the classification of days in regard to ozone concentrations. Data used in this analysis was collected from the Aerometric Information Retrieval System (AIRS) and Interagency Monitoring of Protected Visual Environments (IMPROVE) sites in the southeast (US-EPA, 1993; NPS, 2006). The later two episodes include days from a variety of bins that have high PM$_{2.5}$ concentrations (Figure 3-2).

Meteorology for all three episodes was resolved using the Mesoscale Meteorological Model version 5 (MM5) (PSU/NCAR, 2003). Emissions in each geographic region were developed from FAQS inventories (Hu et al., 2004), and processed using SMOKE version 2.1 (CEP, 2004).

Figure 3-2 Frequency of CART bins. Analysis was performed for the period of Jan. 1, 2000 – Dec. 31, 2003. Filled circles represent modeled days. (Bin 1 occurred 621 times and was also modeled)
3.3 Results and Discussion

Model performance (Figure 3-3) was evaluated by comparing simulated concentrations to observed values using the AIRS and FAQS monitors. Performance was similar to that reported by other similar studies (Seigneur et al., 2000; Seigneur et al., 2004). Results of PM comparison are shown using the approach developed by Boylan et al. (Boylan et al., 2004). Total fine particulate mass, as well as the inorganic components (sulfate, nitrate, and ammonium) individually all performed within the suggested bounds of mean fractional error and mean fractional bias. A low bias in organic carbon (OC) in both 2000 and 2001 is consistent with other studies and is suspected to be due to the underestimation of the formation of secondary organic aerosols (SOA) by the current air quality models (Zhang et al., 2004). Ozone performance was within the EPA recommended modeling guidance during all three episodes (US-EPA, 1999). Performance of DDM-3D for particulates has been evaluated separately elsewhere (Napelenok et al., 2006).
Figure 3-3 Model performance. Total PM$_{2.5}$ during each episode as well as the majority of individual components fall within acceptable limits.
Concentrations and sensitivities in Atlanta were determined as an average of grid
cells that contain the twelve air quality measuring sites in the Atlanta area that report
pollutant levels as part of the Aerometric Information Retrieval System (AIRS) network.
Macon results are for the average of the two cells where the AIRS and the FAQS (Hu et
al., 2004) sites are located. Augusta and Columbus each have one AIRS station that
monitor PM and their grid-cell locations were used in the results.

The largest contributing source to total sensitivity during all three episodes was
the boundary condition of sulfate (Figure 3-4), which accounted for over one quarter of
the total sensitivity. Since the boundary conditions were the result of the larger mother-
domain simulation, this result demonstrates the regional nature of sulfate aerosol. It has
been shown previously that sulfate can have impacts far downwind from sources of its
production (Boylan et al., 2004). Thus, the four Georgia cities are experiencing impacts
of not only local sulfate production, but also the transport from sources beyond
Tennessee, etc. Emissions in the state of Georgia account for the majority of non-
boundary sensitivity. Local emissions of primary organic carbon (OC) and elemental
carbon (EC) are important at the receptor cities. These species dominate in Atlanta
during each episode due to high emissions in the metropolitan area from mobile sources.
Ammonia emissions in mainly Georgia, but also in South Carolina, and Alabama, have a
noticeable impact on the formation of secondary fine particulate mass. Depending on the
conditions in the atmosphere, ammonia was responsible for production of ammonium as
well as the acceleration of sulfur dioxide oxidation in the aqueous phase. Local Georgia
VOC emissions led to the formation of secondary organic aerosol (SOA) in all four cities.
These emissions are dominated by biogenic sources and consist primarily of terpenes and
related compounds. The mostly biogenic Tennessee emission of VOCs, on the other hand, led to a slight negative sensitivity, suggesting that their increase would lead to less PM$_{2.5}$ downwind in Georgia. This is explained by VOCs consuming the hydroxyl radicals reducing sulfur dioxide oxidation (Figure 3-5). Sulfuric acid condenses or grows into Aitken sized particulates. Thus, upwind sources of VOCs in Tennessee led to lower PM mass, in the form of lower sulfate, downwind in the four Georgia cities. However, the formation of SOAs from all VOCs in all regions outweighs their “pseudo-positive” effect on total PM$_{2.5}$ mass at any location, and while sulfate is decreased downwind, SOAs are increased by higher magnitudes locally in all cases. NO$_x$ emissions in the region, while high, did not contribute significantly to the formation of PM during these episodes. Emissions of NO$_x$ in Georgia, South Carolina, and North Carolina have a marginal impact on the formation of nitrate and sulfate and even a lower impact on ammonium.

The results presented here only include modeled species for which the formation mechanisms have been documented and implemented in the current state-of-the-art air quality model. “Unspecified” PM mass is not included in the analysis but its concentrations averaged at around 5.0 µg/m$^3$. Due to its strictly primary nature, its sensitivity would always equal to its concentration.

July 2001 was relatively “cleaner” than the preceding two summer episodes showing lower average concentration in each of the four cities as well as in the entire domain. This is also reflected in the sensitivities that show lower impacts from some of the same geographical sources in the domain.
Figure 3-4 Episode average source contributions to sensitivities. Emissions from each state and boundary conditions are shown as they contribute to primary and secondary fine particulates. (“other” denotes the sum of contributions from the remaining simulated sources that individually were significant)

Figure 3-5 Species sensitivities to Tennessee VOC emissions. VOCs use up the OH radical during daylight hours (a). As a result, less sulfuric acid is produced (b). This leads to less Aitken mode sulfate (c) and ultimately less accumulation mode sulfate (d). In the dark, there is little OH (e) and sulfuric acid (f) activity, but the sulfate sensitivities, in both Aitken (g) and Accumulation (h) modes, are advected towards GA. Thus, in Atlanta, TN VOC emissions have a negative impact on PM, while locally in TN more SOA is produced.
Episode long averages, and their sensitivities, are important for particulate matter, because several counties in Georgia are out of compliance with the annual standard for PM$_{2.5}$ specified by the NAAQS. However, several monitors in the Atlanta metropolitan area also report daily averaged values of PM that are near or above the current standard, and most locations had levels above the proposed more stringent 24-hour standard. Daily variability in source contributions of sensitivities exists (Figure 3-6). Depending on emission rates, but more so on meteorology, gaseous and particulate emissions from specific geographic areas can have a different impact on the receptor cities. For example, during the majority of the August 2000 episode, Columbus was influenced mainly by emissions from Atlanta due to the northeasterly winds. However, after a wind shift on August 18$^{th}$, emissions from Alabama became more important. Similarly, contributions in the other three cities changed significantly on this day. Thus, any emission controls based on the episode averages might be effective in lowering annual PM, while possibly having little effect on some daily maximums.
Secondary fine particulate matter formation from gaseous emissions within the state of Georgia was further analyzed in order to establish the geographical sources of its precursors (Figure 3-7). Averaged over all of the modeled days during the three summer episodes in Atlanta, 3.6 ug/m$^3$ of particulate matter was attributed to gaseous emissions within Georgia out of the total 18.6 ug/m$^3$. The majority of the sensitivities in Atlanta were attributed to local emissions within the metropolitan area. Emissions of ammonia and sulfur dioxide had the most dominant fractions through the formation of sulfate. Biogenic and, to a lesser extent, anthropogenic VOCs formed secondary organic aerosol (SOA) and also had a large signature. Due to the prevalence of mostly northerly winds, only the northern Georgia region had any other significant effect on Atlanta. The other three cities all had more complex source contributions. In each case – Augusta,
Columbus, Macon – local emissions from within the metropolitan area accounted for approximately half of the total sensitivities of secondary PM. A large portion of sensitivity was also attributed to emissions from Atlanta, and the remaining amount came from a mixture of the rest of the defined geographical areas in Georgia.

Figure 3-7 Sources of gaseous precursors emitted in Georgia that lead to the formation of secondary particulate matter in the four cities – a) Atlanta, b) Augusta, c) Columbus, d) Macon. For each city, the total sensitivity that is attributed to GA emissions is shown followed by the total primary and secondary sensitivity sensitivity from all sources in the domain. (“OTHER ” represents the sum of contributions from all other modeled regions).

Speciated components of secondary fine particulate matter were also examined with respect to their precursor emissions. Sulfate is the dominant component of PM in this region (Table 3-1). While the majority of sulfate is attributed to emissions of sulfur dioxide, NOx emissions act to facilitate the oxidation process while excess VOC emissions act to reduce it as was explained previously. The amount of ammonium is
increased through the production of ammonium sulfate and ammonium nitrate due to emissions of SO\(_2\) and NO\(_x\) respectively. Nitrate is produced through the condensation of nitric acid that results from NO\(_x\) emissions, reacting with ammonia. Interestingly, the sensitivity of nitrate to domain-wide emissions of sulfur dioxide is negative. This suggests a PM “replacement” effect where control of SO\(_2\) would reduce sulfate but increase nitrate. To investigate the extent of the “replacement” effect the sensitivity of nitrate to domain-wide emissions of SO\(_2\) were correlated to the sensitivity of sulfate to the same parameter (Figure 3-8). It appears that at the current levels of emissions, the replacement of sulfate by nitrate resulting from SO\(_2\) controls is minor on average, but can be around 10% in some cells in the domain. Examining the ratio of sensitivities of nitrate and sulfate to emissions of SO\(_2\) during the 2000 episode, \(\frac{S_{NO_2^{-}.E(SO_2)}}{S_{SO_4^{2-}.E(SO_2)}}\), revealed that out of 4950 sampled, ground-level cells, 3969 had values of higher than -0.01 (suggesting <1% replacement) and 185 had values lower than -0.10 (suggesting >10% replacement).

<table>
<thead>
<tr>
<th>Table 3-1 Sensitivity of secondary components of fine particulate matter to emissions of their gaseous precursors in Atlanta, GA. The values presented here are averages over all days in the three episodes and the emissions represent total domain-wide amounts.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(µg/m(^3))</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>Sulfate</td>
</tr>
<tr>
<td>Ammonium</td>
</tr>
<tr>
<td>Nitrate</td>
</tr>
<tr>
<td>Anth. SOA</td>
</tr>
<tr>
<td>Biog. SOA</td>
</tr>
</tbody>
</table>
Figure 3-8 Correlation between sulfate and nitrate sensitivities to domain-wide emissions of SO$_2$ – August 2000. Each point on the chart represents the average of all 24-hour PM concentrations during the 2000 episode in each 12-km resolution grid cell. While the correlation between the two variables is poor, there appears to be a minor “replacement” effect where reducing sulfate through SO$_2$ controls would increase nitrate concentrations slightly.

3.4 Summary

Geographically defined sources of primary and secondary particulate matter that impact PM$_{2.5}$ concentrations in Atlanta, Augusta, Columbus, and Macon, Georgia were analyzed using CMAQ outfitted with the Decoupled Direct Method in 3D for computing sensitivities. Three summer-time episodes were considered, which together were found to be representative of high levels of PM$_{2.5}$ during the past 5 years using CART analysis. Each episode can be characterized by stagnant meteorology that led to high concentrations of particulate matter.
The largest contributors to the total PM$_{2.5}$ mass in each city were found to be sulfate produced from the boundary conditions of SO$_2$ and the boundary conditions of sulfate. Since these boundary conditions were established by the larger mother-domain, this result suggests that long-range regional transport is a significant source of PM$_{2.5}$ in the Georgia cities. Elemental and organic carbon were determined to affect only regions immediately near their emissions. VOC emissions in the region led to local formation of secondary organic aerosols but also impeded the oxidation of SO$_2$ downwind to some extent by the consumption of the hydroxyl radical. Ammonia emissions in the region led to increases in the inorganic fraction of secondary PM through the formation of ammonium sulfate and ammonium nitrate. However, the total nitrate sensitivity was found to be low. Daily variability in PM sources was observed during each episode due to changes in meteorology.

A small “replacement” effect was observed with respect to lowering sulfate concentrations through SO$_2$ controls. It appears that in some grid cells in the domain, nitrate concentrations can increase by up to 10% of the magnitude of the sulfate decrease, though it was less than 1% in the majority of the cases. This effect might become more significant as overall level of sulfate (and hence, PM$_{2.5}$) decreases in the domain.

**Acknowledgements**

The authors would like to thank U.S. Environmental Protection Agency for providing funding for this project under Agreements RD82897602, RD83107601, RD83096001 as well as the State of Georgia, through the Fall-line Air Quality Study (FAQS).
References


CHAPTER 4

Regional Source Apportionment of PM$_{2.5}$ in Georgia Using Direct Sensitivities Forecasted to 2007

Abstract

A regional air quality model, CMAQ, with the decoupled direct method for particulate matter (DDM-3D/PM) for computing sensitivities, was used to quantify the impact of sources of primary and secondary PM$_{2.5}$ species in Georgia. DDM-3D/PM sensitivities provide changes in PM$_{2.5}$ components due to incremental changes in emissions. As such, sensitivities can be used directly to approximate the level of emission controls required in order to reach regional air quality goals. The impact of domain wide emissions of primary aerosols was also analyzed to gauge their relative importance. Specific attention is focused on Atlanta, Augusta, Columbus, and Macon, GA, which have PM$_{2.5}$ concentrations near or above the current National Ambient Air Quality Standards (NAAQS). The three cities had similar patterns of impact from local sources as well as regional transport. Wind regimes during the episode played a significant role in the source impacts at each location. Sulfate, formed from SO$_2$ emissions from around the region, was a major component of PM$_{2.5}$ in all three cities. Ammonia emissions also contributed to PM$_{2.5}$ production from direct conversion to ammonium as well as by facilitating SO$_2$ oxidation. The remaining PM$_{2.5}$ mass primarily came from the formation of secondary organics and nitrate as well as primary emissions.

Key Words

Atmospheric Modeling, Sensitivity Analysis, Decoupled Direct Method
4.1 Introduction

As policy makers develop control strategies to achieve or remain in attainment with the National Ambient Air Quality Standards (NAAQS) for particulate matter (PM), they rely upon knowing which PM sources contribute to current PM concentrations. The U.S. EPA has set the NAAQS for PM$_{2.5}$ of 15 ug/m$^3$ (annually) and 65 ug/m$^3$ (daily). Several counties in Georgia have PM$_{2.5}$ concentrations exceeding these values. Furthermore, these standards are currently under review to be lowered, and the daily standard is proposed to be lowered to 35 ug/m$^3$. Identifying effective strategies is complicated, because a large portion of particulate matter (particularly the fraction with aerodynamic diameter less than 2.5 micrometers (PM$_{2.5}$)) is secondary in nature. Sulfate, nitrate, ammonium, and organic carbon compounds are formed from emissions of gaseous species such as SO$_2$, NO$_x$, NH$_3$, and VOCs. Furthermore, these secondary particles interact with each other thermodynamically and physicochemically.

4.2 Method

The Community Multiscale Air Quality (CMAQ) model with DDM-3D/PM was use to calculate concentrations and sensitivities. As described elsewhere (Byun and Ching, 1999), CMAQ is a regional-scale, multiphase model that solves the atmospheric diffusion equation:

$$\frac{\partial C_i}{\partial t} = -\nabla(u C_i) + \nabla(K \nabla C_i) + R_i + E_i$$  \hspace{1cm} (4-1)

where $C_i$ is the concentration of species $i$, $u$ is the fluid velocity, $K$ is the molecular diffusivity tensor, $R_i$ is rate of chemical generation of species $i$, and $E_i$ is rate addition of the species (emissions). CMAQ includes detailed descriptions of gas-phase chemistry
and physics, as well as aerosol dynamics and pertinent heterogeneous chemical reactions. It has been widely applied and evaluated for particulate matter studies (Marmur et al., 2005). Recently, CMAQ was extended to include DDM-3D/PM to directly calculate sensitivities of both gas phase (Cohan et al., 2005) and condensed phase (e.g. PM) pollutants (Napelenok et al., 2006) to precursor emissions. DDM-3D computes first-order sensitivities by solving the following equation:

$$\frac{\partial S_{i,j}}{\partial t} = -\nabla (uS_{i,j}) + \nabla (K\nabla S_{i,j}) + JS_{i,j} + E'_{i} \tag{4-2}$$

where $S_{i,j}$ is the sensitivity of species $i$ to parameter $j$, $J$ is the $i$th row vector in the Jacobian matrix $J$, $(J_{ij} = \partial R_{i}/\partial C_{j})$, which represents the chemical interaction between species, and $E'_{i}$ is the unperturbed emission rate of the sensitivity parameter.

By computing sensitivities of various secondary PM$_{2.5}$ species (sulfate, nitrate, ammonium, and organics) to regional emissions of different gaseous precursors, it is possible to quantify the sources of particulate that impact any point in the domain (such as a PM monitoring station used by a regulatory agency).

DDM-3D/PM enabled to simultaneously compute several sensitivities to emissions of different regions at the same time. DDM-3D/PM sensitivities are local and first order. However, for many species, the near-linearity of the aerosol formation processes suggests these results can be scaled up to levels of emissions reductions that are in line with what is technologically and economically feasible. However, this does not capture “cross-sensitivities” (e.g. second order sensitivities) resulting from interactions between different sources (Hakami et al., 2004).
The domain chosen for this study was a 75 by 66 grid with 12km resolution covering the southeastern United States nested within a 36km grid (Figure 4-1a) as used previously for the Fall Line Air Quality Study (FAQS) (Hu et al., 2004). The inner domain includes the states of Georgia, Alabama, and South Carolina, and portions of Tennessee and North Carolina and northern Florida. Sensitivities of secondary particulates to emissions of SO$_2$, NO$_x$, NH$_3$, and VOC from individual states were calculated using DM 3D/PM. Georgia was further divided into the regions representing the Atlanta, Augusta, Columbus, and Macon metropolitan areas as well as central, northern, and southern Georgia. These divisions follow county lines (Figure 4-1b), similar to non-attainment areas. Furthermore, two coal-burning power plants located in the state of Georgia, Plant Branch and Plant Scherer, were considered separately in order to demonstrate the ability to quantify impacts of individual sources.

A summer episode, July 5 – July 18, 2001, was chosen for detailed study. The meteorology for the period was developed using MM5 version 3.6 (PSU/NCAR, 2003).
Emissions in each geographic region were developed from the 2001 Fall Line Air Quality Study inventory (Hu et al., 2004), and processed using SMOKE version 1.5 (CEP, 2004). A summary of regional emissions of gaseous pollutants shows significant variation in emission strengths, by pollutant, between the states and regions within Georgia (Figure 4-2).

**Figure 4-2 Daily Emissions of** a) **SO₂** b) **NOₓ** c) **NH₃**, and d) **VOC**. ATL, MAC, AUG, and COL categories show emissions in counties belonging to the metropolitan areas of Atlanta, Macon, Augusta, and Columbus respectively. N.GA, S.GA, and C.GA are categories of emissions from North, South, and Central Georgia excluding the above metropolitan areas. SCH and BRA are coal-fired power plants Scherer and Branch. SO₂ emissions are mostly point sources; NOₓ is split between point and mobile sources; NH₃ and VOC are primarily from area sources. The two power plants contribute a significant portion of the regions SO₂ emissions. (Note that total GA emissions would equal to the sum of the first nine table columns)

Concentrations and sensitivities in Atlanta were determined as an average of grid cells that contain the twelve air quality measuring sites in the Atlanta area that report pollutant levels as part of the Aerometric Information Retrieval System (AIRS) network. Macon results are for the average of the two cells where the AIRS and the FAQS (Hu,
Cohan et al., 2004) sites are located. Augusta and Columbus each have one AIRS station
that monitor PM and their grid-cell locations were used in the results to represent the
respective city.

4.3 Results

Simulated concentrations of PM$_{2.5}$ species were compared to air quality
observations at the AIRS and FAQS sites in the domain in order to evaluate model
performance. The performance was similar to other models and applications of CMAQ,
e.g. (Seigneur, Pun et al., 2004; Boylan and Russell, 2006). For ozone, the mean
normalized error was 18.77 and the mean normalized bias was +0.71, both better than the
EPA guidelines for ozone modeling (US-EPA, 1999). PM results typically fall within
guidelines developed by Boylan at al. (Boylan, Odman et al., 2004). Total PM$_{2.5}$, as well
as sulfate, nitrate, and ammonium individually all performed within the suggested bounds
of mean fractional error and mean fractional bias. Elemental carbon and organic carbon
were both under-predicted, but are within the bounds for the air quality modeling
objectives. The performance of DDM-3D/PM has been examined elsewhere (Napelenok,
Cohan et al., 2006).
Figure 4-3  Model Performance of Particulate Matter. Poorer performance of organic carbon is likely caused by the under prediction of the formation of secondary organic aerosols by current air quality models.
Both observations and modeled episode average concentrations (Figure 4-4) find that the majority of secondary PM$_{2.5}$ is composed of sulfate, similar to previous studies in the Southeast during the summer (Hansen, Edgerton et al., 2003). Ammonium and biogenic secondary organics also make up large portions of the total, while nitrate, secondary anthropogenic organics, and elemental carbon concentrations were relatively small.

![Pie charts showing PM$_{2.5}$ composition in different cities](Image)

Figure 4-4 Modeled PM$_{2.5}$ composition in A) Atlanta, B) Macon, C) Columbus, and D) Augusta. Sulfate is the primary component in each city followed by ammonium and biogenic SOA.

Two dominant wind patterns existed during the 12 day episode. During the first half of the simulation, the winds were northwesterly. During the last half, the wind
direction was primarily from the northeast. Since the modeled primary and secondary aerosol species have a residence time in the atmosphere on the order of days, wind direction plays a major role in determining sources that impact pollutant concentrations in each city, as discussed further.

After assuring acceptable model performance and determining the composition of particulate matter in the domain, emissions were adjusted to simulate those expected in the year 2007 and the model was re-run. The year 2007 was chosen because it is not too far in the future and Georgia will begin preparing for some of the newer legislation taking effect such as the Clean Air Interstate Rule (CAIR).

4.3.1 Atlanta

Approximately three-fourths of the PM$_{2.5}$ in Atlanta is simulated to be secondary and half of that was formed from local emissions (Figure 4-5). Tennessee emissions have a large impact during the first several days, while North and South Carolina have a larger impact at the end due to the shift in wind direction. On July 16$^{th}$ and 17$^{th}$, there was also a small contribution from Plant Branch which is located south of Atlanta. This was the only significant sensitivity to the two power plants found for PM in the four cities, although they had noticeable impacts in some rural areas.

Sensitivities to the boundary conditions of all gaseous precursors were calculated, but only sulfur dioxide had a significant impact in Atlanta and the other three cities. The sensitivities to boundary condition sulfate and SO$_2$ are largely due to emissions of these species outside the 12km grid, but are still in the eastern U.S. It appears that high concentrations of SO$_2$ along the northern border of the 12 km nest are responsible for producing the sulfate that, because of its long residence time, is advected to the urban
areas to the south. Boundary conditions of aerosol sulfate were also found to be a large part of the total sensitivity. Boundary conditions of sulfate, SO$_2$ and other species were obtained from the larger 36km resolution grid mother-domain covering the eastern United States.

Volatile organic compounds can have either a positive or a negative influence on aerosol formation. In Atlanta, local VOC emissions (i.e. those emitted from the area in the domain designated as the Atlanta region) add to the total PM$_{2.5}$, primarily from formation of secondary biogenic organic aerosol, while VOC emissions from South Carolina, North Carolina, and Tennessee have a small opposite effect by reducing the amount of sulfate formed, which also lowers ammonium. Sources of primary PM$_{2.5}$ in the domain also had a significant impact, e.g. elemental carbon and organic carbon from area and mobile sources added around 2 µg/m$^3$ on average.
Figure 4-5 Contributions to Atlanta PM$_{2.5}$ (“Other Secondary” represents the sum of the rest of the modeled sources that individually did not amount to over 3% of the total contribution.) *Primary categories are contributions from emissions in the entire domain.

### 4.3.2 Macon

Macon, Georgia is 80 miles south of Atlanta. Given the proximity, the regional contribution of secondary aerosol is similar to Atlanta. During the first part of the episode, Macon is directly in the path of the plume advected from Atlanta. However, after the wind shift, local emissions become more important. Plants Branch and Scherer are located close to the city and had a significant impact on ozone formation but not on PM during this episode (Cohan et al., 2005), because SO$_2$ oxidation takes time, and conversion is limited by the time the emissions reach the city. Macon has a significantly lower population and industrial activity than Atlanta, yet its modeled secondary PM
concentrations are similar. Due to the meteorological conditions throughout the episode, long range transport of SO$_2$, aerosol sulfate, and, to a lesser extent aerosol ammonium, comprise more than half of the total sensitivity of PM$_{2.5}$ on some days, showing the importance of long range transport.

Figure 4-6 Contributions to Macon PM$_{2.5}$ (“Other Secondary” represents the sum of the rest of the modeled sources that individually did not amount to over 3% of the total contribution.) *Primary categories are contributions from emissions in the entire domain.

4.3.3 Columbus

Columbus, Georgia is 100 miles southwest of Atlanta on the Alabama border. The metropolitan area has relatively little industrial activity. Local contributions to secondary PM$_{2.5}$ are small, primarily from ammonia and biogenic organic emissions. During the wind regime of the second part of the episode, Tennessee, South Carolina, and North Carolina emissions have a significant impact here due to the long residence time of
aerosol species in the atmosphere. Again, the boundary conditions of SO\textsubscript{2} and sulfate, as a surrogate for long-range transport into the region, play an important role in the air quality in Columbus. Columbus is closer to the western border of the domain than the other cities, heightening those impacts.

Figure 4-7 Contributions to Columbus PM\textsubscript{2.5} ("Other Secondary" represents the sum of the rest of the modeled sources that individually did not amount to over 3% of the total contribution.)

*Primary categories are contributions from emissions in the entire domain.

4.3.4 Augusta

Augusta, Georgia is 150 miles east of Atlanta on the South Carolina border. Two interesting emission events were registered in Augusta. There is a large fertilizer manufacturing facility near Augusta that releases enough ammonium to be included in the top five ammonia sources in the country. On July 7\textsuperscript{th} and July 13\textsuperscript{th}, there were large amounts of ammonia released from this facility that, due to meteorological and chemical
conditions, led to spikes in the local formation of ammonium and also sulfate. The additional ammonia in the atmosphere made liquid phase aerosol more basic. This effect led to higher oxidation rates of SO₂ by ozone, since these rates respond to the amount of SO³⁻ in the system that would have otherwise been HSO₃⁻ under less basic conditions e.g., (Seinfeld and Pandis, 1998). Aqueous phase sulfate production under the influence of high levels of ammonia can actually contribute more to total PM₂.₅ than the direct production of ammonium. For example, during the peak PM₂.₅ day on July 7 in Augusta (Figure 4-8), local Augusta NH₃ emissions were the major contributor to total PM₂.₅. The emissions resulted in the production of 3.4 ug/m³ of additional sulfate, but only 1.7 ug/m³ of ammonium. Similarly, South Carolina NH₃ emissions lead to 2.7 ug/m³ of sulfate and 1.1 ug/m³ of ammonium in Augusta. This suggests that in Augusta, control strategies designed to lower NH₃ might be appropriate as these will lower both sulfate and ammonium during peak PM₂.₅ days.
Figure 4-8 Contributions to Augusta PM$_{2.5}$ (“Other Secondary” represents the sum of the rest of the modeled sources that individually did not amount to over 3% of the total contribution.) *Primary categories are contributions from emissions in the entire domain.
4.4 Discussion

All four Georgia cities had very similar secondary PM$_{2.5}$ source impacts showing the more regional nature of much of the PM$_{2.5}$ than was found for ozone (Cohan, Hakami et al., 2005). In each city, regional sources and local emissions were about equally important overall. However, the geographic extent of impact is highly variable between the emissions of different species. Primary particulate matter emissions, such as elemental carbon, for example, have very local impacts that are confined to areas around the sources of their emissions (Figure 4-9A). Species such as SO$_2$, on the other hand, are able to influence areas much further from their emissions sources due to the time it takes for them to react (Figure 4-9B).

Figure 4-9 Spatial “foot-print” of different sensitivities. A) shows the sensitivity of sulfate to emissions of SO$_2$ in only Georgia. B) shows the sensitivity of EC to emissions of EC in only Georgia. Sulfate has impacts much further away from the sources of SO$_2$, while primary EC impacts are much more local.
4.5 Summary

Using a three dimensional air quality model, CMAQ, and direct sensitivity analysis, source impacts of primary and secondary PM air pollutants in major Georgia cities were quantified. These cities are either out of attainment with the current PM standard, or could become so with two years of less favorable meteorology or if the daily standard is tightened as proposed. Secondary and primary aerosol composition was very similar in the four cities as were the sources. The majority of secondary mass was sulfate which came primarily from homogeneous and heterogeneous reactions of SO$_2$ released from sources within the state, or advected into the region. Around one-fourth of secondary aerosol mass was composed of ammonium. Higher daily ammonium results coincided with spikes of ammonia emissions from point sources within or near Augusta and parts of South Carolina. Emissions of SO$_2$ also acted to increase ammonium levels through thermodynamic equilibrium interactions. Another one-fourth of secondary mass was attributed by the model to the formation of secondary organic aerosols from emissions of biogenic VOCs (monoterpenes, etc.) Secondary organic aerosol mass resulting from anthropogenic VOC emissions was small. However, the VOC findings are based on the current model assumptions about aerosol formation rates. These are currently under investigation for being underestimated by air quality models, due to much higher atmospheric measurements (Zhang et al., 2004). The remaining, relatively small, portion of mass was nitrate that mostly came from mobile and area sources of NO$_x$. SO$_2$ emissions acted to reduce the amount of nitrate in the region through competition for ammonia. Higher ammonia emissions increased the amount of nitrate in the particle phase, as well as sulfate production.
Sensitivity analysis resulted in some interesting insights into the formation of secondary aerosol in the region. Unlike what occurs in the case of ozone, which in this region is primarily sensitive to emissions of NOx (Zaveri et al., 2003), SO2 plays a much more important role in the total mass of secondary PM$_{2.5}$. In all four cities, biogenic emissions of VOCs can act to reduce the sulfate PM$_{2.5}$. However, the overall mass contribution of VOC emissions from all regions is positive because of SOA formation. Anthropogenic VOC sources were found to impact PM$_{2.5}$ minimally. Ammonia emissions in the region were found to contribute to increased levels of all inorganic secondary species – sulfate, nitrate, and ammonium. Two spikes in the ammonia emissions were also registered in the analysis that had a doubling effect on secondary PM$_{2.5}$ level in Augusta. Increased sulfate concentration following these spikes suggests an increase in heterogeneous sulfate formation.

**Acknowledgements**

The authors would like to thank U.S. Environmental Protection Agency for providing funding for this project under Agreements RD82897602, RD83107601, RD83096001 as well as the State of Georgia, through the Fall-line Air Quality Study (FAQS).

**References**


CHAPTER 5

Area of Influence (AOI) Development: Fast Generation of Receptor-oriented Sensitivity Fields Based on Inversion of Source-oriented Sensitivities*

Abstract

An approach is developed and tested to extend discrete, source-based sensitivity results to provide a complete set of information for source-air quality impacts, as well as inversion of those results to develop receptor-oriented source-impact sensitivities. First, the decoupled direct sensitivity analysis method in 3D (DDM-3D) was used to calculate a finite number of forward sensitivities from discrete points. These results were then interpolated using tessellation to provide a complete set of forward, emissions-based, sensitivities, i.e., how emissions in one grid cell within the domain impact any other cell. Receptor-oriented sensitivities were then found by inverting the set of forward sensitivities and can be used to identify the Area of Influence (AOI). This economically provides results similar to what would be found using an adjoint model. This approach is computationally less intensive than adjoint modeling, and provides both source-oriented and receptor-oriented pollutant response fields that can be used for air quality management and health impact analyses. The forward sensitivity interpolation procedure, as well as the receptor-oriented sensitivities, was evaluated using data withholding.

* This chapter was submitted to Environmental Science and Technology with Florian D. Habermacher, Farhan Akhtar, Yongtao Hu, and Armistead G. Russell as coauthors.
Keywords

Area of Influence, AOI, Sensitivity Analysis, Atmospheric Modeling, Air Quality, Air Pollution

5.1 Introduction

Air pollution, due to human activities or natural causes, originates from a variety of sources, impacting human and ecosystem health. As such, environmental policy makers are tasked with identifying effective measures for improving air quality, but the available resources are scarce and need to be allocated efficiently. To do so, understanding the relationship between emissions in one location and the air quality in other locations is indispensable. Such information is typically developed using either receptor models (Hopke, 1991; Seigneur et al., 1999; Waston et al., 2002) or sensitivity analyses using air quality models (AQM) (Seigneur, 2001; Boylan et al., 2002; Tonnesen, 2004). As an example of the latter, after an AQM has been applied and evaluated for an area, the model can be run with an emission source removed (or added), and the difference in results is taken as the impact of that source on air quality (brute force method). Recently this capability has been built in to some AQMs using direct approaches, e.g. the decoupled direct method in 3D (DDM-3D) (Dunker, 1981; Yang et al., 1997; Odman et al., 2002; Napelenok et al., 2006) including the ability to develop non-linear responses (Hakami et al., 2003). Both the brute force (i.e. difference) approach and the direct method lead to source-oriented sensitivity fields, i.e. the results show how emissions from a specified source (or sources) impact air quality fields.

Forward sensitivities, quantifying the influence of emissions from specific locations on air quality over a domain, have many applications. For example, they are
used to estimate a certain emitter’s contribution to the air pollution in different parts of a region for environmental impact analysis, such as for regional haze and PM non-attainment (US-EPA, 2005) modeling (Odman et al., 2004; Tonnesen, 2004) or Best Available Retrofit Technology (BART) determination (Gesser et al., 2005; US-EPA, 2005). However, reverse, i.e. receptor-specific information, is desired when we want to identify which sources or regions might impact a specific receptor, e.g. locations whose air quality is of specific concern, as is the case for highly populated regions and, in the U.S., Class-1 areas that experience reduced visibility (e.g. National Parks and Wilderness areas) (Patterson et al., 2000; Boylan et al., 2005) and NAAQS-non-attainment-areas (such as Atlanta, GA).

Here we develop a method to calculate the Area of Influence (AOI) for a specified target location. The AOI shows the area in which potential emissions would have a significant impact on the air quality of a specific receptor. Receptor-oriented sensitivity fields are appropriate to designate and quantify such an AOI since they quantify the influence of any source’s emissions on the air quality at the receptor’s location.

One approach for developing receptor-oriented fields is adjoint modeling where receptor-oriented sensitivity fields are directly calculated from extended 3-dimensional AQMs (Sandu et al., 2003; Hakami et al., 2005). Mathematical implementation of the adjoint method is more complicated than the implementation of the method for the forward sensitivities, and calculation of a limited number of forward sensitivities is less time consuming than direct calculation of reverse sensitivities, though for a large number of receptor locations, the adjoint approach can become very efficient (Martien et al., 2006).
Here, we apply spatial interpolation and inversion mapping to calculate reverse sensitivity fields from a set of forward sensitivity fields. Such a method is simple to use and can be completed within seconds on a standard PC once the forward sensitivity fields are found. Forward sensitivity fields can be efficiently calculated using a 3-dimensional AQM extended with DDM-3D.

5.2 Method

5.2.1 Generation of forward sensitivity fields from AQMs

Current AQMs partition the atmosphere into a 3-dimensional grid of cells to simulate the spatial and temporal evolution of pollutant concentrations by solving a discrete version of the atmospheric diffusion equation (ADE):

\[
\frac{\partial c_i}{\partial t} = -\nabla (U c_i) + \nabla (K \nabla c_i) + R_i + E_i \tag{5-1}
\]

where \(c_i\) is the concentration of species \(i\), \(U\) is the wind field, \(K\) is the second order diffusivity tensor, \(R_i\) is the net rate of chemical production of species \(i\), and \(E_i\) is the field of emissions of species \(i\).

A variety of such models exist (e.g. CMAQ (US-EPA, 1999), CAMx (Dunker et al., 2002), EURAD (Schell et al., 2001), TAPOM (Junier et al., 2005), CHIMERE (Hodzic et al., 2004)), and have been widely applied and evaluated (Seigneur et al., 2004). In this study, the Community Multiscale Air Quality (CMAQ) model (US-EPA, 1999), extended to include DDM-3D, is applied. A detailed description of CMAQ and the implementation and evaluation of DDM-3D are presented elsewhere (Cohan et al., 2005; Napelenok et al., 2006), so only a brief discussion of aspects specific to this study follows.
Absolute sensitivity coefficients, \( s_{ij}(x,t) \), are defined as the change in the concentration \( c_i(x,t) \) of a pollutant \( i \) at location \( x \) and time \( t \) that results from a perturbation \( \delta p_j \) of the model parameter \( p_j \) (Cohan et al., 2005):

\[
 s_{ij}(x,t) = \frac{\partial c_i(x,t)}{\partial p_j} \tag{5-2}
\]

In the context of developing an AOI, parameters undergoing perturbation will be emissions. While these perturbations can be complex fields of spatially and temporally varying emission changes (even of multiple emitted species), in this study, in order to simplify the process, perturbations only at specific (virtual) source locations, \( x_k \), and constant in time, will be used, i.e. \( p_j \) is the constant emission, \( E_j(x_k) \), at location \( x_k \) of species \( j \). The perturbed emissions can be a single emitted species, e.g., \( \text{SO}_2 \), or a combination of species, e.g., \( \text{NO}_x \), a mixture of NO and \( \text{NO}_2 \), and if desired, an even more complicated suite of species, combining all compounds emitted by a specific source. As such, the sensitivity of species \( i \) at location \( x \) to an emission of species \( j \) at location \( x_k \) will be expressed as:

\[
 s_{ij,k}(x,t) = \frac{\partial c_i(x,t)}{\partial e_j(x_k)} \tag{5-3}
\]

where \( \partial e_j \) is the rate of the added emission of species \( j \) at location \( x_k \), which, for this work, is constant in time.

Here, direct sensitivity analysis, DDM-3D, is used to find \( s_{ij,k} \). This method has several advantages compared to the brute force method. It directly provides the
sensitivity fields (making it more efficient) and avoids some numerical noise issues. However, sensitivities generated by brute force can also be used.

### 5.2.2 Receptor-oriented, or reverse, sensitivity fields

While environmental policy makers are often concerned with how a specific source(s) impacts air quality, they are also interested in how a specific location (or receptor) is impacted by sources throughout a region. This requires receptor-oriented sensitivity fields. Created for a specific location, i.e. a receptor, a reverse sensitivity field contains the sensitivity of this receptor to emissions from any location in the domain. Receptor-based sensitivity coefficients \( z_{i,r}(\bar{x}_s, t) \) are defined as the change of the concentration \( c_i \) of a pollutant \( i \) at the receptor-location \( \bar{x}_r \) that results from a perturbation \( e_{j,k} \) in the emissions of species \( j \) at location \( \bar{x}_s \):

\[
z_{i,r}(\bar{x}_s, t) = \frac{\partial c_i(x_r, t)}{\partial e_j(x_s)} \tag{5-4}
\]

(\( x_s \) is differentiated from \( \bar{x}_k \), because \( \bar{x}_k \) is used for a discrete source location above and \( x_s \) represents all possible locations, i.e. a field).

Similar to forward sensitivities, the (semi-normalized) relative, receptor-based sensitivity \( z_{ij,r}^*(\bar{x}_s, t) \) is introduced:

\[
z_{ij,r}^*(\bar{x}_s, t) = e_j^*(\bar{x}_s)z_{ij,r}(\bar{x}_s, t) = \frac{\partial c_i(x_r, t)}{\partial e_j(x_s)} \tag{5-5}
\]

where \( e_j^*(\bar{x}_s) \) is the emission of species \( j \), at location \( \bar{x}_s \), constant in time, and \( \partial e_j(x_s) \) is the non-dimensional perturbation factor for the source at \( x_s \).
The magnitude of the perturbation factor does not matter as the sensitivity coefficient is semi-normalized and a linear response is assumed. A more complex form for the emissions field could be used e.g., non-constant or specified for multiple locations.

5.2.3 Generation of reverse sensitivity fields by interpolation and inversion of forward sensitivities

There are a variety of approaches for developing receptor-oriented sensitivity fields from forward sensitivities. One approach would start off by calculating $N$ forward sensitivity fields corresponding to $N$ virtual sources located at various regions in the modeling domain, i.e. find:

$$ s_{v,k}^* (x,t) = \frac{\partial c_j (x,t)}{\partial e_j (x_k)}, k=1,\ldots,N \quad (5-6) $$

Given $N$ forward sensitivities, $s_{v,k}^* (x,t), k=1,\ldots,N$, the reverse sensitivity, $z_{y,r}^* (x_s,t)$ is known, precisely, for $N$ source-receptor pair locations:

$$ z_{y,r}^* (x_k,t) = s_{v,k}^* (x_r,t), k=1,\ldots,N \quad (5-7) $$

That is, the receptor-oriented sensitivity, $z_{y,r}^* (x_k,t)$, for the receptor located at location $\overline{x}_r$ is calculated for each location where a virtual source is placed to find $s_{v,k}^* (x_k,t)$, i.e. at $\overline{x}_k$, $k=1,\ldots,N$. However, the reverse sensitivity is not known at any other points.

Calculating the reverse sensitivity $z_{y,r}^* (x,t)$ for locations other than the $\overline{x}_k$'s ($\overline{x} \notin \overline{x}_k, k = 1,\ldots, N$), can be accomplished by interpolation/extrapolation from the $N$ known reverse sensitivities. This does not utilize the vast majority of the information.
provided by the forward sensitivities. A second approach is to invert the forward sensitivities assuming that the spatial relationship between a receptor and source is preserved, followed by interpolation of those inverted fields (Wilkinson, 2004):

$$z_{ij,r}(x,t) = \sum_{k=1}^{N} w_k(x) s_{ij,k}(\overline{x}_t,t)$$

(5-8)

where $\overline{x}_i$ is the location that has the same distance from the source location $\overline{x}_k$ as the receptor location $\overline{x}_r$ has from $\overline{x}$ ($\overline{x}_i = \overline{x}_k + \overline{x}_r - \overline{x}$), and $w_k(\overline{x})$ is the weight of the source at location $\overline{x}_k$ applied to the sensitivity field for the receptor at $\overline{x}_r$.

The approach used here generates the receptor-oriented, reverse fields based on developing a complete set of forward fields and takes advantage of recognizing that if the forward sensitivity field $s_{ij,s}^*(\overline{x},t)$ is known for all $\overline{x}_s$, i.e. for a source located at any point in the region, according to Eq. 5-7, the complete reverse sensitivity field for any receptor, i.e. $z_{ij,r}^*(\overline{x},t)$ for all $\overline{x}_r$, is known.

Such a field of complete forward fields can be developed by interpolation of the known forward fields $s_{ij,k}^*(\overline{x},t)$, $k=1,\ldots,N$ for any source-location $\overline{x}_s$:

$$s_{ij,s}^*(\overline{x},t) = \sum_{k=1}^{N} w_{s,k}s_{ij,k}^*(\overline{x}_t,t)$$

(5-9)

where $w_{s,k}$ is the weight applied to the sensitivity field developed for location $\overline{x}_k$ to estimate the forward sensitivity field for a source at $\overline{x}_s$, and where $\overline{x}_t$ is the location that has the same positional relationship from the source-location $\overline{x}_k$ as location $\overline{x}$ has from source-location $\overline{x}_s$ ($\overline{x}_t - \overline{x}_k = \overline{x} - \overline{x}_s$). The weights, $w_{s,k}$, are determined by the spatial interpolation approach chosen, and Eq. 5-8 can be rewritten as:
\[
s_{\mathbf{i},\mathbf{s}}^* (\mathbf{x_s} + \delta x, t) = \int_{k=1}^{N} \left( s_{\mathbf{i},k}^* (\mathbf{x}_k + \delta x, t) \right) \]

where \( \int_{k=1}^{N} \left( s_{\mathbf{i},k}^* (\mathbf{x}_k + \delta x, t) \right) \) is the interpolation of the given sensitivities at the positions \( \delta x \) relative to the source locations for location \( \mathbf{x}_s \).

A number of possible interpolation methods were considered, including Nearest Neighbor Interpolation, inverse distance weighting, Kriging and Natural Neighbor Interpolation (NNI). NNI (Sibson, 1981; Boissonnat and Cazals.F, 2002) was found to be the most appropriate. It is an extended nearest neighbor interpolation and takes into account not only the absolutely nearest point, but all the “nearest surrounding” points, which means it is a weighted average of the points that are the “nearest” in different directions from the target location. NNI, here, uses Voronoi Tessellation (Okabe et al., 1992), which partitions a surface into polygons surrounding given points. Voronoi Tessellation is defined as the partitioning of a plane with \( n \) points into \( n \) convex polygons such that each polygon contains exactly one point and every point in a given polygon is closer to its central point than to any other. The actual interpolation is a weighted average of the natural neighbors’ values. The natural neighbors are the points whose polygons are adjacent to the target position polygon when tessellation is performed including the target point. The weight of each neighbor value is equal to the intersection between its polygon from a tessellation performed without the target point and the target location’s polygon from a tessellation performed including the target point.

The NNI method is simple and robust. Even though it doesn’t require parameters that need to be adjusted to the spatial distribution of the points – which makes its application very easy – the model generates reasonable results for densely and/or sparsely
populated areas as well as for areas containing a mixture of both. Since the interpolated value is generated directly by weighting known values, the resulting value always lies within the range of the known values.

Here, NNI was used to calculate interpolated sensitivity fields for a nested domain covering the southeastern United States. CMAQ was applied to a mother domain using a 36 km grid over the Eastern United States, and the same model, extended with DDM-3D and adapted to treatment of particulate matter is applied to a 12 km nested daughter domain over part of the southeast, namely over Georgia (Figure 5-1). Twenty-five virtual sources were placed in a regular grid over the 12 km domain. (It is not necessary to use a regular placement as NNI does not have such a limitation. Indeed, an irregular array may be desirable as discussed below). Pollutant dynamics were simulated for the beginning of August, 1999 to develop sensitivity “plumes” from each virtual source (Figure 5-2). In this case, the virtual sources were 1.0 mole s\(^{-1}\) per 12x12 km\(^2\) grid of the specific pollutant. These kinds of emissions might represent a concentrated point source or an area source of the same strength located within the grid. In the case of NO\(_x\), 0.95 mole NO s\(^{-1}\) per grid and 0.05 mole NO\(_2\) sec\(^{-1}\) per grid of were used or approximately 4.0 tons of NO\(_x\) day\(^{-1}\) per grid. NNI was then used to interpolate the plumes for grid points between the virtual sources such that a complete sensitivity field of source location-impact relationships is available.
Direct interpolation of just the forward sensitivity fields using Eq. 5-10 will lead to exaggerated diffusion in the resulting interpolated sensitivity fields if the original plumes have different main directions (Figure 5-3ab). For the 25 source-oriented sensitivity fields (Figure 5-2ad), we see that the sensitivity “plume” directions can change over relatively short distances, suggesting that inaccuracies can occur even if we use a relatively dense field of virtual sources. This means that mean plume directions have to be taken into account for accurate interpolation. For this, first, the direction of the plume from each source was calculated and then the original fields’ values were interpolated relative to the source positions and relative to their main plume directions. This direction-relative interpolation can be expressed as:

\[
 s_{ij,k}^* (\bar{x}_s + \nabla(\alpha_s, dr, dp), t) = \int_{k=1}^{N} \int_{t_i}^{t_j} \left( s_{ij,k} (\bar{x}_k + \nabla(\alpha_k, dr, dp), t) \right) \, dt \]

(5-11)
where \( \vec{v}(\alpha, dr, dp) \) is the vector with radial length \( dr \) into direction \( \alpha \) and perpendicular length \( dp \) (Figure 5-3cd), as defined in Eq. 5-12.

\[
\vec{v}(\alpha_k, dr, dp) = \begin{bmatrix}
\cos(\alpha_k) & \sin(\alpha_k) \\
\sin(\alpha_k) & -\cos(\alpha_k)
\end{bmatrix} \begin{bmatrix}
dr \\
dp
\end{bmatrix} \tag{5-12}
\]

where \( \alpha_k \) is the mean plume direction (angle) of given field \( k \), calculated as described below, and \( \alpha_s \) is the angle of the interpolated field; it is calculated based on the interpolation of the plume directions of the given fields (5-3):

\[
\alpha_s = \int_{\alpha_k}^{\alpha_k} \left( \alpha_k \right) \tag{5-13}
\]

where \( \int_{\alpha_k}^{\alpha_k} \left( \alpha_k \right) \) is the angular interpolation of the angles \( \alpha_k \) at positions \( x_k \) for location \( x_s \).
Figure 5-2 Superpositions of a regular grid of 25 directly modeled sensitivity fields for concentrations of aerosol nitrate (a) and ozone (d) to emissions of NO$_x$ for August 2, 1999. Directions of the plumes vary significantly even within short distances. (b) and (e) show superpositions of the same fields interpolated using data withholding (see Eq. 5-18). Besides minor differences, the interpolated fields look the same as the original fields. (c) and (f) show superpositions of the inverted, receptor-oriented, AOI sensitivity fields calculated for the same positions for the receptors as the sources’ positions of the forward fields.
Figure 5-3 (a) Calculated sensitivity fields for two virtual sources located at $X_1$ and $X_2$. $dx$ and $dy$ are the cartesian distances from the source locations in the x and y directions, respectively. (b) Sensitivity field for source location $X_0$ derived from interpolation of the original sensitivity fields corresponding to $X_1$ and $X_2$ using Eq. 5-10, i.e. without angular interpolation. (c) Similar to (a), but $dr$ is the distance in the radial direction along the axis of the plume, and $dp$ is the distance perpendicular to the radial direction. (d) Sensitivity field interpolated for $X_0$ using angular interpolation (Eqs. 11-13). Note the artificial diffusion of the plume in (b) vs. (d).
The mean plume direction $\alpha$ of a directly calculated field is calculated as the angular median of the estimated sub-directions $\beta_r$, $r=1,\ldots, R$, where $\beta_r$ is the direction (seen from the source point) to the cell with the maximal sensitivity value among all cells whose rounded distances (in grid cells) from the source location are $r$:

$$\alpha = \text{angular median}(\beta_r, r=1,\ldots, R), \tag{5-14}$$

where

$$\beta_r = \text{angle}(\bar{x}_{m,r} - \bar{x}_s), \tag{5-15}$$

where $\bar{x}_s$ is the source location for which the field $S$ is created, and

$$\bar{x}_{m,r} = \{ x \in \bar{X}_r \mid \bigvee_{\bar{x}_0 \in \bar{X}_r} s(x) \geq s(\bar{x}_0) \}, \tag{5-16}$$

where

$$\bar{X}_r = \{ x \mid \text{round}(\|x - \bar{x}_s\|) = r \} \tag{5-17}$$

$r$ is limited to the distance between the source-location $\bar{x}_s$ and the nearest border of the domain. Interpolation of the forward sensitivities becomes a two stage interpolation: the angle followed by the field. Both steps are done with the same interpolation method. Care is required during the interpolation of plume directions; e.g. the mean direction of $\pi/4$ and $7\pi/4$ is not $\pi$, but $0$. Accounting for the plumes’ directions inhibits spreading during the interpolation (Figure 5-3cd).

5.3 Results

Application and testing of the methods for developing complete forward fields and reverse sensitivity fields (or AOIs) using CMAQ with DDM-3D/PM utilized the August 1-8, 1999 episode. Evaluation utilized data withholding procedures. Application
was done for two locations, Atlanta, GA, which has some of the highest levels of ozone and PM$_{2.5}$ in the region, and Columbus, an area that has pollutant levels near the national standards.

5.3.1 Evaluation

The first step in assessing the approach is to compare how well the interpolation procedure can recreate a forward sensitivity plume using data withholding. A complete sensitivity field can be derived using N-1 sensitivity fields, withholding data from the forward sensitivity calculated for location $x_s = x_k$, for example by adapting the angular approach:

$$s_{ij,s}(x,t) = s_{ij,k}^*(x_s + \nabla(\alpha_k, drdp)t) = \int_{k=1, k \neq 2, x_s, x_k}^{N} (s_{ij,k}^*(x_k + \nabla(\alpha_k, drdp)t)) \quad (5-18)$$

The resulting interpolated field $s_{ij,s}^{int}(x,t)$ is compared against the directly calculated $s_{ij,k=0}^*(x,t)$, where the former is the field interpolated from the N-1 other fields and the latter is the withheld directly calculated forward sensitivity field. In this study, this has been done for the 25 given virtual sources spread regularly over the modeling domain.

The resulting 25 interpolated sensitivity plumes - each calculated for one of the 25 given source locations and based on the remaining 24 given fields - for aerosol nitrate (Figure 5-2b) and for ozone (Figure 5-2e) compare quite well to those calculated directly. Regression of the interpolated and directly calculated values finds a correlation of 0.94 for NO$_2$ and 0.72 for ozone sensitivities to NO$_2$ emissions (Figure 5-4). Typically the higher sensitivity values relatively close to the receptor are very accurately reproduced.
and much smaller values less so. This is encouraging, since it means that the significantly high sensitivity values located near the receptor are well estimated. For ozone, the correlation is negatively impacted by slight offsets in the plume directions and the fact that the sensitivities vary dramatically at the edge of a plume. Averaging over multiple grids reduces this issue. In general, the interpolation procedure would be more accurate than found by data withholding as this approach multiplies the distance between a calculated and interpolated sensitivity by a factor of two or more.

![Figure 5-4 Correlation between the 25 original fields and interpolated fields using a withholding technique for sensitivity of (a) ozone and (b) NO$_2$ to NO$_x$ emissions. A log-log scale is used.](image)

Having now developed the forward sensitivities, receptor oriented sensitivities can be found using the inversion procedure. Receptor oriented sensitivity fields for the locations where the 25 virtual sources were placed shows that the AOI (receptor-oriented plume) is similar to the mirror image of the forward sensitivity (Figure 5-2cf), as might be expected (they should not be identical). In general, there is no limitation to calculating AOIs only for the locations of the virtual sources, as is shown for the two cases below.
Withholding was also used to evaluate the inversion procedure. For the 25
different receptors, reverse sensitivity fields were calculated 25 times (i.e. 25 * 25 fields),
each time withholding one of the 25 calculated forward fields for the sensitivities of
aerosol nitrate and ozone concentrations to NO$_x$ emissions. The resulting reverse fields
(Figure 5-2cf) were compared to the known values, i.e. according to Eq. 5-7, the withheld
field’s values at the receptor location should be equal to the reverse field’s values at the
corresponding source location. Correlation between these values was 0.80 for ozone
sensitivity to NO$_x$ emissions (Figure 5-5). Larger values, which are most critical, agree
best, though scatter is still found.

![Figure 5-5](image)

**Figure 5-5** Comparison of known and interpolated sensitivities found after inversion using data
withholding for ozone sensitivity to NO$_x$ emissions.

### 5.3.2 Area of Influence Calculation for Atlanta and Columbus, GA

Forward, source-oriented, sensitivity fields for areas in the Southeastern US were
previously used to conduct source apportionment in Georgian cities and construct an
optimal control strategy (Cohan et al., 2005). Two specific receptors are chosen for this application: Atlanta and Columbus, GA, neither of which were locations of a virtual source. Atlanta has some of the highest ozone concentrations in the Southeast and is non-attainment for both ozone and PM$_{2.5}$. Columbus is a near non-attainment region, and must be concerned about adding sources in regions that will have significant impacts on its air quality, i.e., an area within the AOI. Ozone is typically highest near or downwind of Atlanta (Figure 5-6). Atlanta is the largest city in the region, and has significant mobile source and industrial emissions, though the surrounding area is dominated by biogenic emissions.

![Figure 5-6 Maximum 8-hour average ozone concentrations over Georgia on August 6th 1999. A represents the location of Atlanta, and C the location of Columbus, GA.](image)

Forward sensitivity/AOIs pairs for Atlanta (Figure 5-7) for August 3 and then on the 8th after a wind reversal, for both ozone to NO$_x$ and sulfate to SO$_2$ emissions, again, find that the AOI is similar to, but not the same as, the mirror image of the forward sensitivities, even though Atlanta was not one of the 25 virtual sources used. The near-field NO$_x$ scavenging is captured on August 8th for ozone. The peak in the ozone AOIs
are about 0.5 ppb ozone per mole s\(^{-1}\) of NO\(_x\) emitted in a specific grid. Peaks in the sulfate AOIs are about 0.03 ug m\(^{-3}\) per mole s\(^{-1}\) of SO\(_2\) emitted.

Columbus, GA, is a medium sized city with relatively little industrial and mobile source emissions and is in a region with significant biogenic sources. Ozone AOIs for Columbus are similar to those for Atlanta, though the peak sensitivities are somewhat higher (about 10%), and there is no zone showing NO\(_x\)-inhibition of ozone formation because of the high biogenic VOC emissions.
Figure 5-8 Receptor-oriented AOI showing ozone sensitivity in Columbus to NO\textsubscript{x} emissions (ppb per mole/sec) on (a) August 3\textsuperscript{rd} and (b) 8\textsuperscript{th} 1999 and also sulfate sensitivity in Columbus to SO\textsubscript{2} emissions (ug m\textsuperscript{-3} per mole/sec) on (c) August 3\textsuperscript{rd} and (d) 8\textsuperscript{th} 1999.  Strong variation between the different fields is apparent, suggesting that decision making based on AOI fields requires data from many different days.

AOIs may be desired for specific days or hours, as shown above, or averaged over multiple days or even a year or more. The former might be the case when considering impacts on peak ozone concentrations which may be at or above the standards, and the latter when concerned about longer term PM impacts. Two different methods for
calculating an average AOI were assessed, with the example of sulfate to SO$_2$ sensitivity of Columbus. First, calculated virtual source forward fields were averaged over the four days, and then inverted as described above, resulting in an AOI showing relatively poor results when compared to known values ($r=0.42$). More correctly, AOIs are calculated individually for the 4 days and averaged afterwards, leading to much better results ($r=0.75$) which is not surprising, since if applying the first method, one is likely to lose information about the mean-plume direction of the forward fields that is found to be important in the interpolation-inversion technique (Figure 5-3, Eq. 5-18) and varying strongly with time, as suggested by data shown for Columbus (Figure 5-8).

5.4 Discussion

Interpolation of forward sensitivity fields, followed by inversion, is used to develop accurate reverse, receptor-oriented sensitivities, or AOIs. The calculation, here, uses CMAQ extended with DDM and can be done quasi instantaneously – only minor computational capacities are required once a finite number of forward sensitivities are known. The use of an extended Natural Neighbor interpolation method that takes into account the mean plume directions, allows an accurate interpolation between the known forward fields. Tests conducted with the withholding technique show that the resulting interpolated forward fields, as well as the complete reverse fields can accurately describe the “exact fields”, and can be improved by increasing the density of virtual sources. The correlation is especially good for the higher values and decreases when in regions with very low sensitivities, which is not a problem because the sensitivity values are spread over a range of several orders of magnitude among which only the highest are of practical concern. In addition to the creation of reverse sensitivity fields, the interpolation method
that is applied in the AOI development can also be useful for the creation of forward
sensitivity fields for any location when such fields initially are known only for a limited
number of places.

Here, a regular grid of virtual sources is used to calculate 25 forward sensitivity
fields. While a regular grid might be preferable in some cases, various reasons can exist
for which a different spatial distribution of virtual sources would be favored: if e.g.
certain parts of a domain contain no emission sources and are unlikely to get high
emissions in the future, one might want to reduce the density of virtual sources. Also, if
there is a main wind-direction dominating in the region of the receptor location, it can be
advantageous to have a more dense field of source-points on the upwind side of various
receptor regions. If the sensitivities are used for exposure-related (impact) studies, one
might distribute the virtual sources based on a population weighted scheme. Another
approach may iteratively minimize the method’s error by first using a uniformly
distributed test sample of virtual sources spread over the domain, and then to distribute
the final virtual sources with a more dense distribution in regions with highest sensitivity
gradients or with extreme sensitivities. Indeed, one might begin with relatively few
virtual sources and then use those results to place additional virtual sources. Using
Chebychev polynomials (Sanchez et al., 1984) and FAST-type placement methods
(McRae et al., 1982) is also possible. While the method performed well using virtual
sources placed 120 km apart and uniformly distributed over the Georgia domain,
evaluation using different densities of known fields and optimization methods based on
parameters such as population density or sensitivity gradients is of interest.
In order to save computational time for the creation of the set of forward sensitivity fields, DDM can be run for a perturbation which includes emission changes at several different spots simultaneously. The resulting “total” sensitivity field will be the sum of the fields that would result when DDM would have been run for perturbations at each location separately. If the virtual sources are distant enough from each other, i.e. if the plumes of the various sources are not significantly overlapping, the “total” sensitivity field can be cut into different sub-domains mainly influenced by one corresponding emission and so a separate sensitivity field can be created for each of the applied perturbation sources, leading to additional computational savings.

The AOI approach presented here should provide results comparable to adjoint models under development, and such results should be compared both in terms of accuracy as well as computational burden. Finally, this method can also be used to develop forward sensitivity fields using receptor-oriented fields developed from adjoint modeling methods.

**Acknowledgments**

This work was supported, in part, by grants from the US EPA, including RD82897602, RD83107601, RD83096001, and by gifts to Georgia Tech from Georgia Power.

**References**


Tonnesen, G., 2004. Regional haze modeling results for the CENRAP region. CENRAP, Oklahoma City, OK.


CHAPTER 6

Area of Influence (AOI) Sensitivity Analysis: Application to Atlanta, Georgia

Abstract

Area of influence (AOI) analysis was applied to determine the geographical extent of the air pollutant precursors contributing to various pollutant levels in the Atlanta metropolitan area. Receptor-oriented sensitivities of ozone and particulate matter (PM) species to emissions of NO\(_x\), SO\(_2\), NH\(_3\), anthropogenic VOC, and elemental carbon were calculated for various combinations of precursor emissions during 1-10 August, 1999. The episode had high observed concentrations of ozone and PM across several days. AOIs differed significantly by day for each sensitivity as well as spatially between pollutants. Ozone sensitivities peaked at 1.0 ppb per 1.0 mol s\(^{-1}\) (or per 4.0 tons d\(^{-1}\)) per 12x12 km\(^2\) model grid of emissions of NO\(_x\), but averaged around 0.1 ppb over much of Atlanta. Sulfate was the major component of PM, with an average sensitivity of 0.03 µg/m\(^3\) per 1.0 mol s\(^{-1}\) (or per 5.5 tons d\(^{-1}\)) per 12x12 km\(^2\) model grid of SO\(_2\) emissions and an average of 0.02 µg/m\(^3\) per 1.0 mol s\(^{-1}\) per 12x12 km\(^2\) of NO\(_x\) emissions. Ammonia had a significant impact on PM through the formation of ammonium sulfate and ammonium nitrate. Elemental carbon had a geographically small area of influence with high values around the receptor.

* This chapter was submitted to *Atmospheric Environment* with Florian D. Habermacher, Farhan Akhtar, Yongtao Hu, and Armistead G. Russell as coauthors.
Key Words

Area of Influence, AOI, Sensitivity Analysis, Atmospheric Modeling, Air Quality, Direct Decoupled Method.

6.1 Introduction

Air quality has improved over the last decade in the United States and Europe, however, there are still regions where large segments of the population are exposed to elevated concentrations of ozone and particulate matter (US-EPA, 2004). Both have been linked to negative impacts on human health (Dockery et al., 1993; Pope et al., 2002). In order to control these pollutants, it is important to identify sources and source regions leading to elevated levels. Ozone and PM concentrations have been simulated using three dimensional, emissions based air quality models such as CMAQ and CAMx, which spatially and temporally resolve these and many other species with good accuracy compared to actual measurements (Russell and Dennis, 2000). Recently, these models were extended to provide sensitivities of air pollutants in addition to concentrations using the decoupled direct method (DDM) (Yang et al., 1997; Dunker et al., 2002; Cohan et al., 2005; Napelenok et al., 2006), as well as adjoint approaches (Hakami et al., 2006). Sensitivity analysis has a wide array of applications ranging from source apportionment (Dunker et al., 2002; Boylan et al., 2004; Cohan et al., 2005), control strategy assessment, and estimation of uncertainty (Fine et al., 2003).

DDM calculates source impacts in a “forward” sense by providing the response of one or more receptors to perturbations in input parameters at the sources (emissions, initial/boundary conditions, etc.). Adjoint analysis provides receptor-oriented sensitivities, where perturbations are originated at a receptor of interest and propagated
backwards in time (Sandu et al., 2005; Hakami et al., 2006). This method is useful in identifying which sources of air pollution precursors influence a particular receptor, such as densely populated urban area or a protected national park. However, the adjoint method is computationally costly to operate and is most efficient for a large number of receptors. As an alternative, the area of influence (AOI) method was developed that provides similar information along with forward sensitivities (Habermacher et al., 2006). AOI calculation takes advantage of the ability of DDM to efficiently calculate several forward sensitivities at once. The forward sensitivities are spatially interpolated and inverted to provide receptor-oriented AOIs.

Combined with concentrations and sensitivities already calculated by current air quality models, AOIs provide additional information on air quality within a region. AOI analysis was applied to calculate receptor-oriented ozone and particulate matter sensitivities in Atlanta, Georgia. Atlanta and its surrounding suburbs are home to over four million people, and have elevated concentrations of zone and particulate matter with aerodynamic diameter of less then 2.5 micrometers (PM$_{2.5}$). Area of influence analysis is ideal for a place like Atlanta, where it is necessary to develop a clear understanding of where emissions of precursors to ozone and particulate matter formation have the greatest impacts, along with the impacts of specific sources (e.g. Cohan et al., 2005; Napelenok et al., 2006).

### 6.2 Method

#### 6.2.1 Area of Influence (AOI)

Described in more detailed elsewhere (Habermacher et al., 2006), the area of influence (AOI) method is used to generate receptor-based sensitivity fields from forward
sensitivities developed using DDM. The AOI of a pollutant \( i \) at a receptor \( \bar{x}_r \) to emissions of \( j \), or \( Z_{ij,r}(\bar{x},t) \), is expressed by the following:

\[
Z_{ij,r}(\bar{x},t) = \frac{\partial C_i(x_r,t)}{\partial E_j(x_j)}
\]  

(6-1)

where \( E_j(x_j) \) is non-dimensional perturbation of the constant emissions of species \( j \) at location \( \bar{x}_s \). AOIs provide relative receptor-based sensitivities to potential emissions at any point, not actual emissions, e.g., the additional amount of pollutant formed if emissions were increased by the specified amount.

### 6.2.2 Application

Area of Influence analysis was applied to a domain centered on Atlanta, Georgia (Figure 6-1). A 57x60 cell grid with 12km resolution was nested within a larger 36km resolution grid used for providing boundary conditions. A similar domain was used previously for the Fall Line Air Quality Study (FAQS) (Hu et al., 2004). A ten day summer episode was selected: 1 – 10 August, 1999. During this period, Atlanta and much of the rest of the state experienced periods of highly elevated ozone and particulate matter concentrations. Meteorology for the episode was developed using the Mesoscale Meteorological Model version 5 (MM5) (PSU/NCAR, 2003). Emissions were developed from FAQS inventories (Hu et al., 2004) and processed using SMOKE version 2.2 (CEP, 2004).
Figure 6-1 Domain used for AOI analysis. a) The larger course grid is 78x66 with 36km resolution and the smaller nested grid is 57x60 with 12km resolution. Urban areas are distinguished by the blue areas. b) Distribution of the preselected sources of forward sensitivities is show as black dots. Sensitivities to emissions of various pollutants were calculated as point sources at these 25 locations and later interpolated for the rest of the grid cells in the domain. Red dots denote the four additional locations used for the refined analysis.

Initial forward sensitivity fields were developed for 25 regularly spaced grid cells within the domain (Figure 6-1) and extrapolated to the rest of the cells (Habermacher et al., 2006). Sensitivities to emissions of SO\textsubscript{2}, NO\textsubscript{x}, NH\textsubscript{3}, anthropogenic VOC, and elemental carbon were calculated. Species examined included ozone, sulfate, nitrate, particulate elemental carbon, anthropogenic secondary organic aerosol, and total PM\textsubscript{2.5}. For ozone, AOIs were calculated for the 8-hour running average at the time of peak concentration, and 24-hour averages were computed for PM\textsubscript{2.5}. 

107
The simulated episode had high observed ozone and PM$_{2.5}$ concentrations. Stagnant air was trapped in the region for an extended period of time due to a high pressure system situated directly over the southeastern United States. The resulting low wind speeds, high temperature, and little precipitation coupled with high emissions in the region presented ideal conditions for poor air quality. Ozone was high around the Atlanta metropolitan area on all days with an observed peak 8-hour average concentration of 139 ppb on 4 August, 1999. Observed 24-hour average PM$_{2.5}$ concentrations in Atlanta were also high throughout the episode.
Figure 6-2 Simulated maximum daily 8-hour ozone concentrations for a) 3 August, b) 5 August, c) 7 August, d) 9 August, 1999. Observed and simulated concentrations exceeded the 8-hour NAAQS of 0.8 for ozone each day.
Figure 6-3 Simulated 24-hour averaged PM$_{2.5}$ concentrations for a) 3 August, b) 5 August, c) 7 August, d) 9 August, 1999. PM$_{2.5}$ is the sum of Aitken and accumulation modes of sulfate, nitrate, ammonium, elemental carbon, primary and secondary organic carbon, and “unspecified” aerosol. Simulated concentrations exceeded the daily averaged NAAQS of 65 ug/m$^3$ on the 7$^{th}$ and were well above the annual standard of 15 µg/m$^3$ each day.

6.3 Results and Discussion

Model performance was evaluated before beginning AOI analysis to insure reasonable results. Simulated concentrations of ozone and each particulate species were compared to observations from the Aerometric Information Retrieval System (AIRS) and
Interagency Monitoring of Protected Visual Environments (IMPROVE) sites in the domain (US-EPA, 1993; NPS, 2006). Ozone had a mean normalized error of 20.3% and a mean normalized bias of -2.69%. Both of these statistics are well within the EPA’s guidelines for air quality modeling (US-EPA, 1999). PM$_{2.5}$ had a fractional error of 28.5% and a fractional bias of -13.0%. Individual PM$_{2.5}$ components also performed similarly (Table 6-1), with the exception of nitrate, which had much higher fraction error (103.4%), but was present in very low quantities (average of 0.6 ug/m$^3$ at all available stations in the domain). Organic carbon was underestimated. Overall, PM$_{2.5}$ performance was similar to that reported by other studies (Boylan et al., 2004; Seigneur et al., 2004).

The performance of DDM-3D in CMAQ (Cohan et al., 2005; Napelenok et al., 2006) and the AOI method (Habermacher et al., 2006) have been evaluated elsewhere.

| Table 6-1 Particulate Matter modeling performance for the 1-10 August, 1999 episode. |
|---------------------------------|-----------------|-----------------|
|                                | Average concentration* (ug/m$^3$) | Fractional error (%) | Fractional Bias (%) |
| Total PM 2.5                   | 29.1            | 28.5            | -13.0            |
| Sulfate                        | 10.3            | 30.7            | 2.72             |
| Nitrate                        | 0.6             | 103.4           | -78.8            |
| Ammonium                       | 4.4             | 37.3            | -26.7            |
| Elemental Carbon               | 1.4             | 52.0            | -9.3             |
| Organic Carbon                 | 7.6             | 50.3            | -41.6            |

* Concentration averages are computed for monitoring stations with available observations.

Simulated fields show extensive areas of elevated ozone that are consistent with observations (Figure 6-2). PM$_{2.5}$ was more uniform throughout the domain with a dramatic peak on 7 August of 79.8 ug/m$^3$ in Atlanta (Figure 6-3). Sulfate and
“unspecified” mass composed the largest fraction (20% and 35% respectively). Elemental and organic carbon contributed around 15% each while secondary organic aerosol (SOA) and ammonium contributed around 10% each.

### 6.3.1 Ozone Area of Influence

Due to large amounts of emissions of biogenic VOCs in the region, ozone formation around the Atlanta metropolitan area is usually NO\textsubscript{x} limited. Prior sensitivity results (Cohan et al., 2005) show a very limited area of VOC emissions impacting ozone. Thus, the ozone AOI for NO\textsubscript{x} emissions is discussed here. Forward fields for ozone were developed as sensitivities to an addition of continuous emissions of 1.0 mole s\textsuperscript{-1} (or approximately 4.0 tons day\textsuperscript{-1}) per 12x12km\textsuperscript{2} model grid of NO\textsubscript{x} at each of the 25 regularly spaced sources in the domain. These kinds of emissions are equivalent to a concentrated point source or an area source of the same net strength within the model grid. The perturbation in emissions resulted in a plume of ozone sensitivities that developed over time originating from each source location (Figure 6-4). A running eight-hour average was computed for all ozone results to correspond to the averaging period of the National Ambient Air Quality Standards (NAAQS). Forward sensitivities for ozone captured titration of NO\textsubscript{x} during the night, resulting in negative sensitivities near the sources during periods without sunlight. As photochemical activity increased, forward sensitivity plumes shifted to positive values. Large variability exists between individual forward fields as well as within each field temporally suggesting complex meteorological and chemical interactions of NO\textsubscript{x} to produce ozone in the region. The forward ozone sensitivities range from around -10 ppb ozone at night to +10 ppb ozone during the day per 1.0 mole s\textsuperscript{-1} per 12x12km\textsuperscript{2} model grid continuous emissions of NO\textsubscript{x}. 

112
Figure 6-4 Forward fields of ozone sensitivity to NO\textsubscript{x} emissions on 5 August, 1999 at a) 01:00 b) 06:00 c) 11:00 d) 16:00 and e) 21:00 (8-hour average). Sensitivities are computed to a 1.0 mole/sec increase in NO\textsubscript{x} emissions at each location. The 25 fields were computed independently, but are presented as a summation. Blue areas indicate ozone titration by NO\textsubscript{x} during night-time, while the red areas represent the formation of ozone in the presence of sunlight.

After the interpolation and the inversion procedures, the area of influence results for Atlanta show significant daily variability (Figure 6-5). The highest contribution to ozone formation by NO\textsubscript{x} is from regions near the receptor. However, on days where concentrations were particularly high (5, 7 August), longer range transport from the rest of Georgia and the neighboring states is evident. In some grid cells, AOI reaches as high as 1.0 ppb ozone per 1.0 mole s\textsuperscript{-1} per 12x12km\textsuperscript{2} model grid continuous NO\textsubscript{x} emissions. However, most of the contribution comes from cells with magnitudes of around 0.1 ppb. Daily variability is also drastic in the AOI plots suggesting that control strategies employing sensitivity analysis will require several days of results in order to get a representative sample.
Figure 6-5 Ozone Area of Influence from emissions of NOx on a) 3 August, b) 5 August, c) 7 August, d) 9 August, 1999. Results are shown for the 8-hour average at 18:00 on each day.

In order to verify the Area of Influence results, the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Hess, 1998) was used to compute reverse wind trajectories from Atlanta (Figure 6-6). While HYSPLIT results neglect chemical interactions accounted for in CMAQ, they are useful in identifying the spatial progression of air parcels that arrive at the receptor during the time of peak ozone. In this case, the trajectories support the general patterns of the AOI plots. On 3 August, the ozone area of influence stretches in the northeasterly direction through South Carolina as do the reverse wind trajectories. Both 5 August and 7 August show evidence of low
speed winds with frequently changing directions. These two days had higher ozone concentrations due to stagnation. 9 August shows fairly constant winds coming from Alabama and the AOI has a similar direction of the sources for NOx that led to ozone formation in Atlanta on that day. Trajectories for all days had very little vertical movement.

Figure 6-6 Reverse wind trajectories as computed by the HYSPLIT model ((Draxler and Hess, 1998)) on a) 3 August, b) 5 August, c) 7 August, d) 9 August, 1999. The 100 meter, 24 hour trajectories are shown arriving in Atlanta at 18:00 (red), 16:00 (dark blue), 14:00 (green), 12:00 (light blue). While a) and d) show fairly constant winds, the other two days evidently experienced frequent changes in wind direction which is reflected in the AOI results.
6.3.2 Particulate Matter Area of Influence

Sensitivities of total particulate matter, as well as its individual components, were calculated for potential emissions of SO₂, NOₓ, NH₃, anthropogenic VOC, and elemental carbon. Since 7 August was such an extreme peak in simulated PM₂.₅ concentrations, AOIs for this day were analyzed (Figure 6-7). Similar to the ozone AOI on this day, a large amount came from south of Atlanta, though, shifting low speed winds during a part of the day led to potential contributions from the north. Sulfate is an important PM₂.₅ component in this region due to SO₂ emissions. The area of influence of sulfate sensitivity to SO₂ emissions is large suggesting the regional nature of this pollutant (Figure 6-7a). This AOI reached a maximum of 0.1 µg/m³ sulfate sensitivity per mole s⁻¹ (or per 5.5 tons per day) per 12x12 km² model grid of SO₂ emissions, but generally ranged from 0.02 – 0.05 µg/m³. NOₓ emissions act to facilitate the oxidation of SO₂ and the subsequent formation of sulfate. However, this effect is less important and thus the AOI for sulfate sensitivity to NOₓ emissions shows a lesser impact (0.02 µg/m³ sulfate per 1 mole s⁻¹ NOₓ emissions (Figure 6-7b)). While SOA produced from biogenic sources are dominant in the region, anthropogenic precursors were considered in the AOI analysis as these are more open to control. Sensitivities to VOC emissions are fairly low, averaging around 0.001 µg/m³ per mole s⁻¹ per 12x12 km² model grid of SOA sensitivity (Figure 6-7c). Ammonium emissions on the other hand, are responsible for a significant fraction of secondary particulate matter produced in the region with peak AOI sensitivity of 2.4 µg/m³ and averaging around 0.1 µg/m³ (Figure 6-7d). The overall sensitivity of PM₂.₅ to ammonia emissions is large, so NH₃ emissions control should be considered in regional control strategies (Figure 6-7e). Effects of primary emissions were considered
by calculating the AOI of elemental carbon emissions to elemental carbon concentrations in Atlanta (Figure 6-7f). The AOI for elemental carbon shows high values peaking at 5.4 μg/m³ per g s⁻¹ per 12x12 km² model grid, however, the spatial extent of high sensitivity around Atlanta is fairly small. EC is typically of concern in areas very near its emission, which is confirmed by the AOI analysis. Other non-reacting aerosol species would have similar AOIs.

Figure 6-7 Area of Influence on 7 August, 1999 of a) sulfate to SO₂ emissions, b) sulfate to NOₓ emissions, c) SOA to anthropogenic VOC emissions, d) ammonium to NH₃ emissions, e) total PM₂.₅ to NH₃ emissions, and f) elemental carbon to elemental carbon emissions. All results are 24-hour averaged.

6.3.3 Upper level emissions

AOI results presented above show the expected changes in concentrations in Atlanta due to changes in emissions in the lowest 20 meters of the domain (model layer 1). Some emissions also occur in the upper levels. For example, SO₂ from electricity
generating units (EGUs) is effectively released at around 500 meters due to high temperatures and exit velocities from power plant stacks. AOIs at the ground level to upper level emissions of SO$_2$ were also calculated (Figure 6-8a,c). On most days, there is little difference between the upper layer and the ground level AOIs. For example, on 7 August, the ground level AOI shows a higher maximum and stronger influence from eastern Tennessee (Figure 6-7a), while the upper level AOI has more areas with a high influence from Georgia (Figure 6-8c), but a lower peak sensitivity.

In order to quantify the current spatial contributions of sensitivity to Atlanta, the product of the AOI field for sulfate sensitivity to SO$_2$ and the actual emissions field of SO$_2$ in the appropriate level ($Z_{\text{ASO}^2^-,\text{SO}_2,\text{ATL}}(\tilde{x},t) \cdot E_{\text{SO}_2}(\tilde{x},t)$) was calculated. It was found that sulfate sensitivity to upper level SO$_2$ emissions are spatially distributed such that the peaks do not always correspond with the AOI peaks on most days (Figure 6-8b,d). This is possible because the emissions peaks during this episode occurred in the area where AOI shows only smaller sensitivities. However, if at any time the emission peaks coincide with AOI peaks, the impacts would be substantial.
Figure 6-8 Area of Influence on a) 5 August and c) 7 August, 1999 of sulfate to SO$_2$ emissions at 500 meters and the corresponding day’s – b), d) – contribution of the same sensitivity (calculated as the product of emissions at 500 meters and the AOI). All results are 24-hour averaged.

6.3.4 AOI Iteration

Area of influence analysis can be further improved by increasing the number of initial forward sensitivity “seed” points and also by developing a better system of determining their locations. In this study, 25 points were located in a regularly spaced grid over the domain. However, several of these points are located in areas of low emissions far away from the target receptor making their contributions insignificant. Four additional points were added in cells (25 35), (11 22), (10 50), and (24 37) (Figure
The addition had a minor impact on the spatial extent of the AOI, but a significant improvement on the ability to capture local sensitivities.

In order to quantify the improvement in performance of AOI, the following relationship was used:

\[
\sum_{c=1}^{N} Z_{ij,c}(x_c, t) \cdot E_j(x_c, t) = S_j(x_r, t) \tag{6-2}
\]

where \( Z_{ij,c}(x_c, t) \) is the AOI field of pollutant \( i \) from emissions of \( j \) at each cell \( c \) in the domain (out of the total \( N \)), \( E_j(x_c, t) \) is the emissions of \( j \) in that cell, and \( S_j(x_r, t) \) is the sensitivity of \( i \) to domain-wide emissions of \( j \) at the receptor location \( r \) for which the reverse field was developed. Adding up the product of the emissions in each cell and that cell AOI contribution should approximately equal the sensitivity in that cell to domain-wide emissions if forward fields were developed from each cell and not interpolated. (The interpolation procedure that was used limits the maximum sensitivities, so it is expected that this test would be biased low.) The results suggest that the addition of just four well-placed forward fields improve the performance significantly. Averaged over the entire length of the episode, 72% of the sulfate sensitivity in Atlanta to ground level emissions of \( \text{SO}_2 \) domain-wide was accounted for using the AOI results and Eq. 6-2 with the extra 4 points compared to 64% calculated in the same way using the original 25 points (Table 6-2). Thus, the method can be used in an iterative fashion with low additional computational resource investment if higher resolution results are desired.
Table 6-2 AOI performance evaluation for sulfate sensitivity in Atlanta to domain-wide emissions of SO$_2$ at the ground level. AOI predicts a higher fraction of the expected sensitivity with four additional points some of which are located up-wind and in areas of high SO$_2$ emissions.

<table>
<thead>
<tr>
<th>Date</th>
<th>Sensitivity (ug/m$^3$)</th>
<th>Predicted Fraction (25 points)</th>
<th>Predicted Fraction (29 points)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Aug.</td>
<td>0.27</td>
<td>67.1%</td>
<td>72.6%</td>
</tr>
<tr>
<td>3 Aug.</td>
<td>0.12</td>
<td>67.1%</td>
<td>71.1%</td>
</tr>
<tr>
<td>4 Aug.</td>
<td>0.22</td>
<td>60.8%</td>
<td>64.9%</td>
</tr>
<tr>
<td>5 Aug.</td>
<td>0.24</td>
<td>56.9%</td>
<td>83.3%</td>
</tr>
<tr>
<td>6 Aug.</td>
<td>0.46</td>
<td>57.1%</td>
<td>68.4%</td>
</tr>
<tr>
<td>7 Aug.</td>
<td>0.44</td>
<td>65.2%</td>
<td>78.4%</td>
</tr>
<tr>
<td>8 Aug.</td>
<td>0.26</td>
<td>78.2%</td>
<td>71.9%</td>
</tr>
<tr>
<td>9 Aug.</td>
<td>0.27</td>
<td>60.4%</td>
<td>68.7%</td>
</tr>
</tbody>
</table>

6.4 Summary

The expanding Atlanta metropolitan area has high mobile and industrial emissions in addition to being surrounded by several coal-fired power plants and biogenic VOC emissions from the vegetation covering a large fraction of the region. This complex mixture of different pollutants in the same location leads to both high ozone and high PM concentrations. Determining the sources of these pollutants is further complicated by complex and variable meteorology. Area of influence analysis as applied to Atlanta provides the geographical extent of the sources that led to formation of both ozone and PM$_{2.5}$ during the 1-10 August, 1999 episode. It was found that while all sensitivity had significant daily variation some had a large footprint (sulfate formation from SO$_2$), while others had only local effects (elemental carbon). Further variation is evident from the effect on the ground level receptors from elevated sources. Sulfate was found to be the major component of PM$_{2.5}$ with high magnitude AOs to SO$_2$ emissions and lower ones to NO$_x$ emissions. Ammonia was found to have a significant impact on Atlanta mainly
from the formation of ammonium. The AOI results are consistent with HYSPLIT model trajectories for sources of air parcels that eventually impacted the receptor (Atlanta) on each day.

Acknowledgements

The support for this project came from U.S. Environmental Protection Agency under Agreements RD82897602, RD83107601, RD83096001.

References


CHAPTER 7

Conclusions and Future Research

7.1 Summary of Findings

This thesis explored sensitivity analysis of particulate matter and specifically provided insights on particulate matter formation and transport in the southeastern United States. Important tools were developed that should provide additional information to those charged with air quality management. The implementation of DDM-3D/PM into CMAQ extends the functionality of this model and the AOI method is a computationally efficient alternative for calculating receptor-oriented sensitivities.

The capability of the CMAQ model to calculate sensitivities of particulate matter is an important tool that should aid policy makers in developing control strategies for these pollutants. DDM-3D/PM, as explained in detail in Chapter 2 and Appendix A, provides results similar to those computed by the traditional difference or “brute force” method. In fact, in some cases, the direct sensitivities are more reasonable and can be explained by real physical and chemical processes while the “brute force” results can be dramatically influenced by discontinuities and nonlinearities in the model. The sensitivity of nitrate to SO$_2$ emissions is one such example. It is expected that SO$_2$ controls would increase average nitrate concentrations slightly, which is confirmed by negative sensitivities throughout the domain calculated by DDM. “Brute force” results, on the other hand, were shown to be erratic and unreasonable. An additional important benefit of using DDM-3D/PM is computational efficiency. While transport algorithms provide no CPU time savings, since each sensitivity field must be advected and diffused
independently, savings come from efficient treatment of chemical processes and aerosol dynamics.

Application of DDM-3D/PM to historical and future projected episodes in the southeastern United States provided important insights on particulate matter source impacts in the region. The investigated episodes had meteorological commonalities. Namely, high pressure systems sitting over the region often prohibited efficient turbulent mixing of the air mass and led to stagnant conditions. Lack of precipitation and high temperatures further contributed to accumulation of PM in the boundary layer. The largest contributor to the total PM$_{2.5}$ mass in Georgia’s cities was the secondary formation of sulfate from long range regional transport of SO$_2$. Elemental and organic carbon also composed a significant fraction of total mass. However, these pollutants came mainly from primary emissions of sources spatially near the examined cities. This occurrence can be explained by the relatively short lifetimes of EC and OC. Investigation of the formation of secondary organic aerosol from VOC emissions uncovered an interesting interaction of this precursor with other inorganic PM species. It was found that high VOC emissions can impede the downwind oxidation of SO$_2$ through consumption of the hydroxyl radical. This effect is small and the contribution of VOCs to total PM$_{2.5}$ concentration is dominated by SOA formation. Another interesting curiosity was observed that could be manifested from SO$_2$ controls. While sulfate concentrations are lowered from lower SO$_2$ emissions, some locations can experience a slight increase in nitrate concentrations. This PM “replacement” is possible from higher availability of ammonia to react with NO$_x$ emissions and ultimately lead to the condensation of nitric acid. Ammonia emissions are interesting in the future projected case, because little is
currently planned in terms on their reductions. Thus, NH$_3$ can be expected to lead to increased sulfate, nitrate, and ammonium production.

Findings resulting from direct sensitivity calculations were also confirmed by the application of the Area of Influence analysis. The development of AOI provides additional insights in the complex physical and chemical interactions of various PM$_{2.5}$ components and their gaseous precursors. This is done through interpolation of forward sensitivity fields originating from pre-selected locations in the modeling domain and inverting them to arrive at reverse or receptor-oriented sensitivities. The method is computationally efficient in that it requires minimal CPU investment after the forward sensitivity fields are available. The number of required forward fields can be minimized by their strategic placement in the domain. The AOI method also takes into account the mean plume direction of the forward sensitivities during interpolation in order to minimize the artifact “diffusion” effect of averaging.

Application of the AOI method to Atlanta for the 1-10 August, 1999 episode showed the spatial extent of the sources around this receptor that led to the formation of PM$_{2.5}$ and also ozone. AOIs for Atlanta were found to have significant daily variation for all pollutants. However, some patterns were apparent. For example, sulfate formation from SO$_2$ had a large spatial footprint, while elemental carbon emissions had dominantly local effects. The variability also extended in the vertical direction and the effects on the ground level receptors were found to be dependent on the elevation of emissions. The reasonableness of the AOI results were also confirmed by tracking air parcels with the HYSPLIT model and through some sensitivity budgeting methods outlined in Chapter 6.
7.2 Future Research

The quality of the information provided by both DDM-3D/PM and AOI depends most on the ability of the underlying air quality model (in this case, CMAQ) to accurately replicate the physical and chemical processes occurring in the real world. The performance of air quality models has been evaluated as a part of this work and by others. Several shortcomings have been identified and need to be addressed. For example, CMAQ generally under-predicts the formation of secondary organic aerosol from both anthropogenic and biogenic emissions of VOCs. It is evident that yields from currently modeled SOA precursors are possibly low and that not all precursors are considered. In CMAQ, monoterpenes appear to have low yields, while compounds like benzene and isoprene are assumed to have negligible formation of SOA. Laboratory experiments and chamber studies are continuously revising aerosol yields. These findings need to be reviewed and incorporated into air quality models. Cloud processing modules could also benefit from updating. CMAQ’s aqueous chemistry routines consist only of SO$_2$ oxidation in the liquid phase and subsequent formation of sulfate through five specific pathways (H$_2$O$_2$, O$_3$, metals, MHP, and PAA). While thermodynamic interactions in the aqueous phase are accounted for by the ISORROPIA module integrated in CMAQ, more detailed chemical interactions between various ions are not considered.

Improvements to underlying air quality models should be accompanied with improvements to direct sensitivity calculation methods. Most apparent improvements are the possible gains in DDM-3D/PM performance improvements from addition of higher order sensitivity calculation capability for particulate species. This had been done already for gaseous species and shows significant improvements in results for ozone
sensitivities. Currently, Area of Influence analysis provides two-dimensional results in the sense that emissions from only one elevation for each AOI are considered. Conceptually, a three-dimensional AOI make more sense. This can be achieved by layering AOIs from different elevations, but a more automated process should be considered. It was shown that elevation of emissions plays an important role in receptor impacts, mainly because transport varies with elevation. A three-dimensional AOI would be beneficial in considering the impacts of elevated sources such as SO$_2$ emissions from power plant stacks. AOI analysis can be further refined by examining the effects of “seed-point” emission strength. In this work, 1 mole/sec of continuous emission of each pollutant was used. This amount corresponds to 4.0 tons/day of NO$_x$ or 5.5 tons/day of SO$_2$. Since chemical interactions with other species plays an important role in the development of the AOI field, the sensitivity of the actual source strength should be further explored and any non-linearity should be identified.

Finally, the development and refinement of these tools (DDM-3D/PM and AOI) necessitates their application to different regions and episodes. Most importantly, winter-time conditions should be studied, since the current work concentrated mainly on summer-time episodes. The meteorology influence can also be further explored by quantifying the effects of stagnation (which were common in the episodes modeled in this work) and also other prevalent meteorological scenarios.
APPENDIX A

SPATIAL COMPARISON OF BRUTE FORCE AND DDM-3D/PM

In order to verify the accuracy of the Decoupled Direct Method in 3D for particulate matter (DDM-3D/PM), a summer time episode was simulated: 6 July – 18 July, 2001 using the CMAQ model. The domain covered entirely the eastern United States using a 36 km grid resolution (66 vertical cells by 78 horizontal cells). Meteorology for the period was developed using MM5 version 3.6 and emissions were processed using SMOKE version 1.5. SAPRC99 was used as the chemical mechanism. Brute force sensitivities were calculated using the difference method as follows:

\[
S_{ij}^{bf} = \frac{C^{+10\%} - C^{-10\%}}{0.2}
\]

where \(C^{+10\%}\) is the simulated concentration at an emissions level 10% higher than the base, \(C^{-10\%}\) is the concentration at emissions 10% lower, and \(S_{ij}^{bf}\) is the approximate first-order, brute force sensitivity. The twenty percent difference was chosen to be large enough to prevent numerical noise, while being small enough to capture the local derivative at the base level of emissions. Sensitivities of sulfate, nitrate, ammonium, anthropogenic secondary organic aerosols (SOA), and biogenic SOA were computed using both the brute force method and DDM-3D/PM to domain wide emissions of \(SO_2\), \(NO_x\), \(NH_3\), anthropogenic VOC, and biogenic VOC. All results were averaged every 24 hours in order to match the regulation time period.

The majority of significant sensitivities (those that are greater in magnitude than 5% of the corresponding concentrations) compared well spatially and temporally. Averaged statistical comparison was shown in Chapter 2, and here three sample days are
shown for each sensitivity parameter: sulfate sensitivity to SO$_2$ (Figure A-1), NO$_x$ (Figure A-2), NH$_3$ (Figure A-3), nitrate sensitivity to SO$_2$ (Figure A-4), NO$_x$ (Figure A-5), NH$_3$ (Figure A-6), ammonium sensitivity to SO$_2$ (Figure A-7), NO$_x$ (Figure A-8), NH$_3$ (Figure A-9), anthropogenic SOA sensitivity to xylene (Figure A-10), and biogenic SOA sensitivity to terpenes (Figure A-11).

The worst comparison was for the sensitivity of nitrate to emissions of SO$_2$ (Figure A-4). As discussed in Chapter 2, there is a possibility of numerical noise effecting the brute force results. In this case, the DDM sensitivity shows values that are more consistent with want might actually happen in the atmosphere. Nitrate levels are expected to decrease with the addition of SO$_2$, partly due to the competition for formation of ammonium nitrate and ammonium sulfate. Sulfate sensitivity to ammonium emissions (Figure A-3) also had a poor averaged statistical comparison. However, the spatial results shown here suggest that the two methods generally agree, since the sensitivity peaks are usually predicted in the same area. In this case, the error comes from lower predictions by the DDM method on most days. Similarly, the difference in magnitude between the two methods introduces a small error in the SOA results. DDM shows slightly higher sensitivities of SOA to both biogenic and anthropogenic emissions. While the statistical comparison shows very high correlation coefficients, the predicted peaks are slightly different. The remaining sensitivities show very good spatial agreement on each day.
Figure A-1 Sulfate sensitivity to domain-wide emissions of SO$_2$ for brute force (left side) and DDM (right side)
Figure A-2 Sulfate sensitivity to domain-wide emissions of NO\textsubscript{x} for brute force (right side) and DDM (left side)
Figure A-3 Sulfate sensitivity to domain-wide emissions of NH$_3$ for brute force (left side) and DDM (right side)
Figure A-4 Nitrate sensitivity to domain-wide emissions of $SO_2$ for brute force (left side) and DDM (right side)
Figure A-5 Nitrate sensitivity to domain-wide emissions of NO\textsubscript{x} for brute force (left side) and DDM (right side)
Figure A-6 Nitrate sensitivity to domain-wide emissions of NH$_3$ for brute force (left side) and DDM (right side)
Figure A-7 Ammonium sensitivity to domain-wide emissions of SO₂ for brute force (left side) and DDM (right side)
Figure A-8 Ammonium sensitivity to domain-wide emissions of NO\textsubscript{x}, for brute force (left side) and DDM (right side)
Figure A-9 Ammonium sensitivity to domain-wide emissions of NH₃ for brute force (left side) and DDM (right side)
Figure A-10 Anthropogenic SOA sensitivity to domain-wide emissions of xylene for brute force (left side) and DDM (right side)
Figure A-11 Biogenic SOA sensitivity to domain-wide emissions of terpenes for brute force (left side) and DDM (right side)
VITA

Sergey L. Napelenok

Sergey L. Napelenok was born in Gomel, Belarus on 13 May, 1978. In 1991, he relocated with his family to the United States. He earned a B.S. in Civil Engineering in 2000 from Washington State University where he was introduced to air quality modeling by Professor Brian Lamb. Sergey earned a M.S. in Civil Engineering in December of 2001 at Georgia Institute of Technology and began his Ph.D. work in the research group of Professor Armistead (Ted) Russell. This portion of his education was facilitated by funding from the Georgia Tech Presidential Fellowship as well as the American Meteorological Society Fellowship. Sergey married Katherine L. Kincaid in 2000 and they both enjoy the companionship of their faithful dog Max.