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Influence of Uncertainties in Vertical Mixing Algorithms

on an Air Quality Model

by

Wei Tang

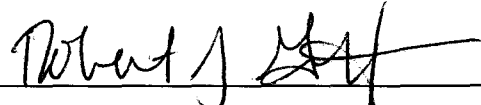A THESIS SUBMITTED

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ABSTRACT

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Vertical diffusion of trace pollutants is a very important physical process that influences pollutant concentrations. However, there are large uncertainties in the numerical modeling of this process, which could affect model predictions of pollutant levels and their responsiveness to emission controls. Uncertainties could result from the formulation of vertical diffusion schemes or from errors in eddy diffusivity and dry deposition velocity parameters associated with this process. Inter-comparisons between different model configurations and sensitivity analysis of model parameters can be used to help quantify these uncertainties. In this study, a comprehensive evaluation of two vertical diffusion schemes, EDDY and ACM2, was performed by comparing ground-level concentrations and vertical profiles generated using the CMAQ model with measurement data from the Texas Air Quality Study II. In addition, new capabilities of conducting sensitivity analysis to dry deposition velocity and eddy diffusivity were implemented into the CMAQ-DDM model. The results show that the ACM2 scheme tends to predict larger secondary pollutant concentrations and smaller primary pollutant concentrations at the surface compared to the EDDY scheme. Differences between the two vertical diffusion schemes and uncertainties in dry deposition velocity may cause temporal variations in the responsiveness of ozone to both NO_x and VOC control respectively.

ACKNOWLEDGEMENTS

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NOMENCLATURE

Abbreviations

ACM	Asymmetric Convective Model
CMAQ	Community Multiscale Air Quality Modeling System
CCTM	CMAQ Chemistry-Transport Model
(H)DDM	(High order) Decoupled Direct Method
EDDY	Eddy Diffusion Model
EPA	Environmental Protection Agency
GoMACCS	Gulf of Mexico Atmospheric Composition and Climate Study
HGB	Houston Galveston Brazoria
ION-6	Intercontinental Transport Experiment Ozonesonde Network Study 2006
M3DDEP	Model-3 DRY Deposition Model
MCIP	Meteorology-Chemistry Interface Processor
MM5	Fifth Generation Mesoscale Meteorological Model
NOAA	National Oceanic and Atmospheric Administration
NAAQS	National Ambient Air Quality Standards
NEI	National Emission Inventory
NO_x	Nitrogen Oxides
NetCDF	Network Common Data Format
PBL	Planetary Boundary Layer
PPM	Piecewise Parabolic Method
RADM	Regional Acid Deposition Model
SIP	State Implementation Plan

SMOKE   Sparse Matrix Operator Kernel Emissions Model

TCEQ   Texas Commission for Environmental Quality

TexAQS II   Texas Air Quality Study II

VOC   Volatile Organic Compounds

Symbols

Δz thickness of layer

K_z eddy diffusivity

f_{conv} partitioning factor

k von Karman constant

h PBL height

L Monin-Obukov Length scale

Pr_0 Prandtl number of neutral stability

β_h coefficients of profile functions for heat

γ_h coefficients of profile functions for heat

u_* friction velocity

w_* convective velocity

z reference height

z_1 height of first model layer

z_0 roughness length

V_d dry deposition velocity

R_a aerodynamic resistance

R_{bh} Quasi laminar boundary layer resistance for heat

R_{bx} Quasi laminar boundary layer resistance for trace species

R_c Canopy resistance

R_s Surface resistance

Sc Schmidt number

z_{SL} surface layer height

z_{dep} deposition height

r_{sx} stomatal resistance

r_{mx} mesophyl resistance

r_{lux} resistance of the outer surface of leaves in the upper canopy

r_{dc} resistance for the gas transfer affected by buoyant convection in canopy

r_{clx} lower canopy resistance

r_{ac} resistance that depends on the canopy height

r_{gsx} resistance of soil, leaf litter

Θ_g potential temperature of the air

Θ_l potential temperature of the ground surface

r_{stb} bulk stomatal resistance

r_{st} stomatal resistance on a leaf layer

r_m mesophyl resistance

r_{cut} dry cuticle resistance

r_{cw} wet cuticle resistance

r_g ground resistance

r_{lc} in-canopy aerodynamic resistance

f_v vegetation fractional coverage

f_w fractional leaf area wetness

LAI   leaf area index

p   a sensitivity parameter

P   unperturbed (base case) value of parameter p

ppb   parts per billion

ppm   parts per million

$\in$ scaling variable for a sensitivity parameter (nominal value 1)

$\Delta\varepsilon$ fractional change in a sensitivity parameter

E   emissions

$S_j^{(1)}$ first-order semi-normalized sensitivity coefficients

$S_{j,k}^{(2)}$ second-order semi-normalized sensitivity coefficients

CHAPTER 1

Introduction

Air quality models are very useful tools in air quality management and atmospheric science studies. They are applied by scientists and policy makers to get a better understanding of the fate and transport of air pollutants and to develop emission control strategies in order to protect human health and mitigate environmental impacts (Carmichael et al., 1991; McKeen et al., 1991; Lu et al., 1997; Bouchet et al., 1999; Kasibhatla and Chameides, 2000). However, due to physical parameterizations, large data requirements, and numerical approximations in air quality modeling, uncertainties cannot be eliminated and may have a significant impact on model performance (Pinder et al., 2009; Zhang et al., 2007; Mallet and Sportisse, 2006). Hence, quantifying the effects of these uncertainties on the model predicted results is essential not only for model validation but also for scientific research and air quality policy analysis. In order to do so, uncertainty analysis is required (Cacuci, 2003).

Structural uncertainty and parametric uncertainty are two types of uncertainties in air quality models. Structural uncertainty results from a lack basic knowledge of fundamental mechanisms in model configurations, such as chemical mechanisms, transport mechanisms, or planetary boundary layer mechanisms. Parametric uncertainty is from measurement error, statistical sampling error, or parameterization error in the model inputs and parameters, such as emission inventories, dry deposition velocities, or eddy diffusivity

(Pinder et al., 2009; Mallet and Sportisse, 2006; Ozkaynak et al., 2009). These

uncertainties would be problematic for the model simulation and policy decision making

because they may cause variations and inaccuracies in model outputs. To assess structural

uncertainties, an ensemble approach, which includes multiple model runs of a single event

through inter-comparisons between varied model configurations, typically is used (Pinder

et al., 2009; Mallet and Sportisse, 2006). To estimate parametric uncertainties, sensitivity

analysis can be used to help characterize the response of concentrations to model input

errors and model parameter errors (Pinder et al., 2009).

Sensitivity analysis is a method used to evaluate the impact of parameter variations on

calculated results (Cacuci, 2003). Sensitivity coefficients calculated via sensitivity analysis

are used to determine quantitatively the response of model prediction to the input

parameter's variation. Numerous methods, such as Brute Force, Green's Function Method

(GFM), Automatic Differentiation in Fortran (ADIFOR), and Decoupled Direct Method

(DDM) have been developed and used to calculate sensitivity coefficients. Compared to

the other methods, DDM is more direct, efficient and stable, and is less subject to

numerical noise. It has been used for many years and has been implemented into many

models for sensitivity analysis (e.g., Yang et al., 1997; Hakami et al., 2003, 2004).

Vertical diffusion is a very important physical process in atmospheric models.

However, studies by Pleim (2006a, 2006b) indicated that large uncertainties still remain

in the numerical modeling of vertical transport of atmospheric properties and chemical

species, especially under the convective boundary layer in both meteorology and air quality models. Uncertainties could come from lack of knowledge in vertical transport mechanisms (structural) and/or from physical parameterization error in dry deposition velocity and eddy diffusivity (parametric), which are two very important parameters associated with vertical diffusion process (Hicks and Wesely, 2000; Wilson 2004).

The Community Multiscale Air Quality Modeling System (CMAQ) model is a third generation, three-dimensional Eulerian air quality model that simulates ozone, acid deposition, visibility, and fine particulate matter in the troposphere (Byun and Schere, 2006). It can simulate multiple pollutants simultaneously in various scales and was designated by the U.S. Environmental Protection Agency (U.S.EPA) for regulatory, policy analysis, and scientific investigation (CMAS 2009). The eddy diffusion scheme (EDDY) and a newly developed asymmetric convective model scheme (ACM2) are the two options for simulating vertical turbulent mixing in CMAQ. The EDDY scheme deals with turbulent mixing only in a sub-grid-scale, and the original ACM scheme considers turbulent mixing only in a super-grid-scale. The ACM2 scheme combines the above two turbulent mixing schemes, enabling the model to simulate vertical transport in both small and large scales (Pleim 2006a). In addition, the ACM2 scheme has recently replaced EDDY as default option in CMAQ. To evaluate the uncertainty in model configurations from using different vertical mixing schemes, comparisons between the modeling results from the two schemes as well as with observation data are required. Although a few

comparisons between EDDY and ACM2 schemes have been conducted previously (Pleim 2006, 2009), more comprehensive evaluations with different scenarios are still highly desirable.

Currently, the sensitivity of pollutant concentrations to initial conditions, boundary conditions, emissions, and reaction rate constants has been determined in CMAQ using DDM technique (Cohan et al., 2005; Jin et al., 2008). However, DDM has not been implemented previously into the newly developed ACM2 scheme, and capabilities of analyzing sensitivities to dry deposition velocity and eddy diffusivity have not been added into CMAQ-DDM. Hence, this model development work has enabled the CMAQ-DDM model to perform sensitivity analysis with the ACM2 scheme and also to calculate sensitivity coefficients for dry deposition velocity and eddy diffusivity in order to qualitatively and quantitatively investigate the parametric uncertainties in the model.

The major accomplishments of this study are: first, DDM was implemented into the ACM2 scheme; second, new features for calculating sensitivities to dry deposition velocity and to eddy diffusivity have been added into CMAQ-DDM; third, EDDY and ACM2 vertical diffusion schemes in CMAQ model were evaluated comprehensively using Texas Air Quality Study II field measurement data; fourth, sensitivity analysis was performed to investigate the effect of uncertainty in dry deposition velocity on predictions of pollutant concentrations and their sensitivities to emission change. Based on this study, the relative strengths of ACM2 and EDDY can be demonstrated, the effect of uncertainty in dry

deposition velocity on CMAQ model simulation can be examined, and the effect of uncertainty in dry deposition velocity on emission controls can be quantified.

In this thesis, Chapter Two reviews current knowledge and literature related to this study; Chapter Three demonstrates the methodology of this study. Chapter Four discusses finding and results from this study, and Chapter Five draws conclusions and recommends future work.

References

Bouchet, V.S., Laprise, R., and Torlaschi, E. (1999) Studying ozone climatologywith a

regional climate model: 2. Climatology. *Journal of Geophysical Research.* 104,

30373–30385.

Byun, D. and Schere, K.L. (2006) Review of the governing equations, computational

algorithms, and other components of the Models-3 Community Multiscale Air

Quality (CMAQ) modeling system. *Applied Mechanics Reviews.* 59, 51-77.

Cacuci, D.G. (2003) *Sensitivity and uncertainty analysis.* Chapman & Hall/CRC, Boca

Raton, Florida.

Carmichael, G. R., Peters, L.K., and Saylor, R.D. (1991) The STEM-II regional-scale acid

deposition and photochemical oxidant model, I. An overview of model

developments and applications. *Atmospheric Environment.* 25A, 2077–2090.

CMAS center. *CMAQ v4.6 operational guidance document.*

(http://www.cmaqmodel.org/op_guidance_4.6/index.cfm. Accessed on October 1st,

2009)

Cohan D.S., Hakami, A., Hu, YT., and Russell, A.G. (2005) Nonlinear response of ozone

to emissions: Source apportionment and sensitivity analysis. *Environmental Science

and Technology.* 39, 6739-6748.

Hakami, A., Odman, M.T., and Russell, A.G. (2003) High-order, direct sensitivity analysis of multidimensional air quality models. *Environmental Science and Technology.* 37, 2442-2452.

Hakami, A., Odman, M.T., and Russell, A.G. (2004) Nonlinearity in atmospheric response: A direct sensitivity analysis approach. *Journal of Geophysical Research.* 109, D15303.

Jin, L., Tonse, S., Cohan, D.S., Mao, XL,. Harley, R.A., and Brown, N.J. (2008) Sensitivity analysis of ozone formation and transport for a central California air pollution episode. *Environmental Science and Technology.* 42, 3683-3689.

Kasibhatla, P. and Chameides, W.L. (2000) Seasonal modeling of regional ozone pollution in the eastern United States. *Geophysical Research Letters.* 27, 1415–1418.

Lu, R., Turco, R.P., and Jacobson M.Z. (1997) An integrated air pollution modeling system for urban and regional scales: 1. Structure and performance. *Journal of Geophysical Research.* 102, 6063–6079.

Mallet, V. and Sportisse, B. (2006) Uncertainty in a chemistry-transport model due to physical parameterizations and numerical approximations: An ensemble approach applied to ozone modeling. *Journal of Geophysical Research.* 111, D01302.

McKeen, S. A., Hsie, E.Y., Trainer, M., Tallamraju, R., and Liu, S.C. (1991) A regional model study of the ozone budget in the eastern United States. *Journal of Geophysical Research.* 96, 10809 –10845.

Ozkaynak, H., Frey, H.C., Burke, J., and Pinder, R.W. (2009) Analysis of coupled model uncertainties in source-to-dose modeling of human exposures to ambient air pollution: A $PM_{2.5}$ case study. *Atmospheric Environment.* 43, 1641-1649.

Pleim, J.E. (2006a) A combined local and nonlocal closure model for the atmospheric boundary layer. Part II: Application and evaluation in a mesoscale meteorological model. *Journal of Applied Meteorology and Climatology.* 46, 1396-1408.

Pleim, J.E. (2006b) A new combined local and non-local PBL model for meteorology and air quality modeling. CMAS conference paper. North Carolina.

Pleim, J.E. Planetary boundary layer modeling for meteorology and air quality. (http://www.epa.gov/AMD/peer/posters/Poster_1.6.pdf   Accessed on September 16th, 2009)

Pinder, R.W., Gilliam, R.C., Appel, K.W., Napelenok, S.L., Foley, K.M., and Gilliland, A.B. (2009) Efficient probabilistic estimates of surface ozone concentration using an ensemble of model configurations and direct sensitivity calculations. *Environmental Science and Technology.* 43, 2388-2393.

Wesely, M.L. and Hicks, B.B. (2000) A review of the current status of knowledge on dry deposition. *Atmospheric Environment.* 34, 2261-2282.

Wilson, R. (2004) Turbulent diffusivity in the free atmosphere inferred from MST radar measurements: A review. *Annales Geophysicae.* 22, 3869-3887.

Yang, YJ., Wilkinson, J.G., and Russell, A.G. (1997) Fast, direct sensitivity analysis of multidimensional photochemical models. *Environmental Science and Technology.* 31, 2859-2868.

Zhang, F. Q., Bei, N. F., Nielsen-Gammon, J. W., Li, G. H., Zhang, R. Y., Stuart, A., and Aksoy, A. (2007) Impacts of meteorological uncertainties on ozone pollution predictability estimated through meteorological and photochemical ensemble forecasts. *Journal of Geophysical Research.* 112, D04304.

CHAPTER 2

Background and Literature Review

This chapter reviews the current knowledge and scientific literature regarding air quality

in Houston, the CMAQ model, vertical diffusion algorithms in CMAQ, vertical eddy

diffusivity, dry deposition velocity, and the DDM-3D method for sensitivity calculation.

2.1 Tropospheric ozone pollution in Houston

Ozone in troposphere is formed through the reactions between nitrogen oxides (NO_x) and

volatile organic compounds (VOCs) in the presence of sunlight (Seinfeld and Pandis,

2002). The Houston-Galveston-Brazoria (HGB) region located in southeast Texas and in

proximity to Gulf of Mexico has five million inhabitants and the largest concentration of

petrochemical facilities in the United States. The large sources of NO_x and VOC emissions

and the meteorological conditions such as extended heat and humidity, and intense solar

radiation makes HGB one of the worst ozone pollution region in the US; it has been

classified by the U.S.EPA as an ozone non-attainment area (Kleinman et al., 2002; Ryerson

et al., 2003; Daum et al., 2004; Rappengluck et al., 2008). Two intensive air quality study

field campaigns were conducted in eastern Texas, as shown in Figure 2.1, to investigate the

sources and the causes of ozone and aerosol formation in the atmosphere (Parrish et al.,

2009). In addition to field measurements, air quality modeling studies also are performed

to better understand atmospheric processes and air pollutants transport and to help the

Texas Commission on Environmental Quality (TCEQ) establish the state implementation

plan (SIP) for complying with U.S. EPA National Ambient Air Quality Standards

(NAAQS) (Byun et al. 2007).
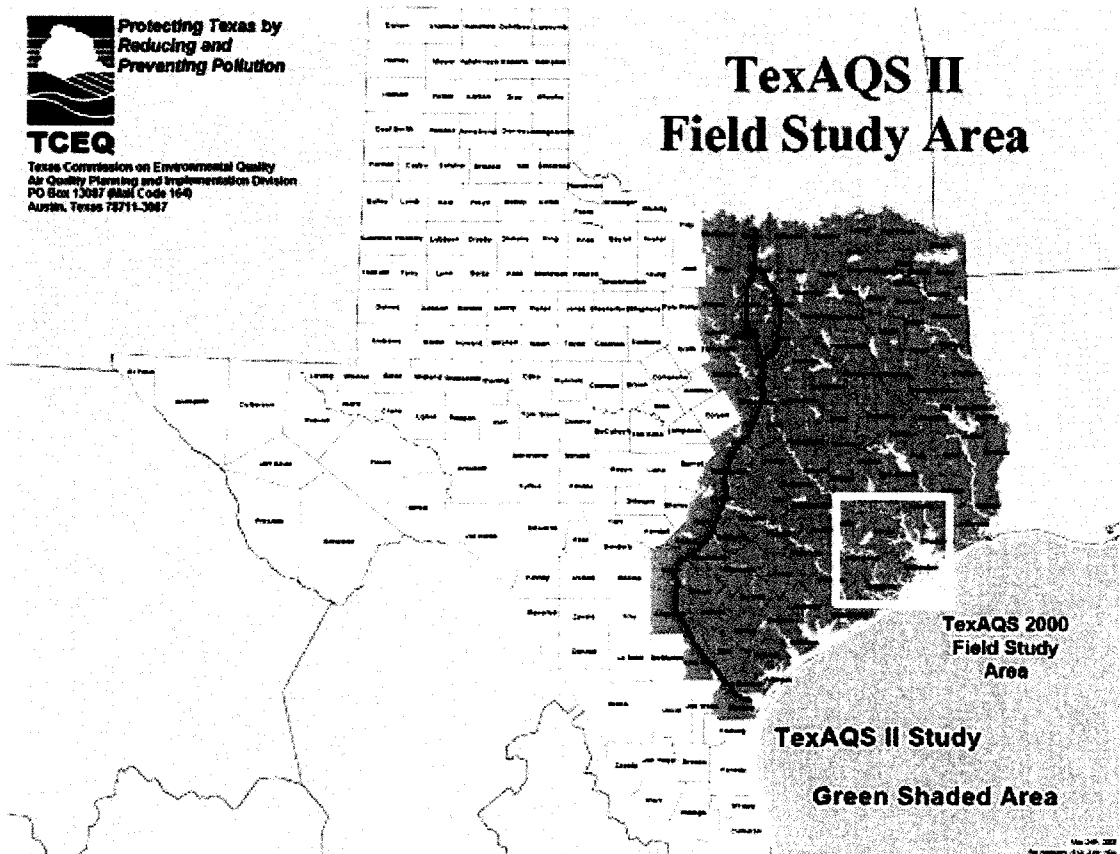
Figure 2.1: TexAQS 2000 and TexAQS II field studies area. (Source: TCEQ, 2009)

The Community Multiscale Air Quality Modeling System (CMAQ) model was used in

this study to simulate an air pollution episode during August 30th to September 5th 2006

associated with TexAQS II air quality field study in eastern Texas.

2.2 Community Multiscale Air Quality Modeling System (CMAQ)

Community Multiscale Air Quality Modeling System (CMAQ) is an Eulerian air quality

model and has been used to simulate ozone, acid deposition, visibility, and fine particulate

matter in the troposphere for regulatory, policy analysis and scientific investigation (Byun

and Schere, 2006). CMAQ separates a modeling domain into many grid cells and

calculates the species concentrations affected by different atmospheric processes using

operator splitting in each grid cell. The processes that were considered as main factors

influencing the species concentrations include emissions from sources, horizontal and

vertical advection, horizontal and vertical diffusion, chemical reaction, and deposition. The

general governing equation for these processes is shown in equation 2.1.

$$\frac{dC}{dt} = [advection] + [diffusion] + [deposition] + [chemistry] + [emission] \tag{2.1}$$

The concentration calculations are conducted by the chemistry-transport model component

of CMAQ (CCTM), which is the last program in CMAQ modeling sequence. The

advection and emission terms as shown in equation 2.1 were calculated using input data

generated by meteorology and emission models, and the deposition, chemical reaction, and

diffusion terms were calculated inside the CCTM (CMAS, 2009). The model framework is

shown in Figure 2.2.
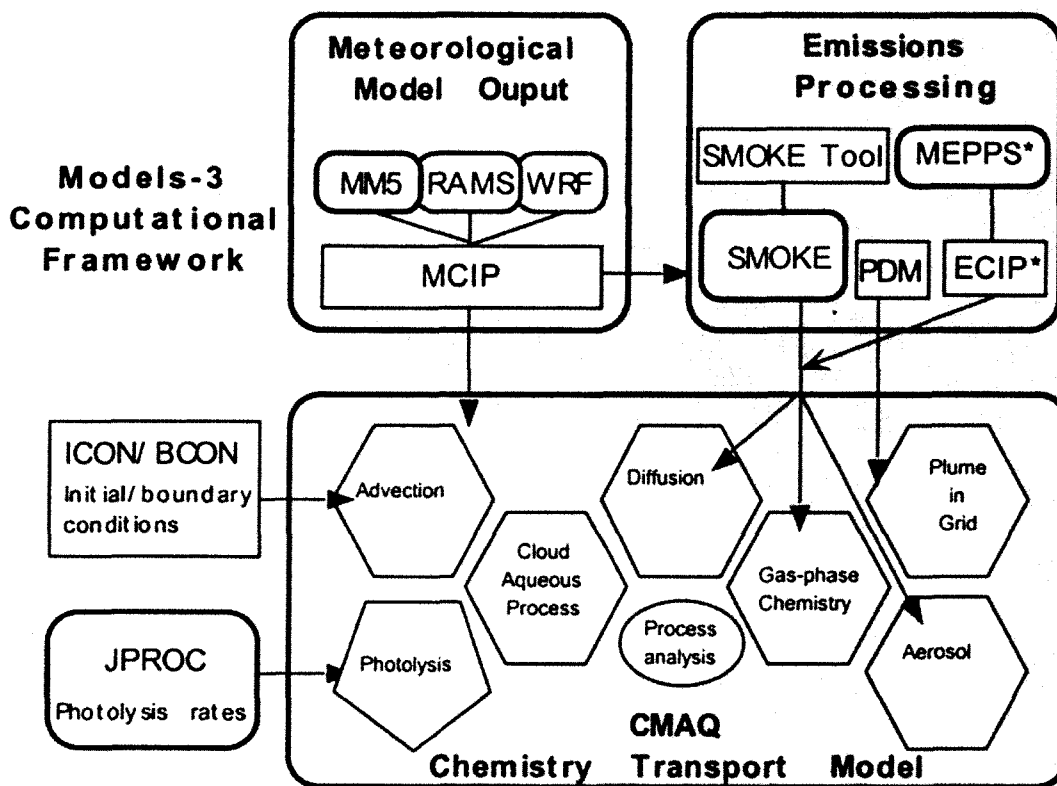
Figure 2.2: Science process modules in Model-3 CMAQ. (Source: Byun and Schere, 2006)

To solve the continuity equation 2.1, initial and boundary condition are required. The initial and boundary conditions for the CMAQ model simulation were generated by the initial condition preprocessor, ICON, and boundary condition preprocessor, BCON, as shown in Figure 2.2. In Figure 2.2, the photolysis rate preprocessor, JPROC, calculates photolysis rate constants that can be used by CCTM to simulate photolysis reactions; the Meteorology-Chemistry interface preprocessor, MCIP, converts meteorology data generated by a meteorology model such as Fifth Generation Mesoscale Meteorological Model, MM5, and Weather Research Forecasting Model, WRF, to a CMAQ-ready

meteorology field. The Sparse Matrix Operator Kernel Emission Model, SMOKE, generates CMAQ-ready emission files (Byun and Schere, 2006; CMAS 2009).

As shown in Figure 2.2, diffusion is one of physical processes simulated by CMAQ that affects concentration fields. In CMAQ, diffusion processes were treated separately as horizontal diffusion and vertical diffusion. Vertical Diffusion generated by heat, momentum, and moisture fluxes is an important component of vertical transport in the atmosphere (Byun and Ching. 1999). However, large source of uncertainties which either come from lack of fundamental knowledge in vertical diffusion mechanisms, or come from the physical parameterization errors in dry deposition velocity and eddy diffusivity associated with vertical diffusion process could reduce the accuracy of numerical modeling in vertical diffusion of atmospheric properties and chemical species under the convective boundary layer in air quality models (Pleim 2006a, 2006b; Wesely and Hicks, 2000; Wilson 2004).

2.3 Vertical diffusion schemes in CMAQ

Eddy diffusion scheme (EDDY) and the newly developed Asymmetric convective model scheme (ACM2) are two options of vertical diffusion mechanisms in CMAQ to simulate vertical transport of atmospheric properties and chemical species. The EDDY scheme interprets turbulent mixing only in sub-grid-scale (local) considering symmetrical vertical mixing based on concentration gradient between adjacent model layers. The original ACM scheme interprets turbulent mixing only in super-grid-scale (non-local) considering

asymmetrical vertical mixing with fast upward buoyant plume and slow broad

compensatory subsidence. The thickness of arrows indicates the quantity of mass flux,

reflecting that the mass fluxes increase during the downward transport. The ACM2 scheme

combines the above two turbulent mixing schemes enabling the model to simulate vertical

transport in both small and large scales. Hence, ACM2 scheme is more realistic in

representing vertical mixing process than the other two schemes (Byun and Ching 1999;

Pleim 2006). The schematic of three types of vertical transport is shown in Figure 2.3.
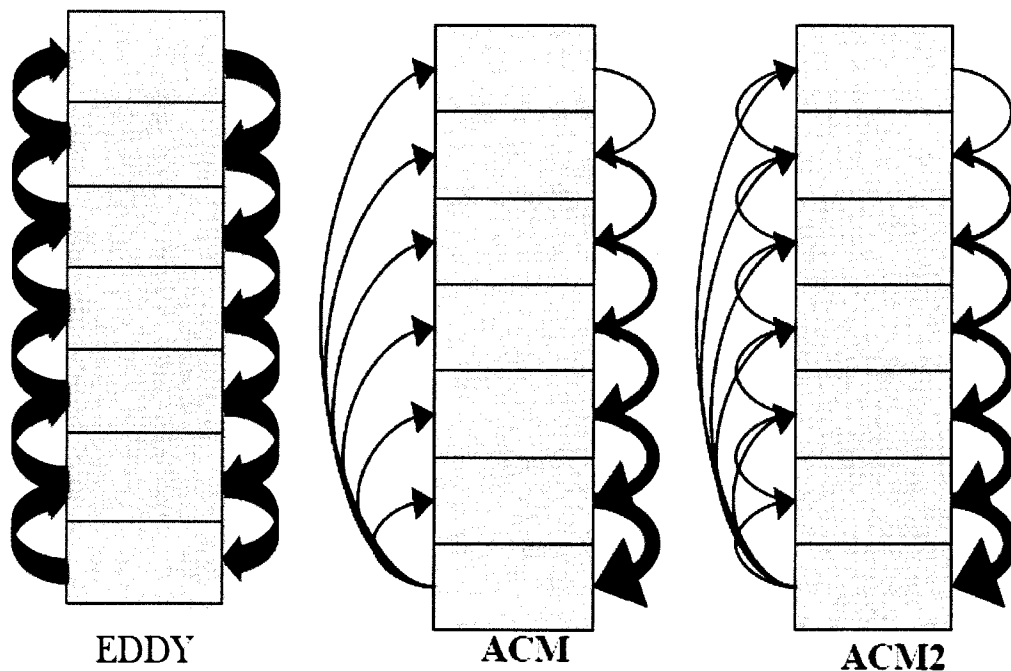
Figure 2.3: Schematic representation of the exchange among model layers in three

schemes. (left) EDDY, (middle) ACM, (right) ACM2

The model formulation for EDDY scheme is shown in equation 2.2

$$\frac{\partial C_i}{\partial t} = \frac{1}{\Delta z_i} \left[\frac{K_{i+1/2}(C_{i+1} - C_i)}{\Delta z_{i+1/2}} + \frac{K_{i-1/2}(C_i - C_{i-1})}{\Delta z_{i-1/2}} \right] \tag{2.2}$$

where C_i is the concentration at layer i; Δz_i is the thickness of layer i; K is the eddy

diffusivity (K_z); i represents the center of the layer; i+1/2 represents the layer interface.

In addition to local mixing, the ACM2 scheme also contains a non-local mixing

component. The model formulation of ACM2 is shown in equation 2.3 (Pleim 2006a)

$$\frac{\partial C_i}{\partial t} = M2uC_1 - M2d_iC_i + M2d_{i+1}C_{i+1} \frac{\Delta z_{i+1}}{\Delta z_i}$$

$$+ \frac{1}{\Delta z_i} \left[\frac{K_{i+1/2}(C_{i+1} - C_i)}{\Delta z_{i+1/2}} + \frac{K_{i-1/2}(C_i - C_{i-1})}{\Delta z_{i-1/2}} \right] \tag{2.3}$$

The first three terms in equation 2.3 represent the asymmetric convective mixing (ACM)

as shown in the middle plot of Figure 2.3. The upward and downward mixing rates are

shown in equation 2.4a and 2.4b, respectively.

$$M2u = \frac{f_{conv}K_z(z_{1+1/2})}{\Delta z_1 (h - z_{1+1/2})} \tag{2.4a}$$

$$M2d_i = M2u(h - z_{i-1/2})/\Delta z_i \tag{2.4b}$$

The K used in local mixing (the fourth term in equation 2.3) is different than that used in

equation 2.2 and is defined as in equation 2.5. The f_{conv} in the equation 2.4a and 2.5 is a

partitioning factor used to control the degree of local and non-local mixing in ACM2

scheme.

$$K(z) = K_z(z)(1 - f_{conv}) \tag{2.5}$$

$$f_{conv} = \left[1 + \frac{k^{-2/3}}{0.1a} \left(-\frac{h}{L} \right)^{-1/3} \right]^{-1} \qquad a = 7.2 \qquad (2.6)$$

In equation 2.6, k is the von Karman constant (k = 0.4), h is PBL height, and L is the

Monin-Obukov Length. When $f_{conv} = 1$, the ACM2 scheme converges to original ACM

scheme; when $f_{conv} = 0$, the ACM2 will return to EDDY scheme. Under stable or neutral

conditions, f_{conv} needs to be zero for pure eddy diffusion.

Using EDDY or ACM2 likely will predict different results in otherwise identical model

simulations. Therefore, one type of structural uncertainty will be generated by choosing

either EDDY or ACM2 in the model configuration. To quantify this uncertainty,

inter-comparisons between modeling results generated from two schemes of a single

process and comparison with observed data are required (Pinder et al. 2009). Pleim (2006b;

2009) have conducted a few modeling comparisons between EDDY and ACM2 schemes in

the CMAQ model, including modeled ground level ozone concentration from two schemes

compared with surface observation data and modeled gas species vertical profiles from two

schemes compared with NOAA P-3 aircraft spiral data. The results indicated that the

ACM2 scheme tends to predict larger concentrations of secondary pollutants and smaller

concentrations of primary pollutants at surface. The ACM2 scheme has a more well-mixed

profile under the PBL than the EDDY scheme. However, the differences between

simulated results from two schemes are not significant. In order to better quantify these two

schemes, more comprehensive evaluations with different scenarios are still highly

desirable.

2.4 Vertical eddy diffusivity (K_z)

Vertical eddy diffusivity, K_z, also called vertical eddy diffusion coefficient is used to

calculate the diffusion rate in the vertical diffusion process. In the lower troposphere, K_z

depends on wind speed, surface roughness, heating of surface, and altitude (Jacob 1999).

Many methods have been developed to estimate K_z, but results lack consistency (Wilson

2004). In the CMAQ model, PBL similarity theory is used to parameterize the vertical eddy

diffusivity (Byun and Ching, 1999). For the surface layer, the non-dimensional profile

functions, ϕ, of the vertical gradient of potential temperature are expressed in equation 2.7

as follows:

$$\phi = \mathrm{Pr}_0(1 + \beta_h \, z\!/\!_L) \quad 1 \geq z/L \geq 0 \qquad \text{moderately stable} \qquad (2.7a)$$

$$\phi = (1 - \gamma_h \, z\!/\!_L)^{-1/2} \quad z/L < 0 \qquad \text{unstable} \qquad (2.7b)$$

$$\phi = \mathrm{Pr}_0(\beta_h + z\!/\!_L) \quad z/L \geq 1 \qquad \text{stable} \qquad (2.7c)$$

In equation 2.7, Pr_0 is the Prandtl number of neutral stability, β_h and γ_h are the coefficients

of profile functions obtained from field measurements, and L is Monin-Obukhov length.

Parameterization for eddy diffusivity at surface layer is shown in equation 2.8.

$$K_z(z) = \frac{ku_* z}{\phi(z/L)} \qquad (2.8)$$

The eddy diffusivity parameterization equation for EDDY and ACM2 schemes are

different in the PBL. For the EDDY scheme, the eddy diffusivity is parameterized with the

expressions as shown in equation 2.9 (Byun and Ching, 1999)

$$K_z(z) = \frac{ku_* z(1 - z/h)^{3/2}}{\phi(z/L)} \qquad \text{z/L>0 (stable)} \qquad (2.9a)$$

$$K_z(z) = kw_* z(1 - z/h) \qquad \text{z/L<0 (unstable)} \qquad (2.9b)$$

An integration method was used to parameterize equations 2.8 and 2.9 at model layer interfaces in order to get more accurate results (Byun and Dennis, 1995). For the ACM2 scheme, the parameterization expressions for eddy diffusivity are shown in equation 2.10 based on the Holtslag and Boville method (Pleim 2006a).

$$K_z(z) = k\frac{u_*}{\phi(\frac{z_s}{L})} z(1 - z/h)^2 \qquad z_s = \min (z, 0.1h) \quad z_s/L<0 \text{ (unstable)} \qquad (2.10a)$$

$$K_z(z) = k\frac{u_*}{\phi(\frac{z_s}{L})} z(1 - z/h)^2 \qquad z_s = z \qquad z_s/L>0 \text{ (stable)} \qquad (2.10b)$$

In the above equations, u* is the friction velocity, w* is the convective velocity, and the values could be obtained by the field measurements. By comparing equation 2.9 and 2.10, we can see that the EDDY scheme uses a quadratic height function to calculate eddy diffusivity and the ACM2 scheme uses a cubic height function. Therefore, EDDY could predict a deeper effective mixing depth than ACM2 (Pleim 2009).

K_z is an empirical quantity. Therefore, uncertainties in eddy diffusivity are unavoidable. Hence, K_z may give parametric uncertainty in the model simulations.

2.5 Dry deposition velocity (V_d)

Dry deposition is the atmospheric process of removing gaseous and particulate species from the atmosphere to the surface of the Earth without precipitation. The dry deposition

rate depends on atmospheric stability, chemical properties of species themselves, and the

surface roughness (Seinfeld and Pandis, 2002). The dry deposition flux at some reference

height, for example 10m above the surface, can be expressed as an equation shown in 2.11.

$$F = -V_d C \qquad (2.11)$$

The process of dry deposition consists three steps: first, aerodynamic transport to a very

thin layer called the quasi-laminar sublayer over the surface with stagnant air; second,

transport through the quasi-laminar sublayer by molecular diffusion; third, uptake by the

Earth surface (Seinfeld and Pandis, 2002). This process is illustrated by analogy to an

electrical resistance analogy as shown in Figure 2.4, with three resistances in series
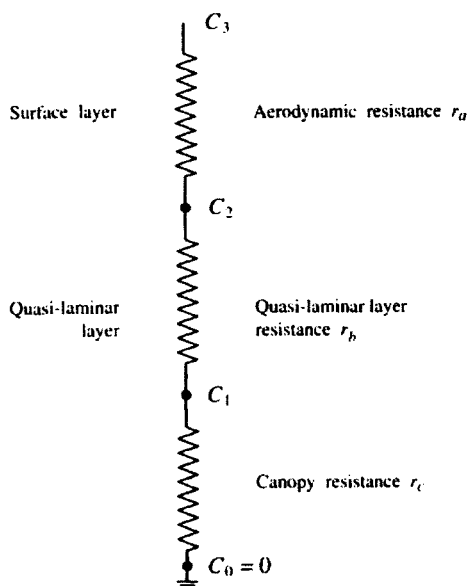
Figure 2.4: Resistance model for dry deposition. (Source: Seinfeld and Pandis, 2002)

In Figure 2.4, aerodynamic resistance, R_a, quasi-laminar layer resistance, R_b, and canopy

resistance, R_c are shown. The dry deposition velocity is expressed as the inverse of the sum

of the resistances as shown in equation 2.12

$$V_d = (R_a + R_b + R_c)^{-1} \tag{2.12}$$

The dry deposition velocities of chemical species can be modeled by using surface

information, surface layer meteorology data, and the dry deposition flux measured in field

observations. However, due to the difficulties associated with long-term dry deposition

flux measurements in various terrain and the inaccuracies in model inputs, as large as

$\pm 30\%$ uncertainty in modeled dry deposition velocity is commonly observed between

measured and modeled data (Brook et al., 1999; Wesely and Hicks, 2000). Therefore, the

dry deposition velocity may also give parametric uncertainty in the model simulations. A

recent uncertainty analysis study conducted by Bergin et al. (1999) indicated that besides

the effects of uncertainties in emissions and reaction rate constants of dominant chemical

reactions, the effect of uncertainty in ozone dry deposition velocity on ozone concentration

simulation is considerable. The uncertainty in NO_2 dry deposition velocity also may have

significant impact on simulated HNO_3 formation and responses to NO_x emission

reductions.

In CMAQ, dry deposition takes place only at the surface layer. The dry deposition

velocities were calculated in MCIP preprocessor and were used by CCTM as inputs.

There are two methods, RADM and M3DDEP, used in MCIP to estimate the dry

deposition velocity (Byun and Ching, 1999). RADM was developed by Wesely (1989) and

estimates dry deposition velocity from horizontal wind components, temperature, and

humidity profiles (Wesely, 1989). The schematic of pathway resistances used in RADM is

shown in Figure 2.5.
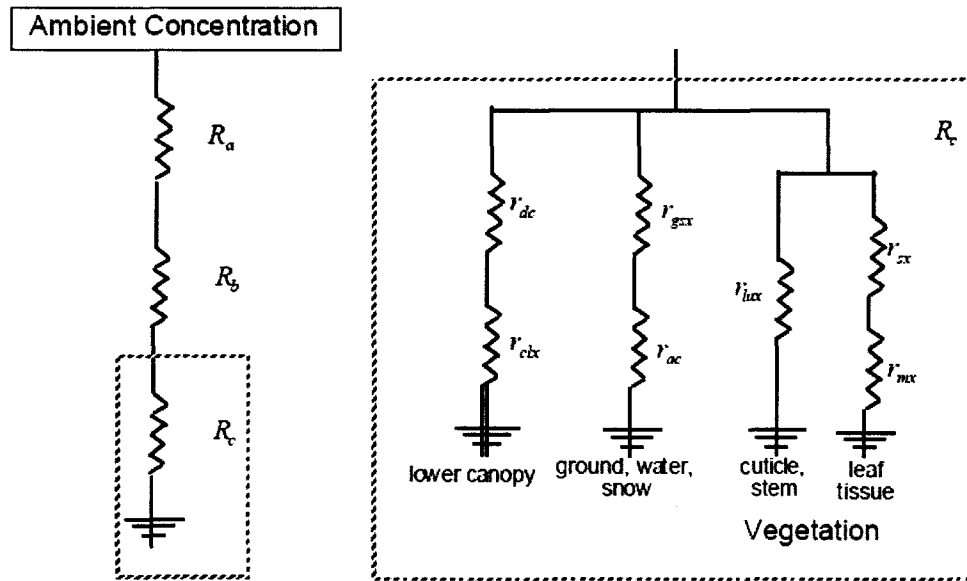
Figure 2.5: Schematic diagram of pathway resistances used in RADM method. (Source:

Byun and Ching, 1999)

Resistances R_a, R_b, and R_c in Figure 2.5 are shown in equations 2.13-2.15 (Byun and

Ching, 1999).

$$R_a = \int_{z_0}^{z} \frac{dz}{K_z(z)} = \int_{z_0}^{z_{SL}} \frac{dz}{K_z(z)} + \int_{z_{SL}}^{z_{dep}} \frac{dz}{K_z(z)} = R_{aSL} + R_{aPBL} \qquad (2.13)$$

$K_z(z)$ is eddy diffusivity, z_{SL} represents surface layer height, and z_{dep} represents deposition

height.

$$R_{bh} = \frac{2}{ku_*} Sc^{2/3} \qquad \text{for heat} \qquad\qquad (2.14a)$$

$$R_{bx} = \frac{2}{ku_*} Sc_x^{2/3} \qquad \text{for trace gas species} \qquad (2.14b)$$

k is von Karman constant, u* is friction velocity, and Sc is Schmidt number.

$$R_c = \left(\frac{1}{r_{sx} + r_{mx}} + \frac{1}{r_{lux}} + \frac{1}{r_{dc} + r_{clx}} + \frac{1}{r_{ac} + r_{gsx}} \right) \qquad (2.15)$$

In equation 2.15, r_{sx} is the stomatal resistance, r_{mx} is the mesophyl resistance, r_{lux} is the resistance of the outer surface of leaves in the upper canopy, r_{dc} is the resistance for the gas transfer affected by buoyant convection in canopy, r_{clx} the lower canopy resistance, r_{ac} is the resistance that depends on the canopy height, and r_{gsx} is the resistance of soil, leaf litter, and other ground materials.

The M3DDEP method was developed by Pleim (2001), and it uses the same resistance components to estimate the dry deposition velocity but with a new land-surface model (Pleim et al., 2001). The schematic of pathway resistances used in M3DDEP is shown in Figure 2.6.

Ambient Concentration

R_a

R_b

Leaf

r_{lc}

r_{st}

r_{cut}

r_g

r_g

r_{in}

R_s

ground, water, ground, water,   cuticle,   leaf
snow   snow   stem   tissue
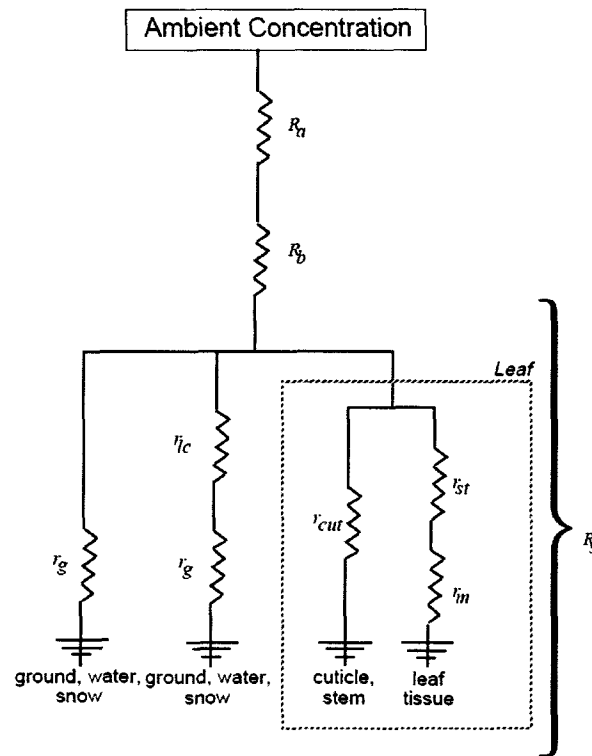
Figure 2.6: Schematic diagram of pathway resistances used in M3DDEP method.

(Source: Byun and Ching, 1999)

In the M3DDEP method, the expression of quasi laminar layer resistances R_b is still the

same as equation 2.14; the new expressions for R_a and R_s (surface resistance) are shown in

equations 2.16-2.17 (Byun and Ching, 1999).

$$R_a = \rho C_p (\Theta_g - \Theta_1) / H - R_{bh}$$ (2.16a)

$$R_a = \frac{Pr_0}{ku_*} \ln\left(\frac{z_1}{z_0}\right) \quad \text{for small sensible heat flux} \quad \left|H /(\rho C_p)\right| < 10^{-15} \quad [K \text{ m s}^{-1}]$$ (2.16b)

In equation 2.16, Θ_g and Θ_1 are the potential temperature in the air and at the ground

surface, respectively in the lowest model layer. z_1 is the height of model layer 1, and z_0 is

roughness length.

$$R_s = \left[\frac{f_v}{r_{stb}} + LAI \left(\frac{f_v(1-f_w)}{r_{cut}} + \frac{f_v f_w}{r_{cw}} \right) + \frac{1-f_v}{r_g} + \frac{f_v}{r_{lc}+r_g} \right]^{-1} \qquad (2.17)$$

In equation 2.17, r_{stb} is the bulk stomatal resistance including the stomatal resistance on a

leaf area r_{st} and the mesophyl resistance r_m as shown in Figure 2.6, r_{cut} is the dry cuticle

resistance, r_{cw} is the wet cuticle resistance, r_g is the ground resistance, and r_{lc} is the

in-canopy aerodynamic resistance. The vegetation fractional coverage is given by f_v, f_w is

the fractional leaf area wetness, and LAI is the leaf area index.

In order to estimate the effects of parametric uncertainties from eddy diffusivity and dry

deposition velocity on model performance, sensitivity analysis associated with random

sampling technique such as Monte Carlo method could be conducted (Hanna et al., 2001;

Pinder et al., 2009). In this study, DDM-3D method was used to calculate the sensitivity

coefficients via sensitivity analysis.

2.6 DDM-3D sensitivity analysis

Sensitivity coefficients calculated via sensitivity analysis have been used to determine

quantitatively the response of model predictions to variations in the model input and

parameters. Numerous methods such as Brute Force, Coupled Direct Method, Green's

Function Method (GFM), Automatic Differentiation in Fortran (ADIFOR), and Decoupled

Direct Method (DDM) have been developed and used to calculate sensitivity coefficients.

Compared to the other methods, sensitivity equations in DDM are derived directly from

concentration equations in the base model, and sensitivity coefficients are computed by

DDM at the same time as concentrations. Hence, DDM is more direct, efficient, and stable, and it suffers from less numerical noise than the other methods. It has been used for many years and has been implemented into many models for sensitivity analysis (e.g., Yang et al., 1997; Hakami et al., 2003, 2004).

The methodology for calculation of sensitivity coefficients in DDM is shown below (Hakami et al, 2003).

Equation 2.1 can be rewritten as shown in equation 2.18

$$\frac{\partial C_i}{\partial t} = -\nabla(uC_i) + \nabla(K\nabla C_i) + R_i + E_i \tag{2.18}$$

The initial and boundary conditions used to solve equation 2.18 are shown in equation 2.19 in below.

$$\text{IC: } C_i = C_{0_i} \tag{2.19a}$$

$$\text{BCs: } uC_i - K\nabla C_i = uC_{b_i} \quad \text{horizontal inflow} \tag{2.19b}$$

$$-\nabla C_i = 0 \quad \text{horizontal outflow} \tag{2.19c}$$

$$V_{g_i}C_i - K_{zz}\frac{\partial C_i}{\partial z} = E_{0_i} \quad z=0 \tag{2.19d}$$

$$-\frac{\partial C_i}{\partial z} = 0 \quad z=H \text{ (top of model domain)} \tag{2.19d}$$

In equation 2.19, u represents wind field, K represents a second-order turbulent sensor, C_{0_i} and C_{b_i} are the initial and boundary concentrations respectively, V_{g_i} is dry deposition velocity, E_{0_i} is ground level emission rate, and i represents species i.

The local sensitivity of a model output to a parameter can be calculated as shown in equation 2.20

$$S_{ij} = \frac{\partial C}{\partial p_j} \qquad (2.20)$$

where p$_j$ represents a model parameter. However, due to the variety in magnitudes and units of different parameters, semi-normalized sensitivity coefficients are defined as in equation 2.21

$$S_{ij}^{(1)} = \tilde{p}_j \frac{\partial C_i}{\partial p_j} = \tilde{p}_j \frac{\partial C_i}{\partial (\epsilon_j \, \tilde{p}_j)} = \frac{\partial C_i}{\partial \epsilon_j} \qquad (2.21)$$

where $\tilde{p}_j$ represents a unperturbed field and ϵ_j is a scaling valuable with a nominal value of 1.

Hence, more intuitively, the first order sensitivity coefficients calculations in the expression of differentiating equation 2.1 can be written as in equation 2.22

$$\frac{dS_{ij}^1}{dt} = \frac{\partial}{\partial \epsilon}[advection] + \frac{\partial}{\partial \epsilon}[diffusion] + \frac{\partial}{\partial \epsilon}[deposition]$$
$$+ \frac{\partial}{\partial \epsilon}[chemistry] + \frac{\partial}{\partial \epsilon}[emission] \qquad (2.22)$$

Meanwhile, equation 2.22 can also be rewritten in the expression of differentiating equation 2.18 as shown in equation 2.23

$$\frac{\partial S_{ij}^{(1)}}{\partial t} = -\nabla(u S_{ij}^{(1)}) + \nabla(K \nabla S_{ij}^{(1)}) + J_i S_j^{(1)} + \frac{\partial R_i}{\partial \epsilon_j} \delta_{5j_1} +$$
$$\tilde{E}_i \delta_{1j_1} \delta_{ij_2} - \nabla(\tilde{u} C_i) \delta_{3j_1} + \nabla(\tilde{K} \nabla C_i) \delta_{7j_1} \qquad (2.23)$$

The initial and boundary conditions used to solve equation 2.23 are shown in equation 2.24 in below.

$$\text{IC: } S_{ij}^{(1)} = \tilde{C}_{0_i} \delta_{0j_1} \delta_{ij_2} \qquad (2.24a)$$

$$\text{BCs: } u S_{ij}^{(1)} - K \nabla S_{ij}^{(1)} = u \tilde{C}_{b_i} \delta_{2j_1} \delta_{ij2} + \tilde{u} C_{b_i} \delta_{3j_1} - \tilde{u} C_i \delta_{3j_1} + \tilde{K} \nabla C_i \delta_{7j_1} \qquad (2.24b)$$

$$-\nabla S_{ij}^{(1)} = 0 \tag{2.24c}$$

$$v_{g_i} S_{ij}^{(1)} - K_{zz} \frac{\partial S_{ij}^{(1)}}{\partial z} = -\tilde{v}_{g_i} C_i \delta_{6j_1} \delta_{ij_2} + \tilde{K} \frac{\partial C_i}{\partial z} \delta_{7j_1} + \tilde{E}_{0_i} \delta_{1j_1} \delta_{ij_2} \tag{2.24d}$$

$$-\frac{\partial S_{ij}^{(1)}}{\partial z} = 0 \tag{2.24e}$$

In equation 2.23, J_i is the ith row vector in the Jacobian matrix of the reaction rates. δ_{j1} is the Kronecker delta function used in DDM to control the sensitivity to input parameters that will be calculated during the simulation process. j_1 could be a number from 0 to 6 referring to initial condition, boundary condition, wind field, diffusivity, dry deposition velocity, and reaction rate respectively. δ_{j2} is used to determine which species will be chosen for sensitivity calculation.

From equation 2.22, we can see that the first order sensitivity considers only the linear model response to input perturbations, as the 'slope' shown in Figure 2.7. In order to evaluate the nonlinearity of model response to input perturbations, as the 'curvature' shown in Figure 2.7, second order sensitivity coefficients need to be computed.
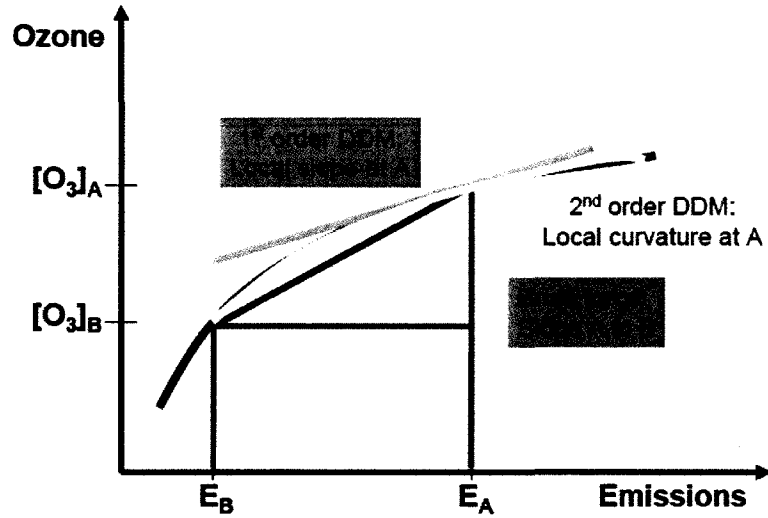
Figure 2.7: Schematic ozone responses to emissions, and brute force and DDM-3D

sensitivities. (Source: Cohan, 2004)

Differentiating equation 2.23 for the same parameter results in the DDM equation for the

second order sensitivity coefficients shown in equation 2.25

$$
\begin{aligned}
\frac{\partial S_{ij}^{(2)}}{\partial t} = &-\nabla(uS_{ij}^{(2)}) + \nabla(K\nabla S_{ij}^{(2)}) + J_i S_j^{(2)} + J_{i,S^{(1)}}^{*} S_j^{(2)} + \\
&2\frac{\partial}{\partial \epsilon_j}(J_{i,\tilde{C}} S_j^{(1)})\delta_{5_{j_1}} - 2\nabla(\tilde{u}S_{ij}^{(1)})\delta_{3_{j_1}} + \nabla(\tilde{K}\nabla S_{ij}^{(1)})\delta_{7_{j_1}}
\end{aligned}
\tag{2.25}
$$

The initial and boundary conditions used to solve equation 2.25 are shown in equation 2.26

$$
\text{IC: } S_{ij}^{(2)} = 0
\tag{2.26a}
$$

$$
\text{BCs: } uS_{ij}^{(2)} - K\nabla S_{ij}^{(2)} = -2\tilde{u}S_{ij}^{(1)}\delta_{3_{j_1}} + 2\tilde{K}\nabla S_{ij}^{(1)}\delta_{7_{j_1}}
\tag{2.26b}
$$

$$
-\nabla S_{ij}^{(2)} = 0
\tag{2.26c}
$$

$$
v_{g_i}S_{ij}^{(2)} - K_{zz}\frac{\partial S_{ij}^{(2)}}{\partial z} = -2\tilde{v}_{g_i}S_{ij}^{(1)}\delta_{6_{j_1}}\delta_{ij_2} + 2\tilde{K}\frac{\partial S_{ij}^{(1)}}{\partial z}\delta_{7_{j_1}}
\tag{2.26d}
$$

In equation 2.25, $J^*_{s^{(1)}}$ is an augmented Jacobian matrix of reaction rate constants; it has

the same structure as $J_{\bar{C}}$ but without all first order reactions.

The cross sensitivity, second order sensitivity in regards to two different sensitivity

parameters, could also be calculated in the same way by differentiating equation 2.23 with

respect to a different parameter, but additional terms may be required.

DDM-3D has been implemented into CMAQ successfully for gaseous species by

Cohan (2004), and expanded to inorganic particulate matter by Napelenok et al, (2006).

CMAQ-DDM can compute the initial condition sensitivity, boundary condition sensitivity,

reaction rate constant sensitivity, and emission rate sensitivity. In this study, new features

of computing the eddy diffusivity sensitivity and dry deposition velocity sensitivity were

also added into CMAQ-DDM. The method of numerical implementation of these two

sensitivity parameters in CMAQ-DDM is discussed in chapter 3.

References

Bergin, M.S., Noblet, G.S., Petrini, K., Dhieux, J.R., Milford, J.B., and Harley, R.B. (1999) Formal uncertainty analysis of a Lagrangian photochemical air pollution model. *Environmental Science and Technology.* 33, 1116-1126.

Brook, J.R., Zhang, L-M., Di-Giovanni, F., and Padro, J. (1999) Description and evaluation of a model of deposition velocities for routine estimates of air pollutant dry deposition over North America. Part I: model development. *Atmospheric Environment.* 33, 5037-5051.

Byun, D.W. and Ching, J.K.S. (1999) *Science algorithms of the EPA Model-3 Community Multiscale Air Quality (CMAQ) modeling system.* Office of research and development, US. EPA. North Carolina.

Byun, D.W. and Dennis, R.L. (1995) Design artifacts in Eulerian air quality models: Evaluation of the effects of layer thickness and vertical profile correction on surface ozone concentrations. *Atmospheric Environment.* 29, 105-126.

Byun, D.W., Kim, S-T., and Kim, S.B. (2007) Evaluation of air quality models for the simulation of a high ozone episode in the Houston metropolitan area. *Atmospheric Environment.* 41, 837-853.

Byun, D. and Schere, K.L. (2006) Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multiscale Air Quality (CMAQ) ,modeling system. *Applied Mechanics Reviews.* 59, 51-77.

CMAS center. *CMAQ v4.6 operational guidance document.*

(http://www.cmaqmodel.org/op_guidance_4.6/index.cfm. Accessed on October 1st,

2009)

Cohan, D.S. (2004) *Photochemical formation and cost-efficient abatement of ozone: high*

order sensitivity analysis. PhD Dissertation. The Georgia Institute of Technology,

Atlanta, Georgia.

Daum, P.H., Kleinman, L.I., Springston, S.R., Nunnemacker, L.J., Lee, Y-N.,

Weinstein-Lloyd, J., Zheng, J., and Berkowitz, C. (2004) Origin and properties of

plumes of high ozone observed during Texas 2000 Air Quality Study (TEXAQS

2000). *Geophysical Research Letter.* 109, D17306.

Hakami, A., Odman, M.T., and Russell, A.G. (2003) High-order, direct sensitivity analysis

of multidimensional air quality models. *Environmental Science and Technology.* 37,

2442-2452.

Hakami, A., Odman, M.T., and Russell, A.G. (2004) Nonlinearity in atmospheric response:

A direct sensitivity analysis approach. *Journal of Geophysical Research.* 109,

D15303.

Hanna, S.R., Lu, Z., Frey, H.C., Wheeler, N., Vukovich, J., Arumachalam, S., and Fernau,

M. (2001) Uncertainties in predicted ozone concentration due to input uncertainties

for the UAM-V photochemical grid model applied to the July 1995 OTAG domain.

Atmospheric Environment. 35, 891-903.

Jacob, D.J. (1999) *Introduction to atmospheric chemistry.* Princeton Press. New Jersey.

Kleinman, L.I., Daum, P.H., Imre, D., Lee, Y-N., Nunnemacker, L.J., and Springston, S.R. (2002) Ozone production rate and hydrocarbon reactivity in five urban areas: A case of high ozone concentration in Houston. *Geophysical Research Letter.* 29(10), 1467.

Napelenok, S.L., Cohan, D.S., Hu, Y-T., and Russell, A.G. (2006) Decoupled direct 3D sensitivity analysis for particulate matter (DDM-3D/PM). *Atmospheric Environment.* 40, 6112-6121.

Parrish, D.D., Allen, D.T., Bates, T.S., Estes, M., Fehsenfeld, F.C., Feingold, G., Ferrare, R., Hardesty, R.M., Meagher, J.F., Nielsen-Gammon, J.W., Pierce, R.B., Ryserson, T.B., Seinfeld, J.H. and Williams, E.J. (2009) Overview of the second Texas Air Quality Study (TexAQS II) and the Gulf of Mexico Atmosphere Composition and Climate Study (GoMACCS). *Journal of Geophysical Research.* 114, D00F13.

Pinder, R.W., Gilliam, R.C., Appel, K.W., Napelenok, S.L., Foley, K.M., and Gilliland, A.B. (2009) Efficient probabilistic estimates of surface ozone concentration using an ensemble of model configurations and direct sensitivity calculations. *Environmental Science and Technology.* 43, 2388-2393.

Pleim, J.E. (2006a) A combined local and nonlocal closure model for the atmospheric boundary layer. Part II: Apllication and evaluation in a mesoscale meteorological model. *Journal of Applied Meteorology and Climatology.* 46, 1396-1408.

Pleim, J.E. (2006b) A new combined local and non-local PBL model for meteorology and air quality modeling. CMAS conference paper. North Carolina.

Pleim, J.E. Planetary boundary layer modeling for meteorology and air quality.

(http://www.epa.gov/AMD/peer/posters/Poster_1.6.pdf Accessed on September

16th,2009)

Pleim, J.E., Xiu, A., Finkelstein, P.L., and Otte, T.L (2001) A coupled land-surface and dry

deposition model and comparison to field measurements of surface heat, moisture,

and ozone fluxes. *Water Air Soil Pollution. Focus.* 1, 243-252.

Rappengluck, B., Perna, R., Zhong, S., and Morris, G.A. (2008) An analysis of the vertical

structure of the atmosphere and the upper-level meteorology and their impact on

surface ozone levels in Houston, Texas. *Journal of Geophysical Research.* 113,

D17315.

Ryerson, T.B., et al. (2003) Effect of petrochemical industrial emissions of reactive alkenes

and NO_x on tropospheric ozone formation in Houston, Texas. *Journal of*

Geophysical Research. 108, D8, 4249.

Seinfeld, J.H and Pandis, S.N (2002) *Atmospheric chemistry and physics.* John Wiley &

Sons, INC. New Jersey.

TCEQ. *TexAQS II field study map.*

(http://www.tceq.state.tx.us/implementation/air/airmod/texaqs/texaqs_overview.ht

ml Accessed on October 1st, 2009)

Wesely, M.L. (1989) Parameterization of surface resistances to gaseous dry deposition in

regional-scale numerical models. *Atmospheric Environment.* 23, 1293-1304.

Wesely, M.L. and Hicks, B.B. (2000) A review of the current status of knowledge on dry deposition. *Atmospheric Environment*. 34, 2261-2282.

Wilson, R. (2004) Turbulent diffusivity in the free atmosphere inferred from MST radar measurements: A review. *Annales Geophysicae*. 22, 3869-3887.

Yang, Y.J., Wilkinson, J.G., and Russell, A.G. (1997) Fast, direct sensitivity analysis of multidimensional photochemical models. *Environmental Science and Technology*. 31, 2859-2868.

CHAPTER 3

Methodology

The methodology of this modeling work is described in this chapter. The following

description includes three subsections: Model development, Model evaluation, and

Sensitivity and uncertainty analysis. In the model development part, the Crank-Nicolson

method that is used to solve the advection-diffusion equation in CMAQ is demonstrated;

the numerical implementation of dry deposition velocity and eddy diffusivity sensitivities

into the CMAQ-DDM model, and the accuracy test method for the newly implemented

code are described. In the model evaluation part, the CMAQ configurations in this study

and the data comparison methods are introduced. In the sensitivity and uncertainty analysis

part, the sensitivity coefficient calculations and the Taylor expansion equations used in

uncertainty analysis are illustrated.

3.1 Model development

3.1.1 Crank-Nicolson scheme

The model formulation of two vertical diffusion schemes, EDDY and ACM2, was

described in Chapter Two. To solve the vertical advection-diffusion equation, as shown in

equation 3.1, the Crank-Nicolson finite-difference approximation was applied to these two

vertical diffusion schemes in CMAQ. Compared to the Forward Euler and Implicit

finite-difference methods, which are commonly used in solving differential equations, the

Crank-Nicolson method, as shown in equation 3.2, has second order approximations in both time and space, and it is unconditionally stable for all values of u and K (Jacobson 2005).

$$\frac{\partial N}{\partial t} + \frac{\partial (wN)}{\partial z} - \frac{\partial}{\partial z}(K_{zz}\frac{\partial N}{\partial z}) = 0 \tag{3.1}$$

$$\frac{N_{i,t} - N_{i,t-h}}{h} + \left[\mu_c \frac{(wN)_{i+1,t} - (wN)_{i-1,t}}{2\Delta z} + (1-\mu_c)\frac{(wN)_{i+1,t-h} - (wN)_{i-1,t-h}}{2\Delta z}\right]$$

$$-K\left[\mu_c \frac{N_{i+1,t} - 2N_{i,t} + N_{i-1,t}}{\Delta z^2} + (1-\mu_c)\frac{N_{i+1,t-h} - 2N_{i,t-h} + N_{i-1,t-h}}{\Delta z^2}\right] = 0 \tag{3.2}$$

In equation 3.2, μ_c is the Crank-Nicolson parameter. When μ_c equals 0, the equation reduces to the forward Euler method; when μ_c equals 1, the equation reduces to the implicit method. In our case, μ_c equals 0.5. The μ_c term enables this method to evaluate some terms at time t and the others at time t-h. Hence, it improves the order of approximation in time to second order. The matrix corresponded to equation 3.2 could be written as follows:

$$\begin{bmatrix} B_1 & D_1 & 0 & 0 & \cdots & 0 & 0 & 0 \\ A_2 & B_2 & D_2 & 0 & \cdots & 0 & 0 & 0 \\ 0 & A_3 & B_3 & D_3 & \cdots & 0 & 0 & 0 \\ 0 & 0 & A_4 & B_4 & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & B_{i-2} & D_{i-2} & 0 \\ 0 & 0 & 0 & 0 & \cdots & A_{i-1} & B_{i-1} & D_{i-1} \\ 0 & 0 & 0 & 0 & \cdots & 0 & A_i & B_i \end{bmatrix} \begin{bmatrix} N_{1,t} \\ N_{2,t} \\ N_{3,t} \\ N_{4,t} \\ \vdots \\ N_{i-1,t} \\ N_{i-2,t} \\ N_{i,t} \end{bmatrix} =$$

$$\begin{bmatrix} F_1 & G_1 & 0 & 0 & \cdots & 0 & 0 & 0 \\ E_2 & F_2 & G_2 & 0 & \cdots & 0 & 0 & 0 \\ 0 & E_3 & F_3 & G_3 & \cdots & 0 & 0 & 0 \\ 0 & 0 & E_4 & F_4 & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & F_{i-2} & G_{i-2} & 0 \\ 0 & 0 & 0 & 0 & \cdots & E_{i-1} & F_{i-1} & G_{i-1} \\ 0 & 0 & 0 & 0 & \cdots & 0 & E_i & F_i \end{bmatrix} \begin{bmatrix} N_{1,t-h} \\ N_{2,t-h} \\ N_{3,t-h} \\ N_{4,t-h} \\ \vdots \\ N_{i-1,t-h} \\ N_{i-2,t-h} \\ N_{i,t-h} \end{bmatrix} + \begin{bmatrix} E_1 N_{0,t-h} - A_1 N_{0,t} \\ 0 \\ 0 \\ 0 \\ \vdots \\ 0 \\ 0 \\ G_i N_{i+1,t-h} - D_i N_{i+1,t} \end{bmatrix} \tag{3.3}$$

$$A_i = -\mu_c h(\frac{w}{2\Delta z} + \frac{K_{zz}}{\Delta z^2})_{i-1} \quad B_i = 1 + \mu_c h(\frac{2K_{zz}}{\Delta z^2})_i \quad D_i = \mu_c h(\frac{w}{2\Delta z} - \frac{K_{zz}}{\Delta z^2})_{i+1}$$

$$E_i = (1-\mu_c)h(\frac{w}{2\Delta z}+\frac{K_{zz}}{\Delta z^2})_{i-1} \quad F_i = 1-(1-\mu_c)h(\frac{2K_{zz}}{\Delta z^2})_i \quad G_i = -(1-\mu_c)h(\frac{w}{2\Delta z}-\frac{K_{zz}}{\Delta z^2})_{i+1}$$

Due to the operator splitting method used in the model, the EDDY and ACM2 codes only

simulate vertical diffusion, that is, the $K_{zz}/\Delta z^2$ term. The vertical advection term, w/2Δz, is

being simulated by another code called ZADV. Both schemes discretized their diffusion

equations into a tridiagonal matrix system, as shown in equation 3.3, and use the Thomas

algorithm (tridiagonal solver) to solve the matrix.

3.1.2 Numerical implementation

As described in Chapter Two, the DDM equation for the time evolution of first order

sensitivity coefficients is given by equation 3.4 (Hakami et al. 2003)

$$\frac{\partial S_{ij}^{(1)}}{\partial t} = -\nabla(uS_{ij}^{(1)}) + \nabla(K\nabla S_{ij}^{(1)}) + J_i S_j^{(1)} + \frac{\partial R_i}{\partial \epsilon_j}\delta_{5 j_1} + \tilde{E}_i\delta_{1 j_1}\delta_{ij_2} - \nabla(\tilde{u}C_i)\delta_{3 j_1} + \nabla(\tilde{K}\nabla C_i)\delta_{7 j_1} \tag{3.4}$$

Equation 3.5 is one of the boundary conditions required to solve the first order sensitivity

coefficients, and it is also the equation used to calculate the sensitivity to emission, dry

deposition velocity, and eddy diffusivity.

$$v_{g_i}S_{ij}^{(1)} - K_{zz}\frac{\partial S_{ij}^{(1)}}{\partial z} = -\tilde{v}_{g_i}C_i\delta_{6 j_1}\delta_{ij_2} + \tilde{K}_{zz}\frac{\partial C_i}{\partial z}\delta_{7 j_1} + \tilde{E}_{0_i}\delta_{1 j_1}\delta_{ij_2} \tag{3.5}$$

V_g, K_{zz} and E represent the dry deposition velocity, eddy diffusivity and emission,

respectively. The Kronecker delta function, δ_{j1}, is used in DDM to control the sensitivity to

input parameters that will be calculated during the simulation process. In this work, $6j_1$ and

$7j_1$ refer to dry deposition velocity and eddy diffusivity, respectively. δ_{j2} is used to

determine which species will be chosen for sensitivity calculation. The dry deposition

velocities, like emission rates, have different values for different species; hence, the term

δ_{j2} needs to be applied to the dry deposition velocity sensitivity calculation. However, δ_{j2} is

not necessary for calculating the eddy diffusivity sensitivity because eddy diffusivity does

not depend on the properties of species. The DDM code for calculating the emission, dry

deposition velocity, and eddy diffusivity sensitivities in equation 3.5 can be implemented

into the code that is used to simulate the vertical diffusion process in CMAQ by following

the logic of calculating concentrations. The DDM code already has been implemented into

the EDDY scheme for emission sensitivity calculation only, but it has not been

implemented yet into the newly developed ACM2 scheme. Hence, by analogy to the DDM

implementation in the EDDY scheme, the DDM also could be added to the ACM2 scheme.

Meanwhile, the first order sensitivities to dry deposition velocity and eddy diffusivity also

could be added to the CMAQ-DDM model similarly.

In equation 3.5, for the first order sensitivity, there are three terms on the right hand

side. The E_i term already has been added to DDM in the EDDY scheme as mentioned

above. Hence, by following the same logic, the other two terms, $\tilde{v}_{g_i} C_i \delta_{6_{j_1}} \delta_{ij_2}$ and

$\tilde{K} \dfrac{\partial C_i}{\partial z} \delta_{4_{j_1}}$, are included directly after the E_i term in the code. The capability of calculating

dry deposition velocity sensitivity for different species at a particular time and in a given

region and the capability of calculating eddy diffusivity sensitivity for different layers at a

particular time and in a given region were also added to the DDM code.

After differentiating equation 3.4 for the same parameter, the DDM equation for the

second order sensitivity coefficients is shown in equation 3.6 .

$$\frac{\partial S_{ij}^{(2)}}{\partial t} = -\nabla(uS_{ij}^{(2)}) + \nabla(K\nabla S_{ij}^{(2)}) + J_i S_j^{(2)} + J_{i,S^{(1)}}^{*} S_j^{(2)} +$$
$$2\frac{\partial}{\partial \epsilon_j}(J_{i,\tilde{C}} S_j^{(1)})\delta_{5_{j_1}} - 2\nabla(\tilde{u}S_{ij}^{(1)})\delta_{3_{j_1}} + \nabla(\tilde{K}\nabla S_{ij}^{(1)})\delta_{7_{j_1}}$$

(3.6)

Equation 3.7, as one of the boundary condition for 3.6, can be used as guidance for the

implementation of the second order sensitivities to dry deposition velocity and eddy

diffusivity.

$$v_{g_i} S_{ij}^{(2)} - K_{zz} \frac{\partial S_{ij}^{(2)}}{\partial z} = -2\tilde{v}_{g_i} S_{ij}^{(1)} \delta_{6_{j_1}} \delta_{ij_2} + 2\tilde{K}_{zz} \frac{\partial S_{ij}^{(1)}}{\partial z} \delta_{7_{j_1}}$$

(3.7)

The emission term in equation 3.5 does not appear in equation 3.7, because it has

concentration term (C_i) for dry deposition and eddy diffusion in the first order sensitivity

calculation, the additional terms with first order sensitivities appear in equation 3.7 for

second order sensitivities to dry deposition velocity and eddy diffusivity calculation.

Similarly, second order terms also could be added into DDM by following the same

protocol that has been used in the first order sensitivity implementation.

For the second order sensitivity, two additional terms were required for HDDM,

$-2\tilde{v}_{g_i} S_{ij}^{(1)}\delta_{6_{j_1}}\delta_{ij_2}$ and $2\tilde{K}_{zz}\frac{\partial S_{ij}^{(1)}}{\partial z}\delta_{4_{j_1}}$, as shown on the right hand side of equation 3.7. The

implementation of second order terms is very similar to that for the first order terms. The

only difference is that the concentration terms in first order sensitivities calculations were

replaced by the corresponding first order sensitivity terms. Notice that the logic in equation

3.7 is only for the same sensitivity parameter. For second order of different sensitivity

parameters, such as cross sensitivity of dry deposition with emission, the term on the right

hand side of equation 3.7 should be replaced by $-\tilde{v}_{g_i}\delta_{6j_1}\delta_{ij_2}S_{ik}^{(1)}$, where $S_{ik}^{(1)}$ indicates the other sensitivity parameter, here referring to emission.

For the DDM implementation of the first order and second order sensitivities to dry deposition velocity and eddy diffusivity, the logic and the way of coding are almost identical for the EDDY and ACM2 schemes. The only difference is that the non-local turbulence diffusion terms under the convective boundary layer also need to be considered in the DDM for eddy diffusivity sensitivity calculation for the ACM2 scheme.

3.1.3 Accuracy test

After new code is implemented into DDM, an accuracy test is essential for model validation. Commonly, the sensitivity coefficients calculated by DDM are compared with a Brute Force approximation to evaluate the accuracy (Hakami et al., 2004). Sensitivity coefficients calculated by a Brute Force approximation are derived from Taylor series expansion and are shown in equations 3.8-3.10. Equation 3.8 can be used for first order sensitivity comparison, equation 3.9 can be used for second order sensitivity comparison, and equation 3.10 can be used for cross sensitivity comparison

$$S_j^{(1)} \approx \frac{C_{+\Delta\epsilon_j} - C_{-\Delta\epsilon_j}}{2\Delta\epsilon_j} \tag{3.8}$$

$$S_{j,j}^{(2)} \approx \frac{C_{(+\Delta\epsilon_j\, p_j)} - 2C_0 + C_{(-\Delta\epsilon_j\, p_j)}}{(\Delta\epsilon_j)^2} \tag{3.9}$$

$$S_{j,k}^{(2)} \approx \frac{C_{(+\Delta\epsilon_j\, p_j,+\Delta\epsilon_k\, p_k)} - C_{(+\Delta\epsilon_j\, p_j,-\Delta\epsilon_k\, p_k)} - C_{(-\Delta\epsilon_j\, p_j,+\Delta\epsilon_k\, p_k)} + C_{(-\Delta\epsilon_j\, p_j,-\Delta\epsilon_k\, p_k)}}{4\Delta\epsilon_j\, \Delta\epsilon_k} \tag{3.10}$$

$\Delta \in$ in above equations indicates the perturbation of model input parameters in the Brute Force approximation. In this study, $\pm 10\%$ perturbation was chosen for the first order sensitivity coefficients calculation by the Brute Force approximation, and $\pm 50\%$ perturbation was chosen for the second order and cross sensitivity coefficients calculation.

3.2 Model evaluation

3.2.1 Model configurations

CMAQ model version 4.5 was used in this study to simulate a seven-day episode from August 30th to September 5th in eastern Texas at a resolution of 4km grid cell. All model inputs were provided by University of Houston. The model configurations are shown in Figure 3.1 (University of Houston IMAQS. 2009):
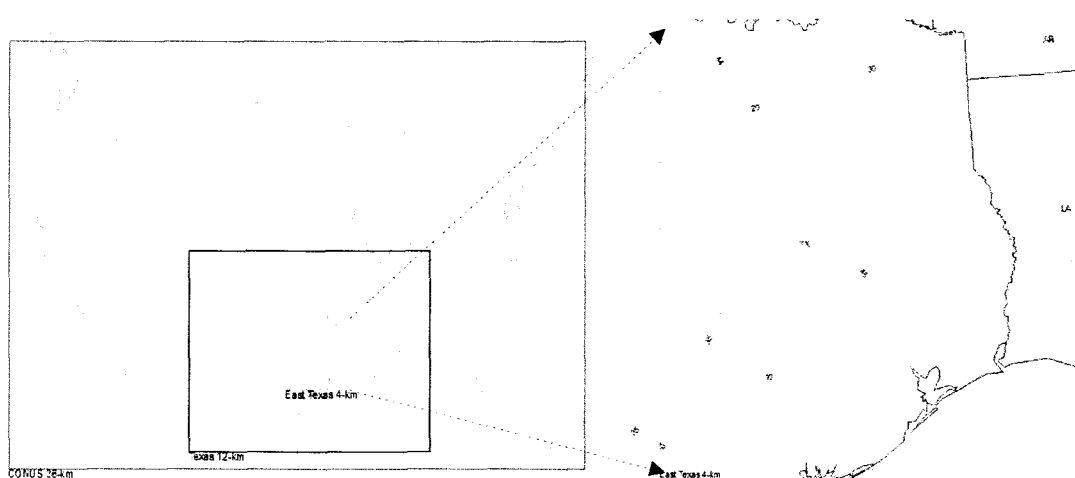

Figure 3.1: Modeling domain of East Texas (source: IMAQS 2009)

The NCAR/Penn State (National Center for Atmospheric Research/Pennsylvania State University) Mesoscale Model, Version 5, release 3.6.1 (MM5V3.6.1), was used to generate the meteorological field in this study, and a 43-layer vertical structure was set up in MM5. The Meteorology-Chemistry Interface Processor Version 2.3 (MCIP2.3) was used to create CMAQ-ready meteorology data from the files generated by MM5, and the 43 vertical layers used in MM5 were reduced to 23 for CMAQ by MCIP. The Sparse Matrix Operator Kernel Emissions (SMOKE) model, version 2.1 was used for emission processing as shown in Figure 3.2. The projected air quality forecast emissions inventory including Point, Mobile, and Area sources at level of year 2005 based on year 2000 and 2007 emissions from TCEQ was used in this study. The biogenic emission inventory is taken from TCEQ's Land Use and Land Cover (LULC) data after processed by the GloBEIS 3.1 model for emission normalizing and by BEIS3 model for meteorology conditions adjustment.
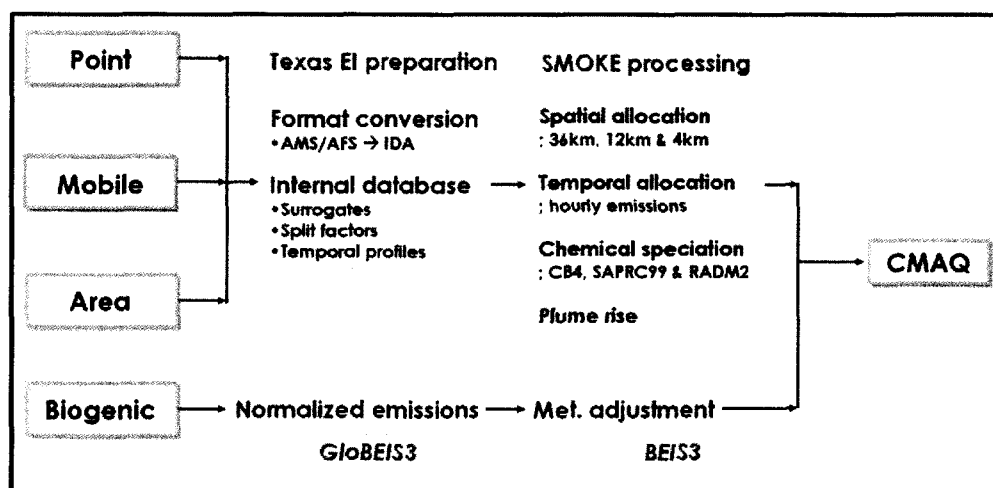

Figure 3.2: SMOKE emissions processing (source: IMAQS 2009)

The CMAQ model configuration is shown in Table 3.1.

Table 3.1: CMAQ science options (source: IMAQS 2009)

Options	Parameters
Domain	Eastern Texas 4-km
CMAQ	Version 4.5
MCIP	Version 2.3
SMOKE	Version 2.1
Chemical Mechanism	CB4 (cb4_aq_ae4)
Emissions	Texas Emissions Inventory (TCEQ) projected for 2005 + NEI99
Boundary Condition	Downscale linkage from GEOS-CHEM
Advection Scheme	Piecewise Parabolic Method (PPM)
Horizontal Diffusion	Multiscale
Vertical Diffusion	Eddy
Cloud Scheme	RADM
Forecasting hours	48 hours (+ 6-hr spin-up)

3.2.2 Data comparisons

In this study, the modeling results generated by using different vertical diffusion

schemes, EDDY and ACM2, were compared with the field measurement data from a

TexAQS 2006/Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS)

field campaign conducted from August to October 2006. The measurement sites located in

our modeling domain are shown in Figure 3.3.

Figure 3.3: Field measurement locations (top) and surface sites (bottom) inside modeling

domain.

Comparisons in this study include those with surface data, ozonesonde data, and aircraft data. As shown in Figure 3.3, the red rectangle represents ground site measurements, and the data were downloaded from TECQ website (http://www.tceq.state.tx.us/compliance/monitoring/air/monops/hourly_data.html). The green circle and blue ship sign represent the ozonesonde measurements conducted at University of Houston and the Houston Ship Channel, respectively, and the data were downloaded from World Ozone Data Centre website (ftp://ftp.tor.ec.gc.ca/Projects-Campaigns/ions06/). The air plane sign represents NOAA P-3 Aircraft measurements, and the data were downloaded from NOAA website (http://www.esrl.noaa.gov/csd/tropchem/2006TexAQS/).

The measurement data were compared to the modeling results from CMAQ extracted from output netCDF files for the corresponding grid cell, hour, and layer.

3.3 Sensitivity and Uncertainty analysis

In this study, the sensitivity analysis and the uncertainty analysis in dry deposition velocity for both EDDY and ACM2 schemes were investigated. However, the uncertainty analysis in eddy diffusivity was not performed, because K_z is a meteorological parameter, and if only considers the variation in CMAQ alone, it may cause model inconsistency error between MM5 and CMAQ.

3.3.1 Sensitivity analysis

As described in Chapter Two, the semi-normalized first order sensitivity coefficients

can be written as equation 3.11. Similarly, the semi-normalized second order sensitivity

coefficients for the same and different parameters can be also defined as equation 3.12

and 3.13, respectively.

$$S_j^{(1)} = P_j \frac{\partial C}{\partial p_j} = P_j \frac{\partial C}{\partial(\in_j P_j)} = \frac{\partial C}{\partial \in_j} \tag{3.11}$$

$$S_{j,j}^{(2)} = P_j \frac{\partial}{\partial p_j}(P_j \frac{\partial C}{\partial p_j}) = \frac{\partial^2 C}{\partial \in_j^2} \tag{3.12}$$

$$S_{j,k}^{(2)} = P_j \frac{\partial}{\partial p_j}(P_k \frac{\partial C}{\partial p_k}) = \frac{\partial^2 C}{\partial \in_j \partial \in_k} \tag{3.13}$$

The P_j and P_k in above equations represent the input or model parameters such as emission

rate, dry deposition velocity, or boundary condition. The p_j and p_k represent the variations

of model parameters such as P_j and P_k, and are defined as $p = \in P$. $\in$ is a scaling variable

with nominal value 0 to 1.

The first order sensitivity coefficients evaluate the responsiveness of pollutant

concentration to infinitesimal perturbations of model parameters; the second order

sensitivity coefficients quantify the nonlinearity of the pollutant concentration response;

the cross sensitivity coefficients analyze the effectiveness of pollutant concentration

response to one sensitivity parameter influenced by the other sensitivity parameter

(Cohan et al., 2005). In this study, the first order and second order ozone sensitivities to

anthropogenic NO_x emission, to anthropogenic VOC emission and to dry deposition

velocity of all species were analyzed.

By looking at the first order ozone sensitivities to anthropogenic NO_x, $\partial[O_3]/\partial \in_{E,\,NO_x}$, and to anthropogenic VOC, $\partial[O_3]/\partial \in_{E,\,VOC}$, the different emission control beneficial regions could be determined for policy applications. For example, where

$\partial[O_3]/\partial \in_{E,\,NO_x} < 0$, controlling VOC will be effective for ozone reduction; where

$\partial[O_3]/\partial \in_{E,\,NO_x} > \partial[O_3]/\partial \in_{E,\,VOC} > 0$, controlling NO_x will be effective for ozone

reduction; where $\partial[O_3]/\partial \in_{E,\,VOC} > \partial[O_3]/\partial \in_{E,\,NO_x} > 0$, controlling VOC will be more

beneficial than controlling NO_x for ozone reduction (Jin et al., 2008).

By looking at the second order ozone sensitivities to NO_x, $\partial^2[O_3]/\partial \in_{E,NO_x}^2$, to VOC ,

$\partial^2[O_3]/\partial \in_{E,VOC}^2$, and to dry deposition velocity, $\partial^2[O_3]/\partial \in_{V_{dep}}^2$, the nonlinear response in

ozone concentration to these sensitivity parameters can be quantified. By looking at the

cross sensitivity of ozone to emission crossed with dry deposition velocity,

$\partial(\dfrac{\partial[O_3]}{\partial \in_E})/\partial \in_{V_{dep}}$, the effect of variation in dry deposition velocity on emission control can be

evaluated.

3.3.2 Uncertainty in dry deposition velocity

Based on the sensitivity coefficients calculated by DDM, the pollutant concentration

with any fractional perturbation can be projected from the base case scenario via Taylor

expansion (Hakami et al., 2004; Cohan et al., 2005). The expression of Taylor expansion

in this study can be written as equation 3.14

$$C_j \mid_{P_j = P_j + \Delta \in_j P_j} \approx C_0 \mid_{P_j = P_j} + \Delta \in_j S_j^{(1)} + \frac{1}{2}\Delta \in_j^2 S_{j,j}^{(2)} \qquad (3.14)$$

Hence, the effect of uncertainty in dry deposition velocity on model simulation results can be evaluated via Taylor expansion. In this analysis, equation 3.14 was revised and expressed as shown in equation 3.15.

$$C_{\Delta V_{dep}} \approx C_0 + \Delta \varphi_{V_{dep}} \times S_{V_{dep}}^{(1)}$$ (3.15)

$C_{\Delta V_{dep}}$ in equation 3.15 is the adjusted concentration by considering the effect of uncertainty in dry deposition velocity. $\Delta \varphi$ represents uncertainty in dry deposition velocity, a value of $\pm 30\%$ (Wesely and Hicks 2000) will be used in this study.

In addition, the effect of uncertainty in dry deposition velocity on emission control strategies also can be quantified via Taylor series expansion.

$$C(x_0 + \Delta \varepsilon_1, y_0 + \Delta \varepsilon_2) \approx C(x_0, y_0) + \Delta \varepsilon_1 S_{\varepsilon_1}^{(1)}(x_0, y_0) + \frac{(\Delta \varepsilon_1)^2}{2} S_{\varepsilon_1 \varepsilon_1}^{(2)}(x_0, y_0)$$ (3.16)

In equation 3.16, x_0 can be considered as emission rate, y_0 can be considered as dry deposition velocity, $\Delta \varepsilon_1$ can be considered as control percentage in emission, and $\Delta \varepsilon_2$ can be considered as uncertainty in dry deposition velocity. In equation 3.16, $\Delta \varepsilon_2$ equals to 0. However, if the parameter y_0 varies ($\Delta \varepsilon_2 > 0$), then more terms must be accounted for equation 3.16 as shown in equation 3.17.

$$C(x_0 + \Delta \varepsilon_1, y_0 + \Delta \varepsilon_2) \approx C(x_0, y_0) + \Delta \varepsilon_1 S_{\varepsilon_1}^{(1)}(x_0, y_0) + \Delta \varepsilon_2 S_{\varepsilon_2}^{(1)}(x_0, y_0)$$
$$+ \frac{(\Delta \varepsilon_1)^2}{2} S_{\varepsilon_1 \varepsilon_1}^{(2)}(x_0, y_0) + \frac{(\Delta \varepsilon_2)^2}{2} S_{\varepsilon_2 \varepsilon_2}^{(2)}(x_0, y_0) + (\Delta \varepsilon_1)(\Delta \varepsilon_2) S_{\varepsilon_1 \varepsilon_2}^{(2)}(x_0, y_0)$$ (3.17)

In order to make the left hand side of equation 3.16 equals to that of equation 3.17, the term, $S_{\varepsilon_1}^{(1)}(x_0, y_0)$, in equation 3.16 needs to be updated to the term as in equation 3.18

$$S_{\varepsilon_1}^{(1)}(x_0, y_0) = S_{\varepsilon_1}^{(1)}(x_0, y_0) + \Delta \varepsilon_2 S_{\varepsilon_1 \varepsilon_2}^{(2)}(x_0, y_0)$$ (3.18)

Therefore, analog to equation 3.18, we could get the mathematical expressions for

quantifying the effect of uncertainty in dry deposition velocity on NO_x and VOC controls

as shown in equations 3.19 and 3.20, respectively.

$$S_{E_{NO_x}}^{(1)} = (\frac{\partial [O_3]}{\partial \in_{E,NO_x}})_{new} = (\frac{\partial [O_3]}{\partial \in_{E,NO_x}})_{old} + \Delta \varphi_{V_{dep}} \frac{\partial^2 [O_3]}{\partial \in_{E,NO_x} \partial \in_{V_{dep}}} \tag{3.19}$$

$$S_{E_{VOC}}^{(1)} = (\frac{\partial [O_3]}{\partial \in_{E,VOC}})_{new} = (\frac{\partial [O_3]}{\partial \in_{E,VOC}})_{old} + \Delta \varphi_{V_{dep}} \frac{\partial^2 [O_3]}{\partial \in_{E,VOC} \partial \in_{V_{dep}}} \tag{3.20}$$

References

Cohan D.S., Hakami, A., Hu, YT., and Russell, A.G. (2005) Nonlinear response of ozone to emissions: Source apportionment and sensitivity analysis. *Environmental Science and Technology.* 39, 6739-6748.

Hakami, A., Odman, M.T., and Russell, A.G. (2003) High-order, direct sensitivity analysis of multidimensional air quality models. *Environmental Science and Technology.* 37, 2442-2452.

Hakami, A., Odman, M.T., and Russell, A.G. (2004) Nonlinearity in atmospheric response: A direct sensitivity analysis approach. *Journal of Geophysical Research.* 109, D15303.

Jacobson, M.Z. (2005) *Fundamentals of Atmospheric Modeling.* Cambridge University Press, New York.

Jin, L., Tonse, S., Cohan, D.S., Mao, XL,. Harley, R.A., and Brown, N.J. (2008) Sensitivity analysis of ozone formation and transport for a central California air pollution episode. *Environmental Science and Technology.* 42, 3683-3689.

UH IMAQS. *Air Quality Forecasting Model Configurations.* (http://imaqs.uh.edu/ModelSetup.html. Accessed on October 15th, 2009)

Wesely, M.L. and Hicks, B.B. (2000) A review of the current status of knowledge on dry deposition. *Atmospheric Environment.* 34, 2261-2282.

CHAPTER 4

Results and Discussions

In this chapter, modeling results will be illustrated and discussed. It includes four parts: accuracy test, vertical diffusion scheme evaluation, sensitivity analysis, and effect of uncertainty in dry deposition velocity.

4.1 Accuracy test results

As described in Chapter Three, sensitivity coefficients calculated by a Brute Force approximation are used as a benchmark of DDM accuracy. The equations for sensitivity coefficients calculation from the Brute Force approximation are shown in equation 3.8-3.10 in Chapter Three. The comparisons of sensitivity coefficient calculation between DDM and the Brute Force approximation approach are presented in this section. The first order sensitivity coefficients of ozone to ozone dry deposition velocity, ozone to eddy diffusivity, and ozone to NO_x dry deposition velocity, the second order sensitivity coefficient of ozone to NO_x dry deposition velocity, and the cross sensitivity coefficient between NO_x dry deposition velocity and NO_x emission are tested for both EDDY (Figure 4.1a) and ACM2 (Figure 4.1b) schemes.
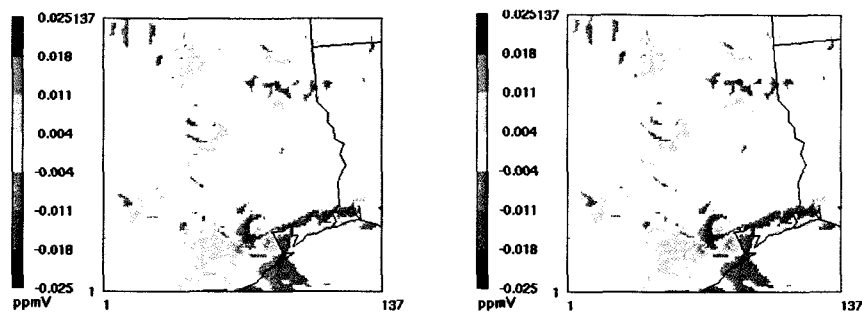
$\partial[O_3]/\partial \in_{V_{O_3dep}}$ (ozone sensitivity to ozone dry deposition velocity)
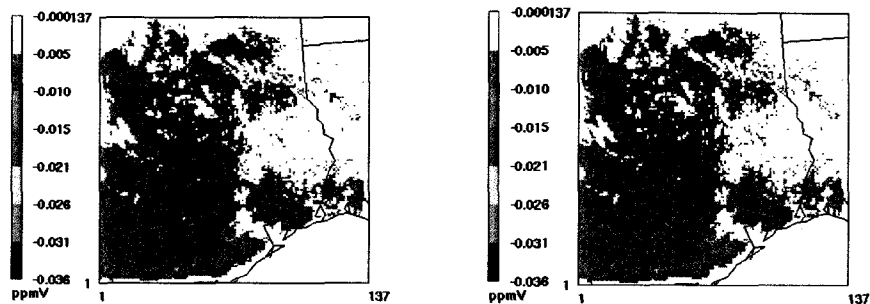
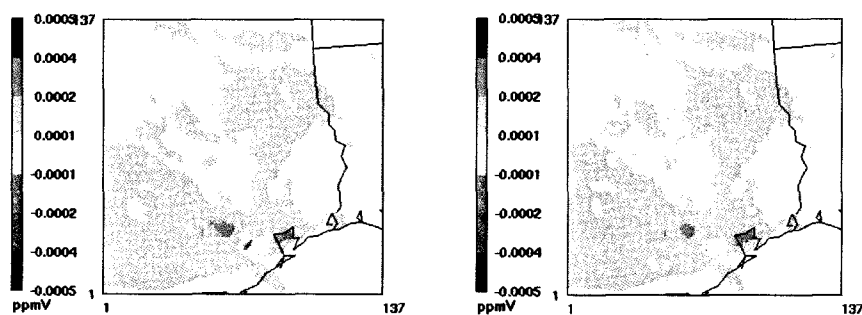$\partial[O_3]/\partial \in_{V_{NO_xdep}}$ (ozone sensitivity to NO_x dry deposition velocity)
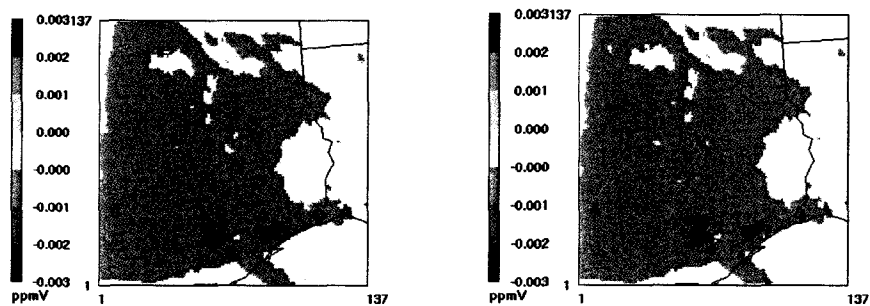
$\partial[O_3]/\partial \in_{K_{zz}}$ (ozone sensitivity to eddy diffusivity)

$\partial^2[O_3]/\partial \in_{V_{NO_xdep}}^2$ (second order ozone sensitivity to NO_x dry deposition velocity)

$\partial^2[O_3]/\partial \in_{E_{NO_x}} \partial \in_{V_{NO_x dep}}$ (cross sensitivity to NO_x emission and NO_x dry deposition velocity)
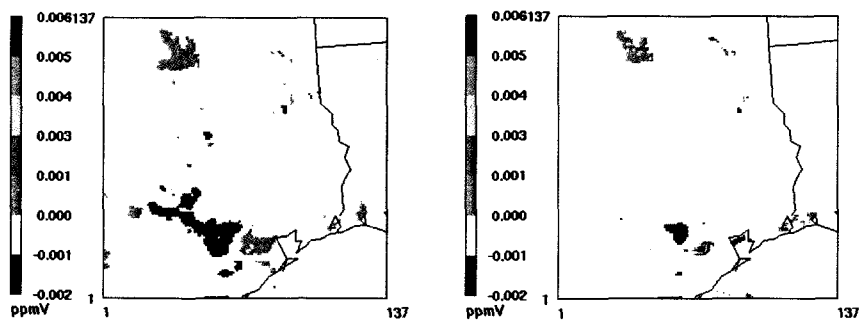

Figure 4.1a: Sensitivity coefficients from DDM (left) and Brute Force (right) of EDDY

scheme at the time of peak ozone (4:00PM CST) on August 31st, 2006.

$\partial[O_3]/\partial \in_{V_{O_3 dep}}$ (ozone sensitivity to ozone dry deposition velocity)

$\partial[O_3]/\partial \in_{V_{NO_x dep}}$ (ozone sensitivity to NO_x dry deposition velocity)

$\partial[O_3] / \partial \in_{K_{zz}}$ (ozone sensitivity to eddy diffusivity)

$\partial^2[O_3] / \partial \in^2_{V_{NO_x dep}}$ (second order ozone sensitivity to NO_x dry deposition velocity)

$\partial^2[O_3] / \partial \in_{E_{NO_x}} \partial \in_{V_{NO_x dep}}$ (cross sensitivity to NO_x emission and NO_x dry deposition velocity)

Figure 4.1b: Sensitivity coefficients from DDM (left) and Brute Force (right) of ACM2

scheme at the time of peak ozone (4:00PM CST) on August 31st, 2006.

Table 4.1. Sensitivity coefficients of 1-hour ozone with respect to dry deposition velocity, eddy diffusivity, and emission, and statistical consistency of Brute Force and DDM-3D results

Sensitivity Parameters	DDM vs. Brute Force (EDDY)[a]			DDM vs. Brute Force (ACM2)[a]		
	R^2	Bias%[f]	Error%[g]	R^2	Bias%[f]	Error%[g]
O_3 dry deposition velocity[b,c]	0.9991	-0.19	0.94	0.9989	-0.72	1.2
NO_X dry deposition velocity[b,d]	0.9953	2.17	3.02	0.9955	2.04	3.05
Eddy diffusivity[b,e]	0.9932	-1.72	3.91	0.9911	3.3	5.91
1st order domain wide NO_X emission[b]	0.9975	-1.60	3.22	0.9975	-1.39	3.1
2nd order dry deposition velocity[d,h]	0.9595	0.59	6.77	0.9046	10.58	17.99
Cross sensitivity (E_{NOx} and V_{dNOX})[i]	0.9676	16.64	13.74	0.845	21.25	33.1

Note: a Comparing for each day and grid cell. Averaged over domain for Aug. 31-Sep 5 episode.

b Calculated using ±10% perturbation

c O_3 sensitivity to O_3 dry deposition velocity

d O_3 sensitivity to NO_X dry deposition velocity

e O_3 sensitivity to eddy diffusivity in all layers

f Normalized mean bias $\Sigma(DDM\text{-}Brute\ force)/\Sigma(Brute\ force)$

g Normalized mean error $\Sigma|(DDM\text{-}Brute\ force)|/\Sigma|(Brute\ force)|$

h Calculated using ±50% perturbation

i Calculated using ±10% perturbation for emission, ±50% perturbation for dry deposition velocity

The first order sensitivity coefficients calculated by DDM and the Brute Force method are almost identical for both schemes. The second order sensitivity and cross sensitivity coefficients calculated by DDM seem to be less accurate but still have good agreement compared with Brute Force (Figure 4.1). The statistical analysis results (Table 4.1) show the same conclusions as those illustrated in Figure 4.1. The statistical comparisons between DDM and BF in Table 4.1 were calculated cell-by-cell for each hour in a day and were averaged over six days of the episode. A ±50% perturbation was used in the Brute Force approximation for second order sensitivity to dry deposition velocity in order to reduce the

numerical noise from model simulations. The first day statistical results were excluded in the calculations to minimize influence of the initial conditions. The statistical results show R^2 close to one and very small values of normalized mean bias (NMB) and normalized mean error (NME) for the first order sensitivity coefficients comparisons. However, the second order and cross sensitivity coefficients have slightly less statistical consistency than the first order coefficients, most probably due to truncation error and model inconsistency error from the Brute Force approximation (Hakami et al., 2004). Notice that the second order and cross sensitivity coefficients from ACM2 scheme showed remarkable inaccuracy. Hence, the HDDM code for the second order and cross sensitivity of dry deposition velocity in ACM2 requires further investigation. Additionally, weak consistency was observed in modeling cases with a grid size larger than 8km because of the convective cloud process during the simulation. Scientists at U.S. EPA are addressing this weakness (Sergey, N.L, personal communications, 2009).

4.2 Vertical diffusion schemes evaluation

The CMAQ model simulation results with two different vertical diffusion schemes for the same episode are evaluated in this section. The data comparisons between modeling and measurements include those with surface, ozonesonde, and regional aircraft data.

4.2.1 Regional ozone modeling

Ozone formation and transport in eastern Texas from August 30th to September 5th were simulated by CMAQ 4.5. The maximum 1-hr average simulated ozone in the episode occurs downwind of the Houston Ship Channel at 4:00PM (CST) on August 31st, 2006, and the predicted ozone concentration reaches 133ppb in EDDY scheme and 147 ppb in ACM2 scheme. The eastern Texas county map and HGB ozone non-attainment area are shown in Figure 4.2. The wind conditions and PBL height over the study domain at the time of peak ozone are shown in Figure 4.3.
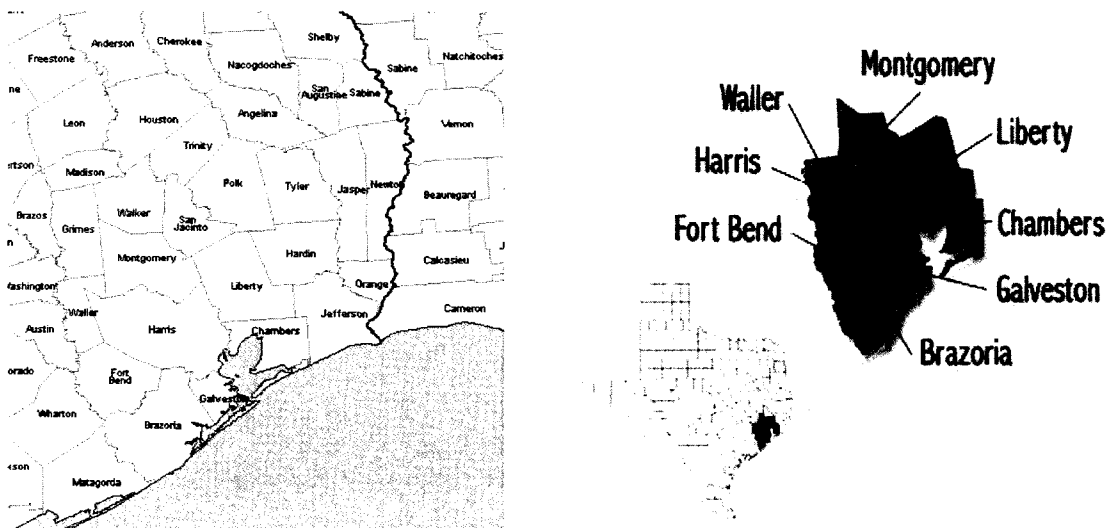
Figure 4.2: Eastern Texas county map (left) and HGB ozone non-attainment area (right).

(Source: TCEQ 2009)
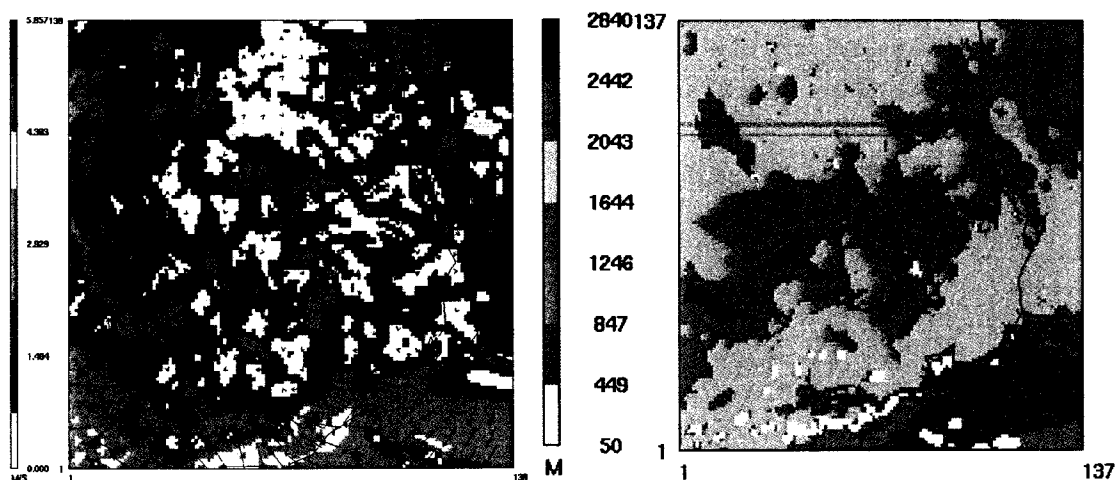
Figure 4.3: Wind conditions (left) and PBL height (right) at ozone peak time (4:00PM CST), August 31st, 2006.

The domain ozone distribution at the time of peak ozone for the episode for both EDDY and ACM2 schemes is shown in Figure 4.4.
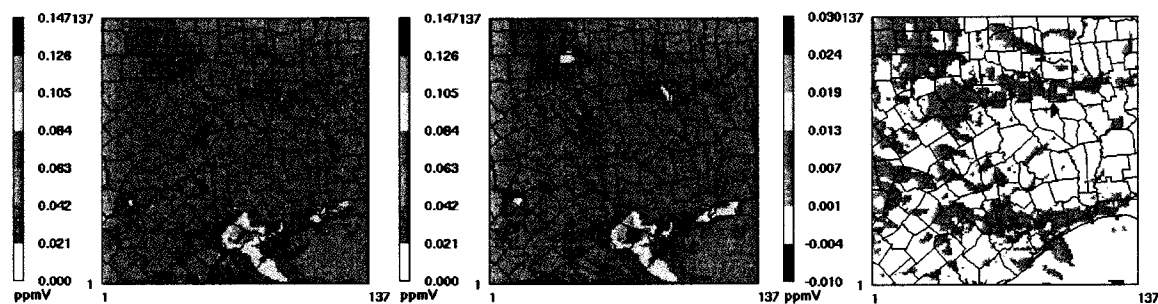

Figure 4.4: Ozone concentration at peak time (4:00PM CST), August 31st, 2006. (left) EDDY scheme; (middle) ACM2 scheme; (right) Difference (ACM2-EDDY)

The maximum ozone occurs downwind of Houston in Fort Bend County at 4:00pm (Figure 4.2, 4.4) most probably due to the meteorological conditions at that time. The wind plot (Figure 4.3) indicates that at 4:00pm, the northeasterly wind transports the pollutants

from the Houston Ship Channel, where one of the largest petroleum industries in the US

located, to the downwind area. It also indicates that the sea breeze transports the ozone

from the sea to inland at that time and that the low wind speed in Fort Bend County causes

pollutant accumulation. The high temperature and humidity in the afternoon also enhances

the ozone formation. The difference of predicted ozone concentrations from two vertical

diffusion schemes (Figure 4.4) also illustrates that the ACM2 scheme tends to predict more

surface ozone than the EDDY scheme.

4.2.2 EDDY and ACM2 modeling data comparisons

The pollutant concentrations simulated by CMAQ with two different schemes are

analyzed here. Figure 4.5 shows the comparisons of simulated ground level primary and

secondary pollutants when using the EDDY or ACM2 schemes. Figure 4.6 shows the

corresponding comparisons of vertical profiles.

The EDDY scheme tends to predict large concentrations of primary pollutants (CO, NO_x)

but smaller concentrations of secondary pollutants (O_3) at the surface compared to the

ACM2 scheme (Figure 4.5). One possible reason is that the ACM2 scheme has faster

vertical mixing under the convective boundary layer, leading to enhanced vertical transport

of emitted primary pollutants. However, the EDDY scheme tends to predict smaller O_3

concentration near the surface than the ACM2 scheme, most probably due to more NO_x

($NO+NO_2$) being predicted at surface, leading to increased O_3 titration (Pleim 2009).
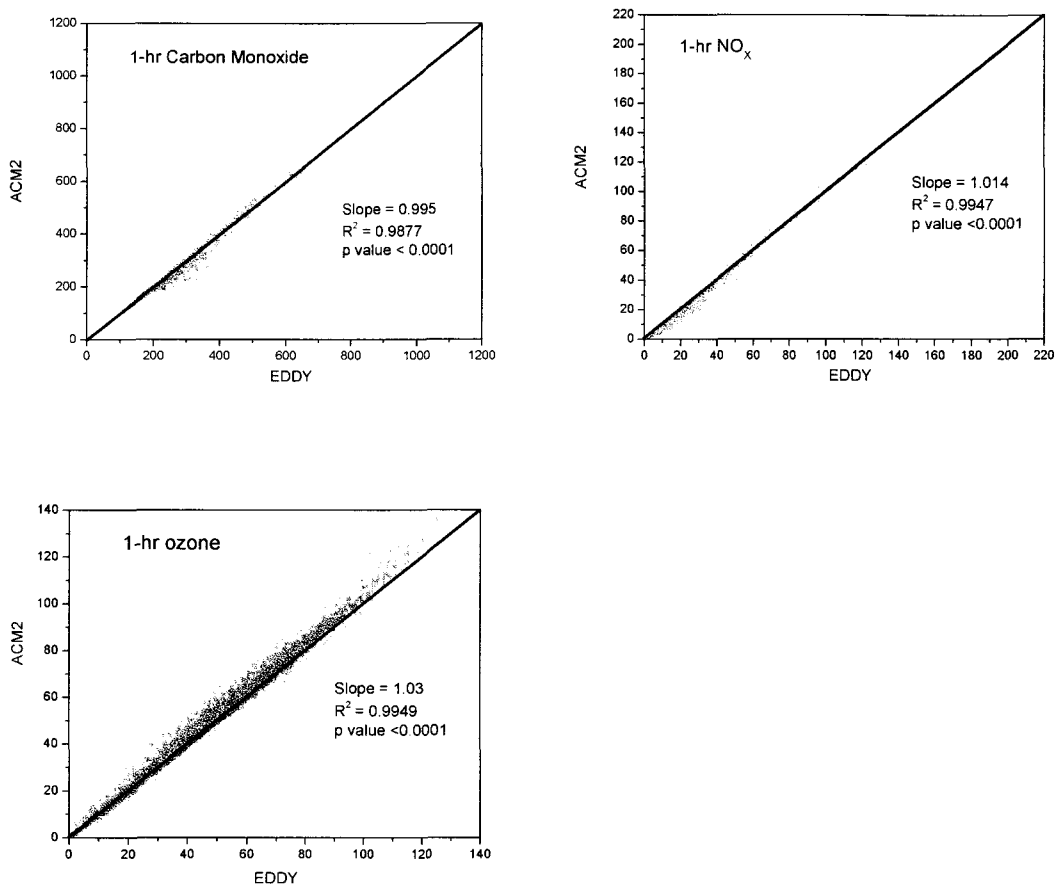
Figure 4.5: Regression between 1-hr average pollutant concentrations for all days in the episode modeled using EDDY and those modeled using ACM2.
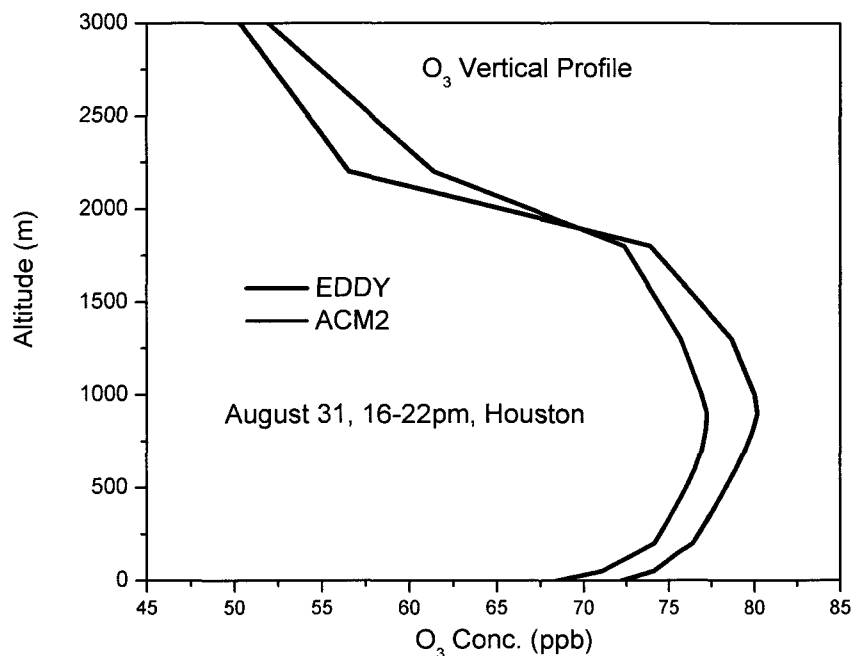
Figure 4.6 shows the comparisons of vertical profiles produced by the EDDY and ACM2 schemes for NO_x and O_3 mixing ratios averaged over 4pm to 10pm on August 31st, 2006, in Houston. The ACM2 scheme has a more well-mixed profile under a convective PBL than EDDY because ACM2 considers turbulent diffusion under the PBL, making mixing more rapid than EDDY. The EDDY scheme has a deeper mixing depth than ACM2 because the EDDY scheme uses a quadratic height function to calculate eddy diffusivity, while the

ACM2 scheme uses a cubic height function (Pleim, 2009). In addition, EDDY tends to

predict more NO_x near the surface, but less NO_x aloft than ACM2, most probably due to the

faster upward mixing feature in ACM2 scheme causing smaller mixing ratios at surface but

larger mixing ratios aloft. Again, the ACM2 scheme produces more O_3 than EDDY scheme

under the PBL. In addition to the NO_x titration reason discussed above, another possible

reason is that NO_x in ACM2 is better mixed than EDDY under the PBL, making more

ozone yields.
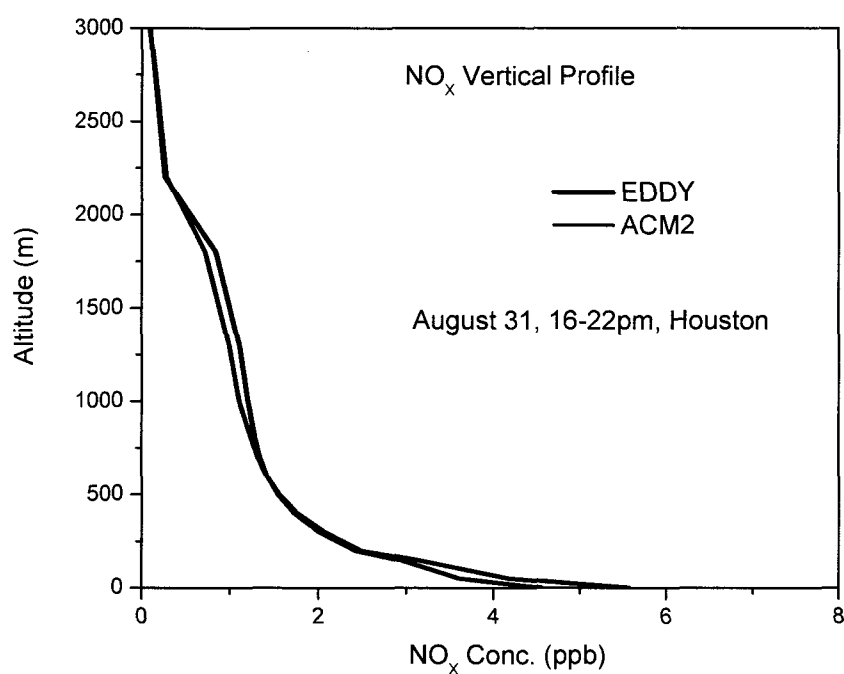
Figure 4.6: Vertical profiles produced by the EDDY and ACM2 schemes for NO_x (top) and

O_3 (bottom) mixing ratios averaged over 4pm to 10pm on August 31st, 2006 in Houston.

4.2.3 Comparison with surface measurements

The comparisons of modeled O_3, NO_x and CO concentration with surface measurement

data are presented in this section. Figure 4.7 shows the scatter plots of modeled ground

level 1-hr average ozone versus measured 1-hr surface ozone for the whole episode at all

ground measurement sites shown in Figure 3.3, in the domain.
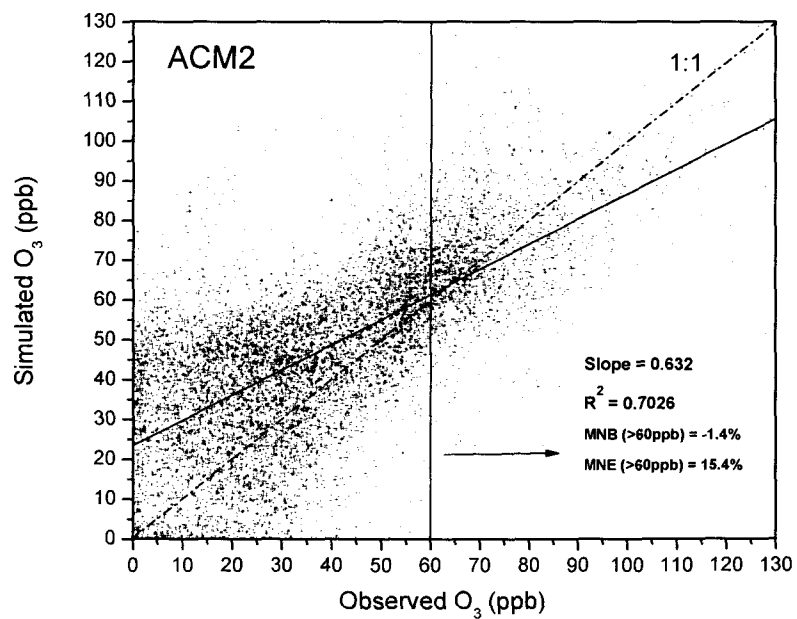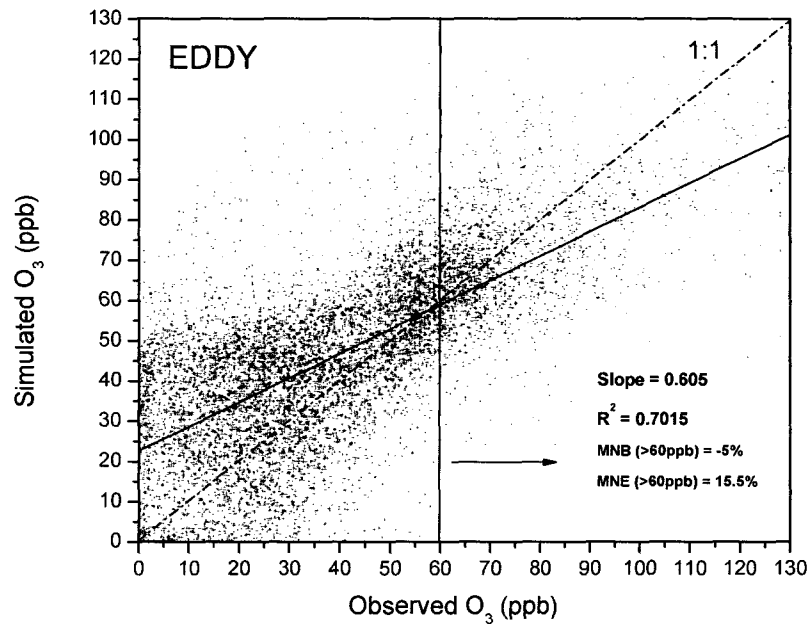
Figure 4.7: Scatter diagram of modeled 1-hr O₃ versus observed data, (top) EDDY, (bottom) ACM2.

Both vertical diffusion schemes simulated O_3 quite well generally, as correlation

coefficients approach 0.7 (Figure 4.7). However, Figure 4.7 shows that the model

performed weakly in predicting both very small and very large O_3 concentration in this

case. The mean normalized bias (MNB) and mean normalized error (MNE) also have been

calculated for the O_3 concentration value greater than 60 ppb. It shows that the simulation
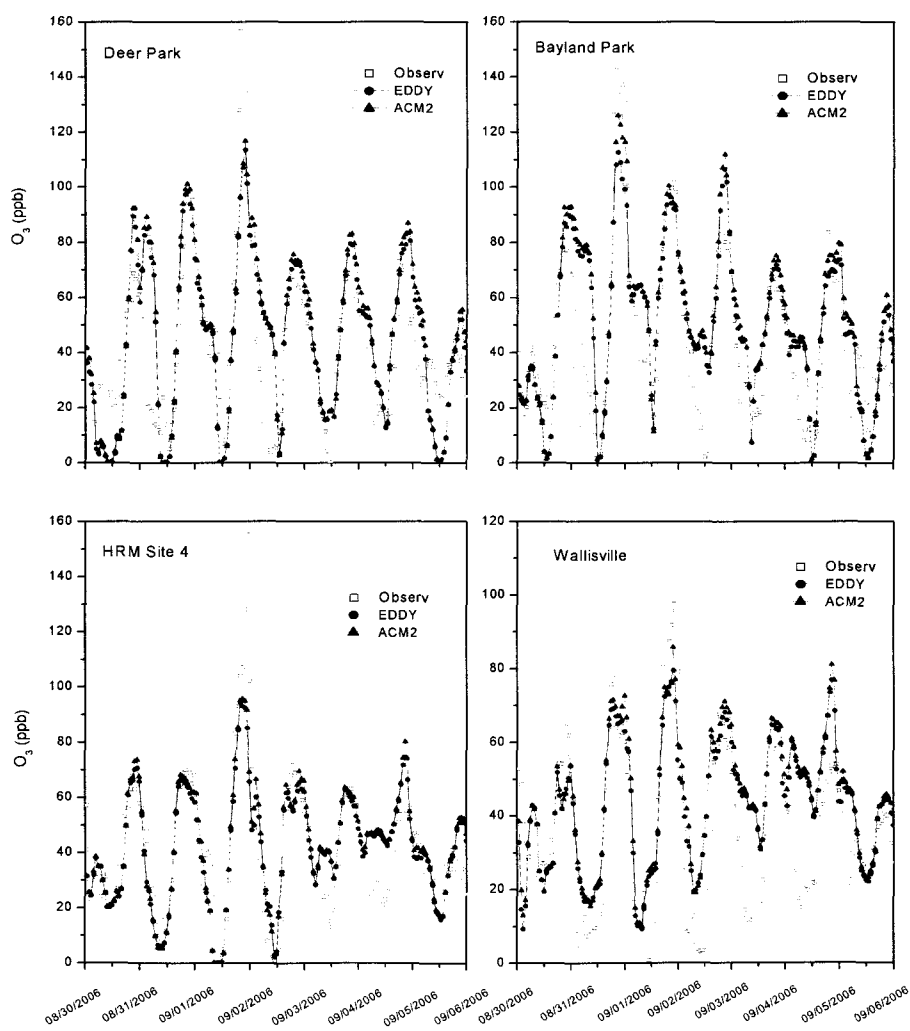
results from ACM2 and EDDY are virtually identical.

Figure 4.8: Time series (UTC) of predicted and observed ozone at four sites.

The temporal profiles of 1-hr average predicted and observed ozone at four measurement

sites which have very high observed ozone concentration and inside the model domain,

over seven days episode are shown in Figure 4.8, which indicate that the model mostly

underpredicted the large daytime ozone concentrations (later afternoon) and overpredicted

small nighttime ozone concentrations. The ACM2 scheme predicts larger ozone

concentrations than the EDDY scheme, but the difference between the two schemes is

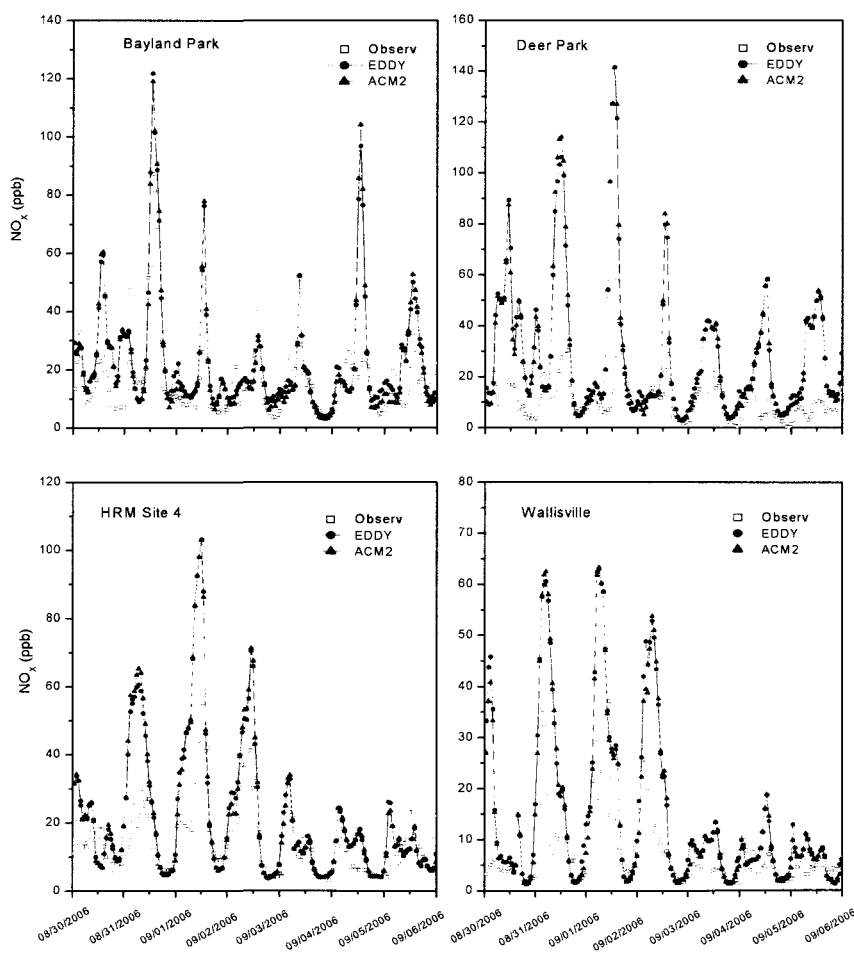small, averaging 2ppb and with a maximum value of 6ppb.

Figure 4.9: Time series (UTC) of predicted and observed NO_x at four sites.

The 1-hr average predicted and observed NO_x ($NO+NO_2$) at four measurement sites

inside the model domain over seven days are shown in Figure 4.9, which indicate that both

schemes simulated small NO_x concentration at nighttime very well, but significantly

overpredicted peak daytime NO_x (early morning) at most sites. The ACM2 scheme

predicts smaller NO_x concentration than the EDDY scheme, but the difference between

two schemes is small, averaging 1ppb, with a maximum value of 3ppb.
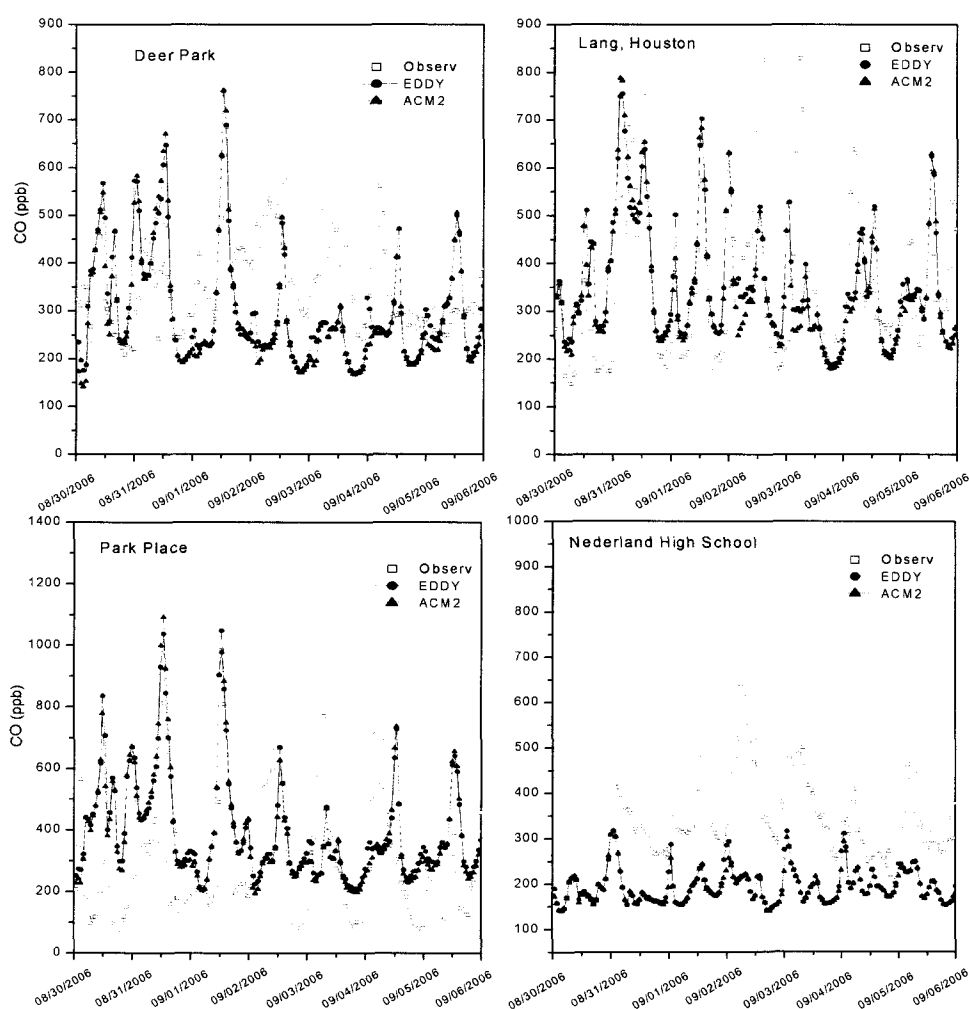

Figure 4.10: Time series (UTC) of predicted and observed CO at four sites.

Due to data availability, four measurement sites inside the model domain are chosen for the 1-hr average predicted and observed CO comparison (Figure 4.10), which indicates that both schemes performed poorly in simulating CO concentration. It shows that CO was significantly underpredicted at Deer Park and Nederland High School sites and that the simulations did not capture the largest and the smallest CO concentration at the Park Place and Lang sites. The ACM2 scheme predicts smaller CO concentration than the EDDY scheme, and the difference of simulated values between two schemes averages 30ppb, with a maximum value of 100ppb.

4.2.4 Comparison with ozonesonde measurements

Ten ozonesonde measurements made within the model domain were chosen for the vertical profiles comparisons. The data were obtained from Intercontinental Transport Experiment Ozonesonde Network Study 2006 (ION-6) campaign (Parrish et al., 2009). Six ozonesondes were launched at the University of Houston (UH), and four ozonesondes were launched from the NOAA R.H Brown vessel. Figure 4.11a shows measured and modeled data for six ozonesondes launched from UH. Figure 4.11b shows the corresponding information for the four ozonesondes launched from R.H Brown vessel.
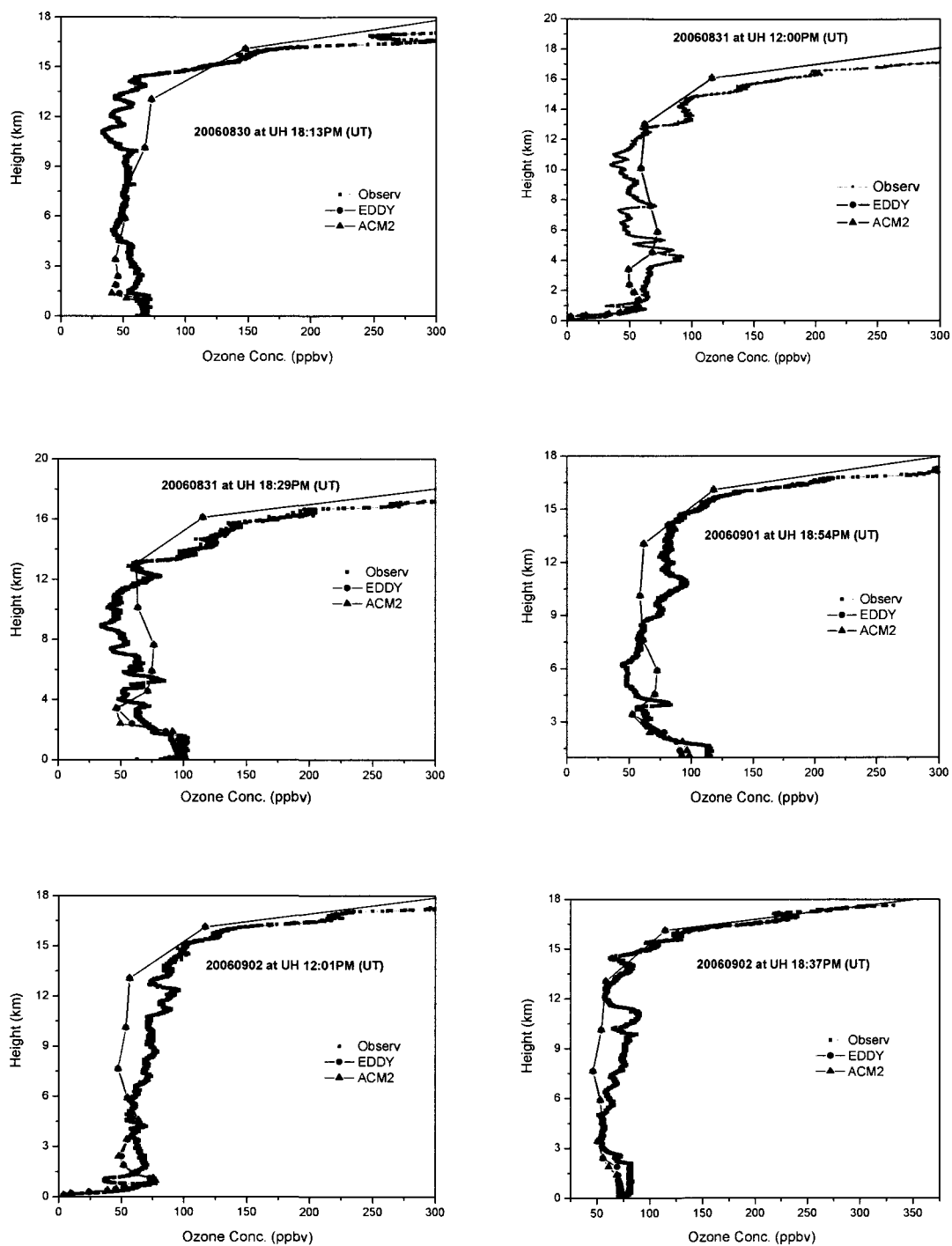
Figure 4.11a: Measured and modeled data for ozonesondes launched from University of
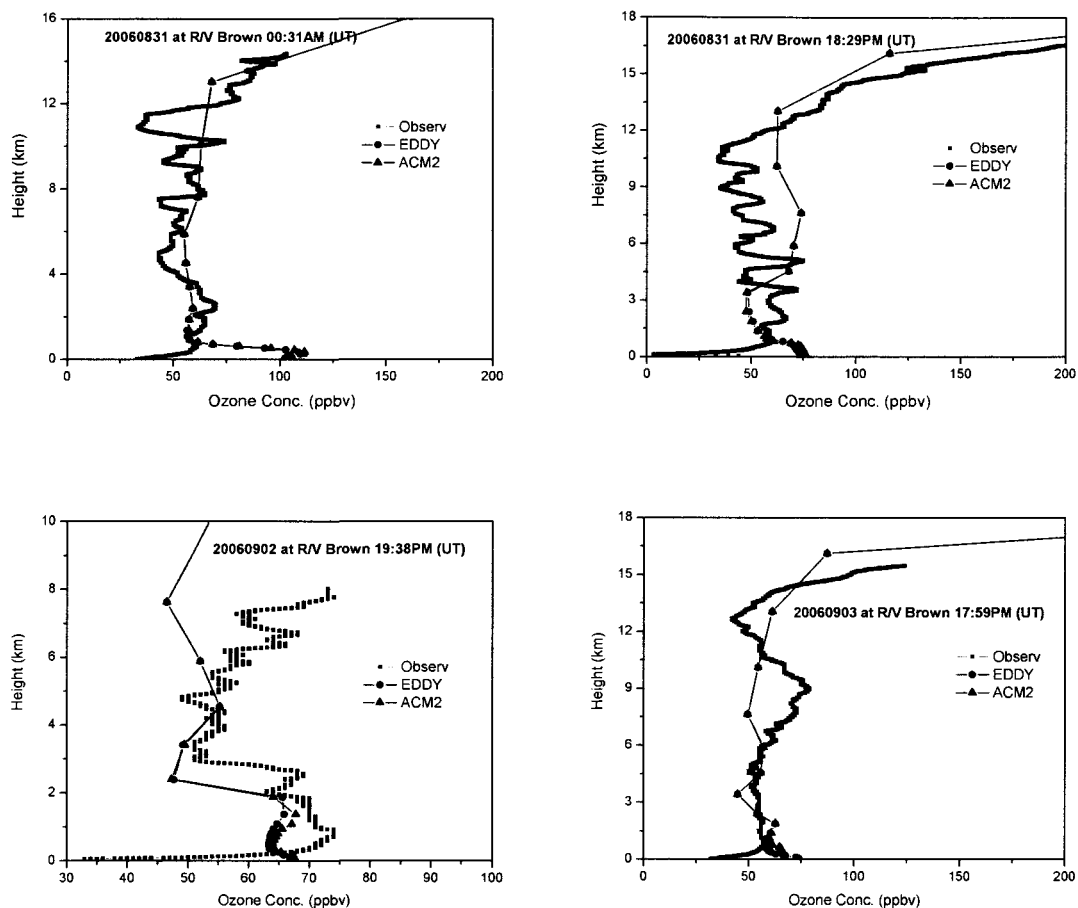
Houston.

Figure 4.11b: Measured and modeled data for ozonesondes launched from R.H Brown.

Figure 4.11 shows that both vertical diffusion schemes in the model were capable of capturing the qualitative features of ozone vertical profiles measured by ozonesondes in each case. The ACM2 scheme continuously shows larger predicted ozone mixing ratios under the PBL, and the simulated vertical profiles by two schemes do not have significant difference above 3km. In Figure 4.11b, there are large discrepancies between modeled and observed profiles in the R.H Brown ozonesonde data. One possible reason is surface losses caused by measurement uncertainty (G.A. Morris, personal communication, 2009). In

addition, sudden increase of measured ozone concentration under the PBL shown in Figure

4.11a on August 31st and September 1st likely resulted from background ozone transported

from both the continental and the sea (Rappengluck et al. 2008).

4.2.5 Comparison with regional aircraft measurements

Aircraft measurements conducted by the NOAA WP-3D aircraft (Parrish et al., 2009)

also are compared to modeling results. A part of the P-3 aircraft track measurement data

collected at 3:00pm (CST) on August 31st, 2006, (Figure 4.12) from 500 meters to 3000

meters height were used for comparison. The chemical species O_3, NO, NO_2, and CO

measured by aircraft during 20 minute periods from 3:00pm to 4:00pm with 1 second

resolution were compared with the extracted 1-hr average modeling data from each grid

cell that the aircraft passed through at the corresponding time.
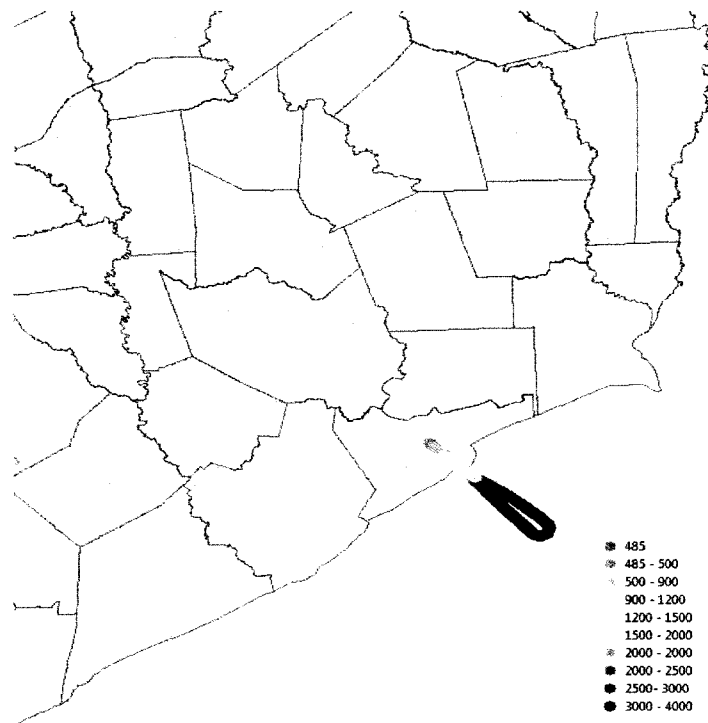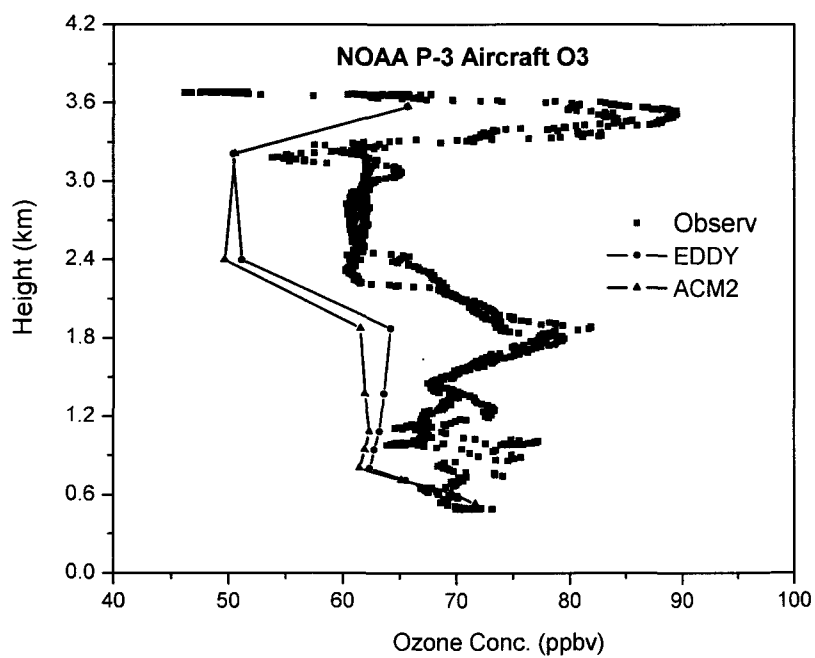
Figure 4.12: P-3 Aircraft track at 3:00pm on August 31st, 2006. (Color represents
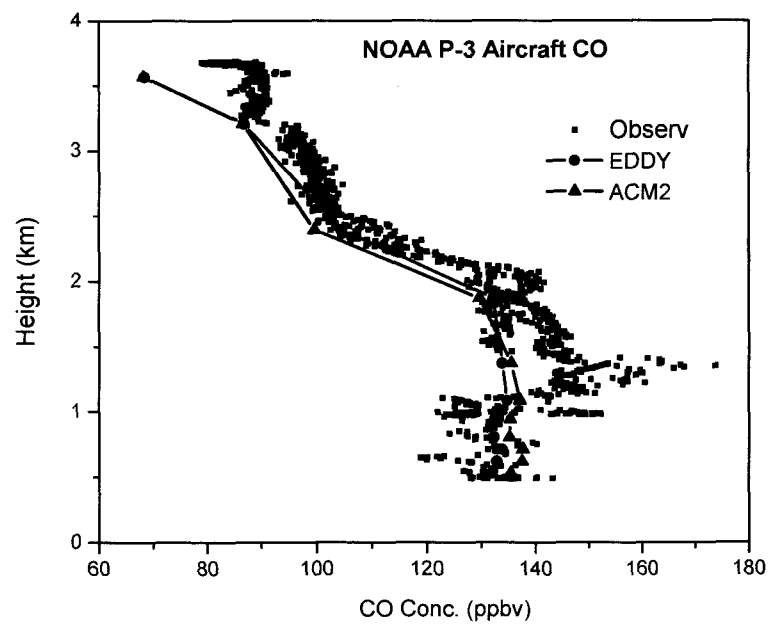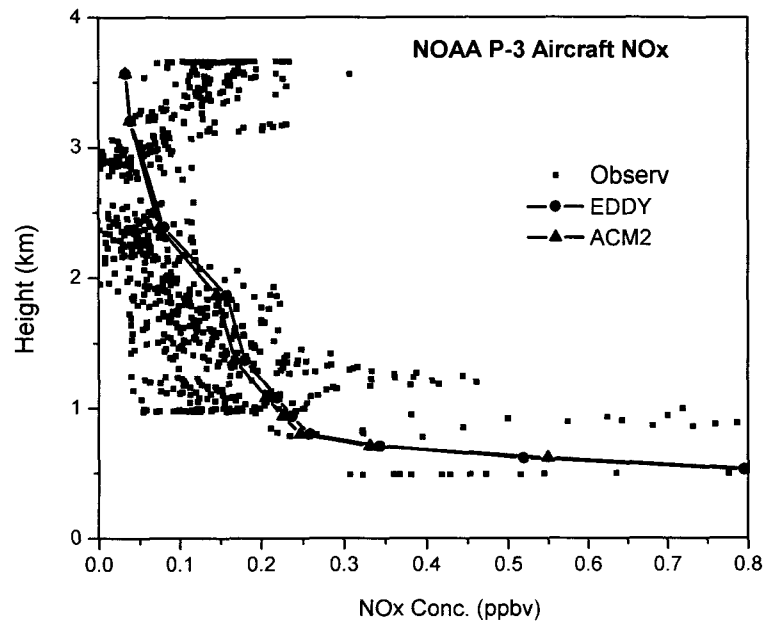
different altitude)

Figure 4.13: Modeled and P-3 aircraft data for O_3 (top), NO_x ($NO+NO_2$) (middle), and CO (bottom).

The modeled vertical profiles from both schemes virtually matched the observed ones quite well, especially for NO_x and CO modeling (Figure 4.13). The ACM2 scheme predicted larger concentrations of pollutant from 500m to the height of the PBL and predicted smaller concentrations of pollutant from the height of the PBL to 3km, and above 3km, there is no significant difference for the predicted concentrations between the EDDY and ACM2 schemes. The results are quite similar to those in Figure 4.6.

The discrepancies between modeled and observed data are much more significant than the differences between predicted concentrations using the two different vertical mixing schemes. Hence, the discrepancy between modeled and observed data cannot be rectified by changing the vertical mixing scheme. It is also not possible to determine which scheme is better on the basis of comparing modeling and observations.

4.3 Sensitivity analysis

The results of the analysis to determine the sensitivity of ozone to model input parameters are presented here. The first and second order ozone sensitivities to dry deposition velocity, to anthropogenic NO_x, and to anthropogenic VOC and the cross sensitivity of ozone to anthropogenic NO_x and anthropogenic VOC emission with dry deposition velocity were calculated by CMAQ-DDM. The DDM results are illustrated below.

$\partial[O_3] / \partial \in_{V_{depall}}$ (ozone sensitivity to dry deposition velocity of all species)
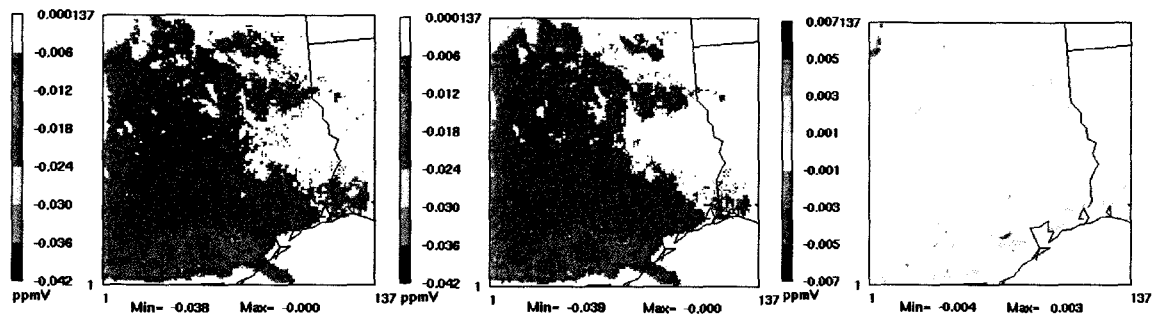
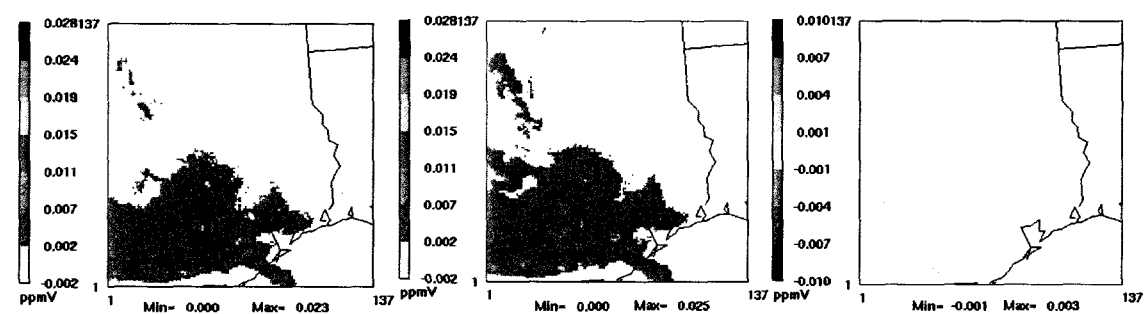$\partial^2[O_3] / \partial \in_{V_{depall}}^2$ (second order ozone sensitivity to dry deposition velocity)

Figure 4.14a: Ozone sensitivity to dry deposition velcoity at 4:00pm CST on August 31st, 2006. (left) EDDY, (middle) ACM2, (right) difference (ACM2-EDDY)
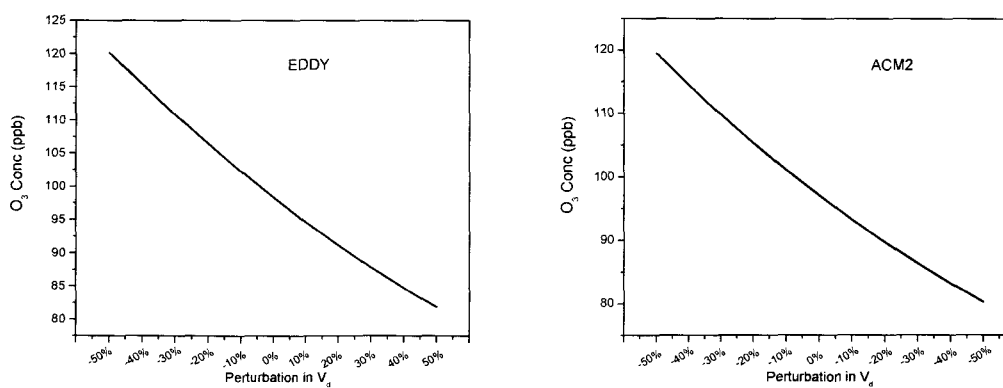

Figure 4.14b: Responsiveness of ozone to dry deposition velocity at 4:00pm CST.

The first order ozone sensitivity to dry deposition velocity (Figure 4.14a) is negative

because enhanced dry deposition velocity decreases atmospheric concentrations. The

second order ozone sensitivity to dry deposition velocity (Figure 4.14a) is positive because

of the convex response of ozone to dry deposition velocity at that time (Figure 4.14b). It

also indicates that the nonlinearity in ozone response caused by dry deposition velocity is
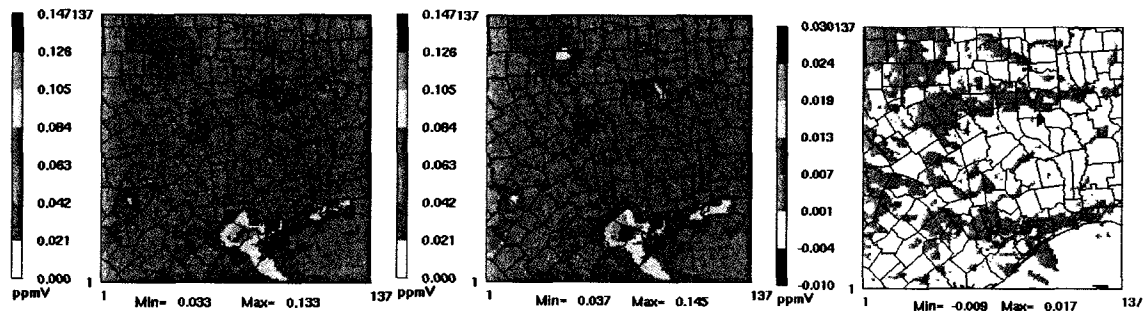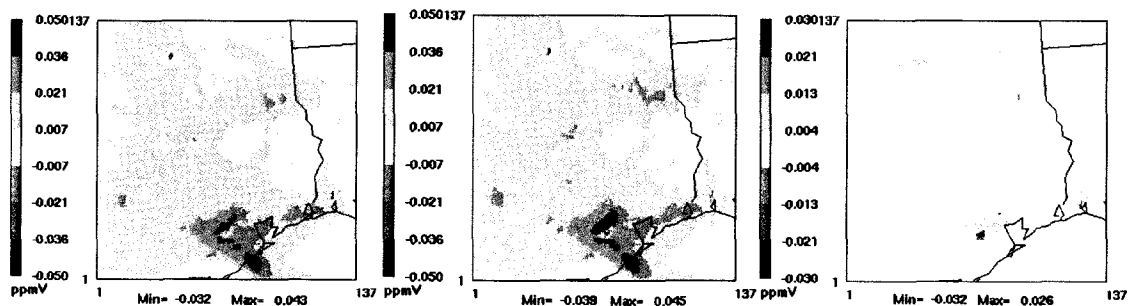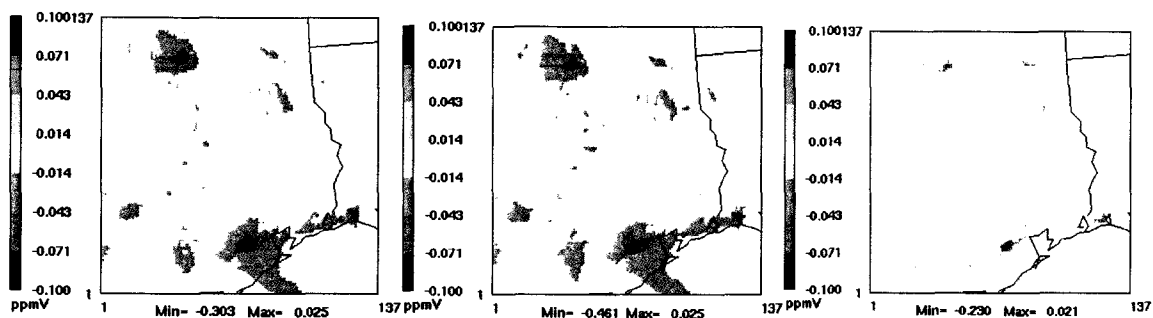
small.

Figure 4.15a: Ozone concentration at peak time (4:00PM CST), August 31st, 2006. (left)

EDDY scheme; (middle) ACM2 scheme; (right) Difference (ACM2-EDDY)

$\partial [O_3] / \partial \in_{E,ANO_x}$ (ozone sensitivity to anthropogenic NO_x emission)

$\partial^2 [O_3] / \partial \in^2_{E,NO_x}$ (second order ozone sensitivity to anthropogenic NOx emission)

$\partial [O_3] / \partial \in_{E,AVOC}$ (ozone sensitivity to anthropogenic VOC emission)

$\partial^2 [O_3] / \partial \in^2_{E,AVOC}$ (second order ozone sensitivity to anthropogenic VOC emission)

Figure 4.15b: Ozone sensitivities to anthropogenic NOx and VOC at peak time (4:00PM

CST), August 31st, 2006. (left) EDDY scheme; (middle) ACM2 scheme; (right) Difference

(ACM2-EDDY)

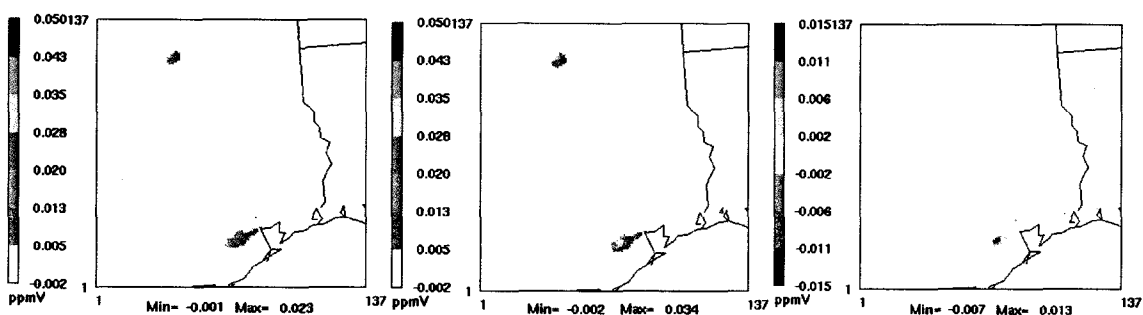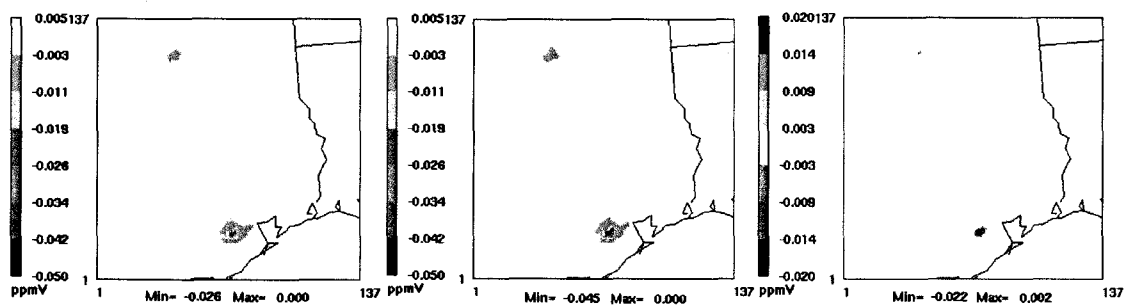The maximum ozone concentration occurs downwind of Houston in Fort Bend County at

4:00pm (Figure 4.15a). From the Figure 4.15b, the first order ozone sensitivity to

anthropogenic NO_x, $\partial[O_3]/\partial \in_{E.\Lambda NO_x}$, is negative indicating that VOC control will be

effective for ozone reduction in that area and at that time (how to distinct control region has

already been discussed in Chapter Three). The response of ozone calculated from the

ACM2 scheme (Figure 4.15b) seems to be more sensitive to anthropogenic NO_x and VOC

than the EDDY scheme, indicating that different emission controls may be designed as

different vertical diffusion schemes are used. Compared with the first order sensitivities,

the second order sensitivities become more localized. The second order ozone sensitivity to

anthropogenic NO_x, $\partial^2[O_3]/\partial \in^2_{E.\Lambda NO_x}$, shows predominantly negative value indicating large

nonlinear and concave response of ozone. The second order ozone sensitivity to

anthropogenic VOC, $\partial^2[O_3]/\partial \in^2_{E.\Lambda VOC}$, shows a much smaller magnitude than

$\partial^2[O_3]/\partial \in^2_{E.\Lambda NO_x}$ indicating less degree of nonlinearity in ozone response (Hakami et al.,

2004; Cohan et al., 2005).

$$\frac{\partial}{\partial \epsilon_{V_{depall}}}(\frac{\partial [O_3]}{\partial \epsilon_{E_{.ANO_x}}})$$
$$\frac{\partial}{\partial \epsilon_{V_{depall}}}(\frac{\partial [O_3]}{\partial \epsilon_{E_{.AVOC}}})$$
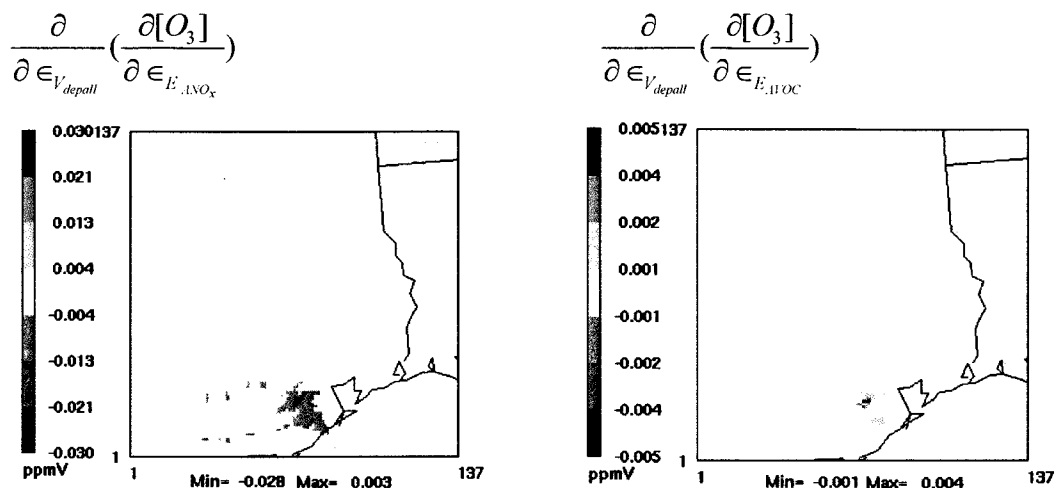

Figure 4.16: Cross sensitivity coefficients of ozone to dry deposition velocity and anthropogenic NO_x (left), and anthropogenic VOC (right) at 4:00pm on August 31st, 2006.

The cross sensitivity coefficients calculated by the EDDY scheme are shown in Figure 4.16. The result from the ACM2 scheme is not shown because it was not reliable as discussed in Section 4.1. The cross sensitivity of ozone to anthropogenic NO_x emission and dry deposition velocity shows negative value at that time, indicating that if dry deposition velocities for all species are underpredicted, ozone becomes more sensitive to ANO_x. In contrast, the cross sensitivity of ozone to anthropogenic VOC emission and dry deposition velocity shows positive value at that time, indicating that if dry deposition velocities for all species are underpredicted, ozone becomes less sensitive to AVOC. The magnitude of cross sensitivity coefficients are much smaller than the first order and second order sensitivities as showed above, but these terms will become much important in uncertainty analysis as discussed below.

4.4 Uncertainty analysis in dry deposition velocity

As described in Chapter Two, recent studies indicate that the uncertainty in dry

deposition velocities could be as large as ±30% (Wesely and Hicks 2000). Therefore, it is

essential to analyze the impact of uncertainty in dry deposition velocity on model

performance. The effects of uncertainty in dry deposition velocity on model simulation and

on emission control are discussed here.

4.4.1 Effect on model simulations

Based on equation 3.15, the effect of ±30% uncertainty in dry deposition velocity for

all depositing species on model simulation results can be quantified. The effects of

uncertainty in dry deposition velocities on surface ozone modeling and on ozone, sulfur

dioxide, and nitric acid simulated vertical profiles are evaluated in Figure 4.17 and 4.18,

respectively.
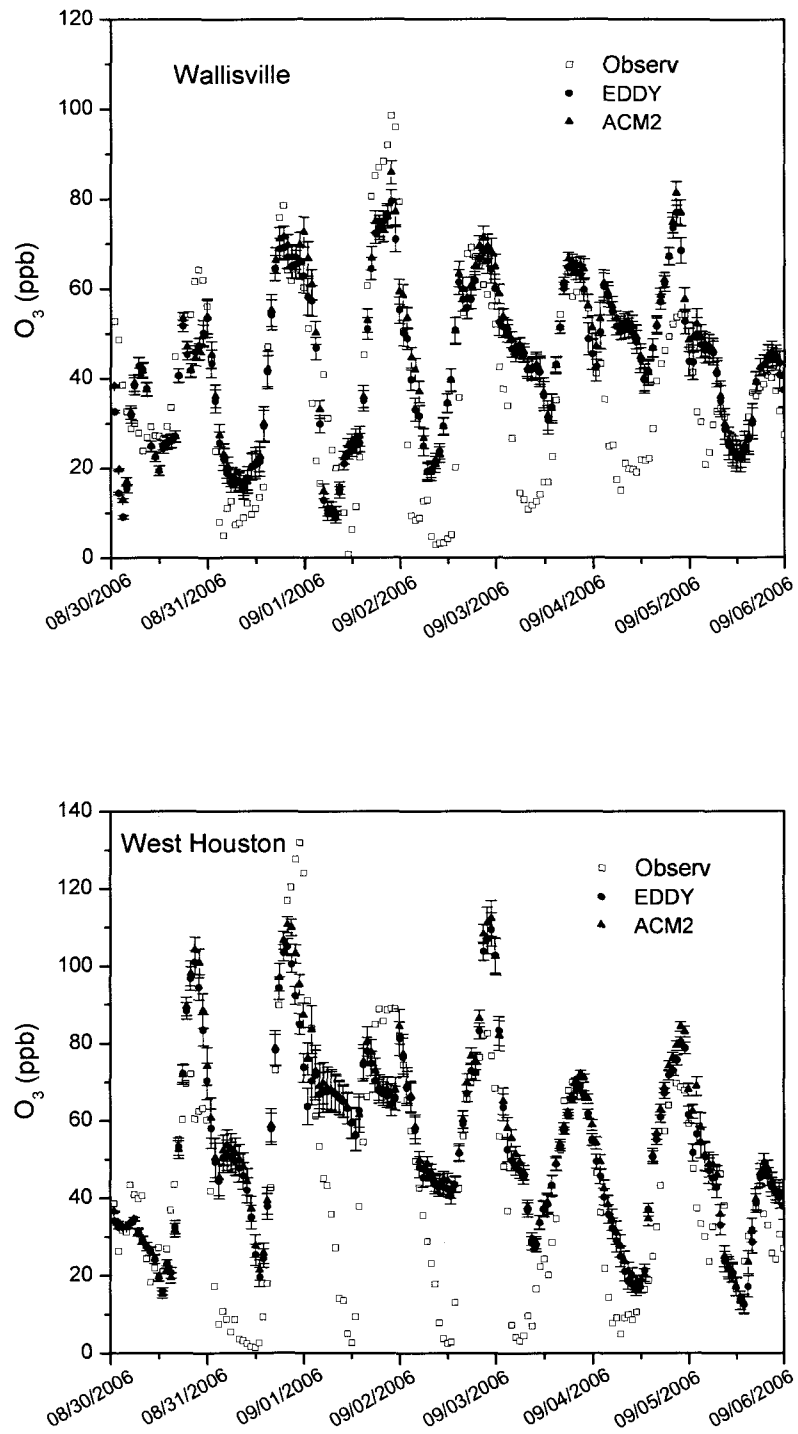
Figure 4.17: Effect of uncertainty in O_3 dry deposition velocity on surface O_3 modeling.

As discussed above, when the dry deposition velocities decrease, the species

concentrations increase. The higher and lower error bars in Figure 4.17 represent ozone

concentration adjusted by -30% and +30% uncertainties in dry deposition velocity. The

results indicate that compared to the discrepancy between modeled and observed results,

the effect of uncertainty in dry deposition velocity on simulated surface O_3 is small.

Figure 4.18a: Effect of uncertainty in dry deposition velocity on O_3 vertical profile.

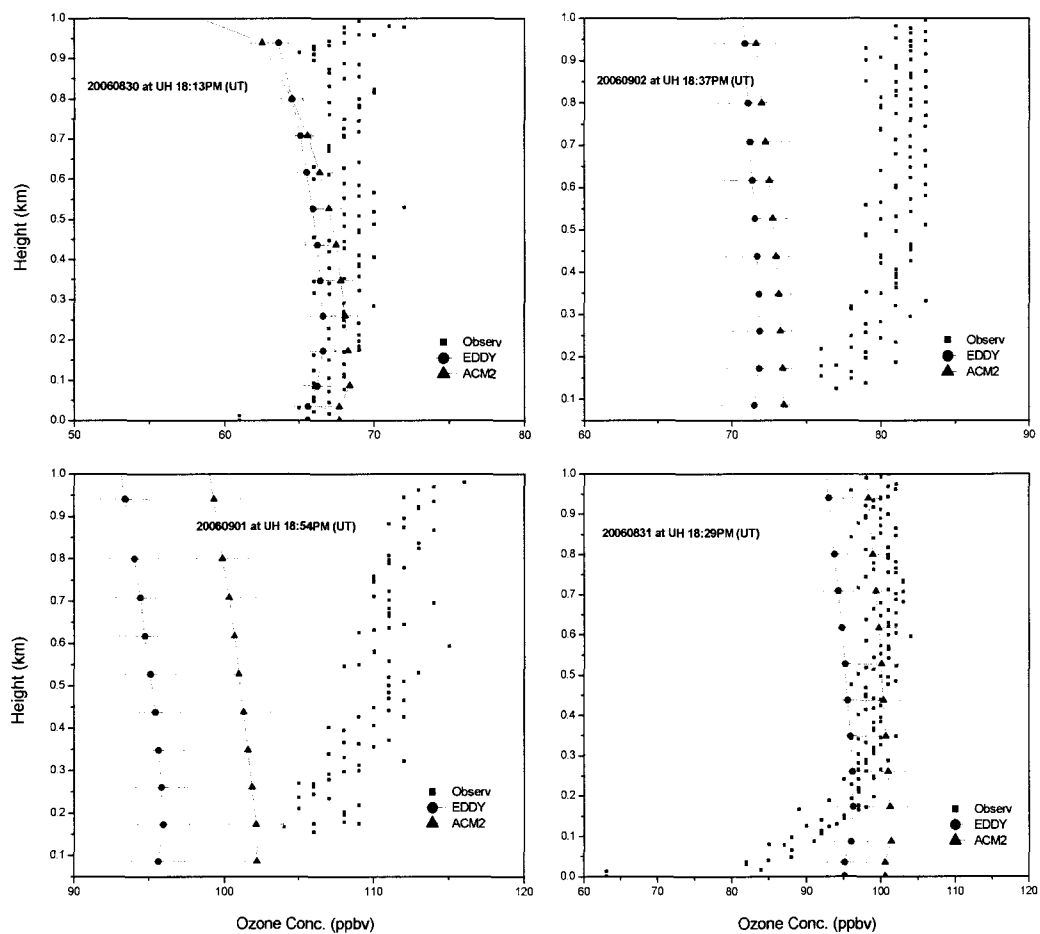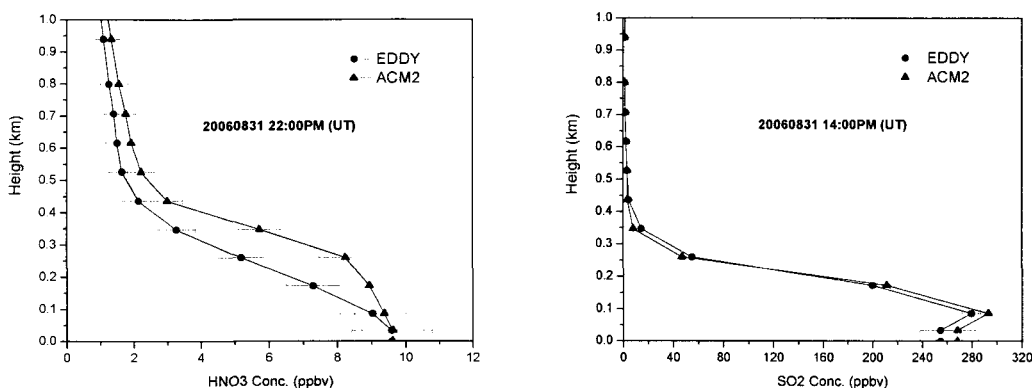**Figure 4.18b:** Effects of uncertainty in dry deposition velocities on HNO_3 (left) and SO_2 (right) vertical profiles.

However, Figure 4.18a illustrates that considering the uncertainty in O_3 dry deposition velocity may make the modeled O_3 vertical profile closer to the observed values after adjusting the profile, but the uncertainty in O_3 dry deposition velocity is certainly not the driving force causing the discrepancy between modeled and observed profile in this case. However, Figure 4.18b demonstrates that for species with larger dry deposition velocity, such as HNO_3 or SO_2, the effect of uncertainty in dry deposition velocity on modeled results at lower layer is more significant.

4.4.2 Effect on emission control strategy

As discussed in chapter 3, uncertainties in inputs such as dry deposition velocities can influence the sensitivity of ozone to NO_x and VOC emission controls. Based on the equations 3.19 and 3.20 derived in chapter 3, the effect of dry deposition velocity on

emission control strategy can be evaluated. Figure 4.19 shows the effect of uncertainty in

choosing different vertical mixing schemes on both NO_x and VOC emission controls, and

Figure 4.20 shows the effect of uncertainty in dry deposition velocity on both NO_x and

VOC emission controls, at the Bayland Park and Deer Park ozone monitoring sites in

Houston. The Bayland Park site is in a suburban area in the west of Houston, and the Deer

Park site is in the Ship Channel area in the east of Houston. Both sites have predicted future

ozone designed values that exceed 84 ppb (TCEQ 2009). The average hourly sensitivity

coefficients of ozone to NO_x and VOC emission were calculated for the 7-day episode in

this case.
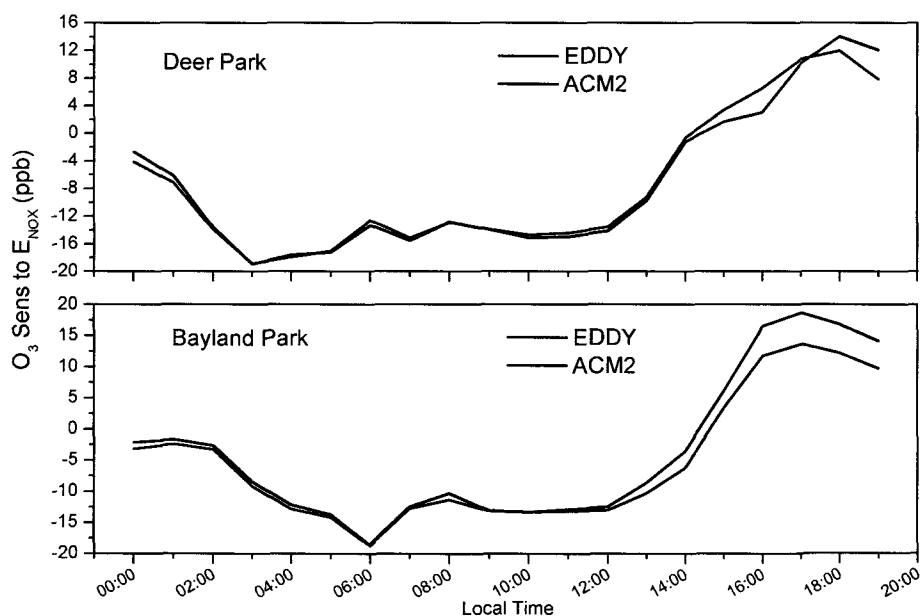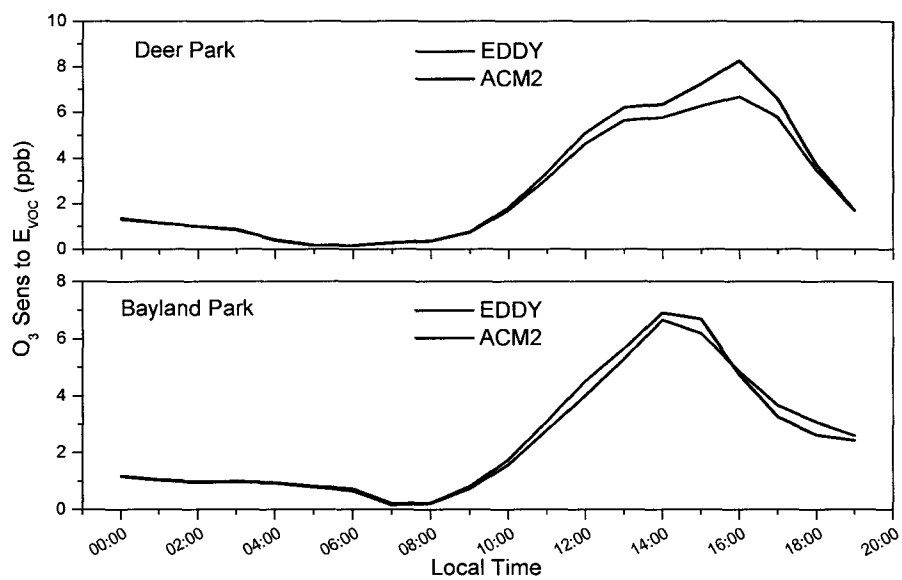
Figure 4.19: Effects of uncertainty in different vertical mixing schemes on O_3 sensitivity

to anthropogenic NO_x (top) and to anthropogenic VOC (bottom) emissions.
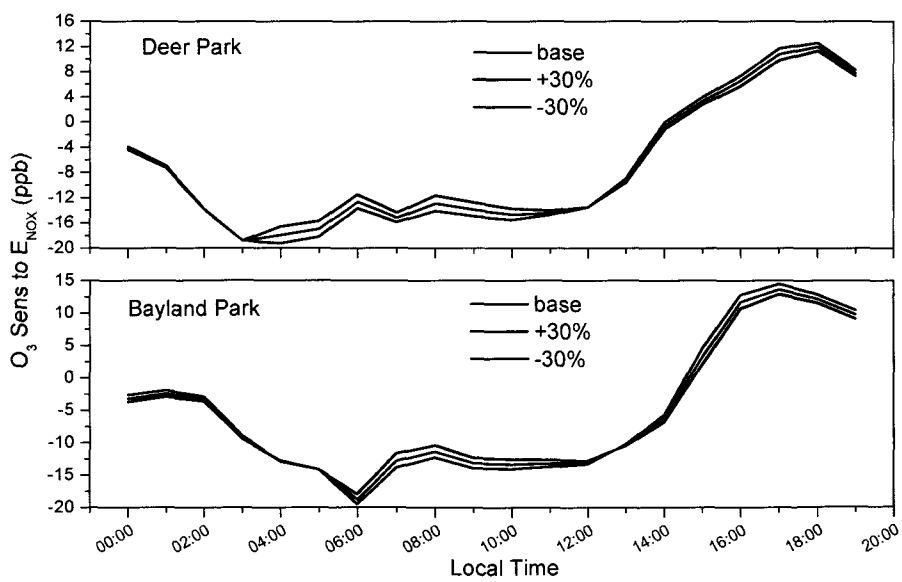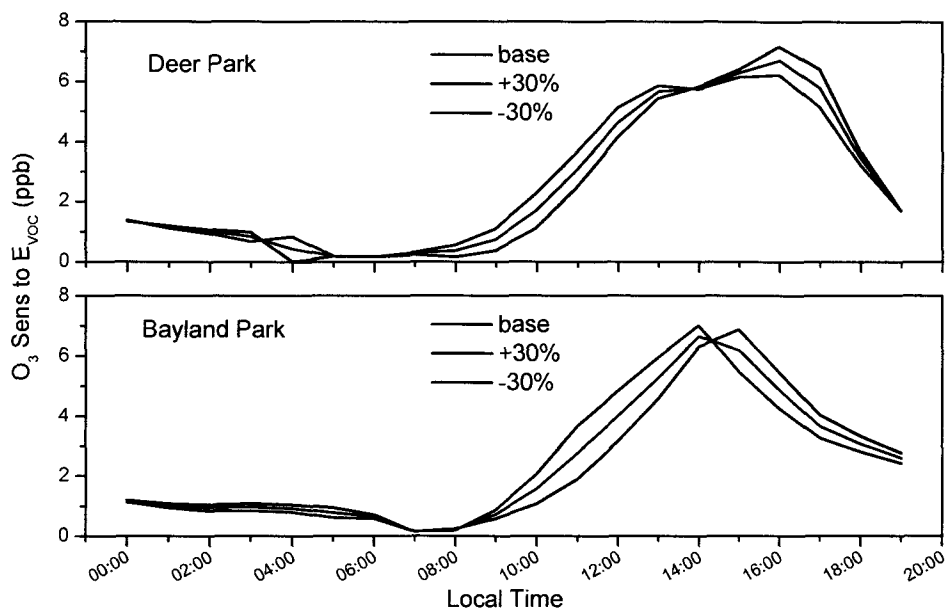
Figure 4.20: Effects of uncertainty in dry deposition velocity on O_3 sensitivity to

anthropogenic NO_x (top) and to anthropogenic VOC (bottom) emissions.

Table 4.2: Effects of uncertainties on emission control (Deer Park)

Emission Control	EDDY scheme	ACM2 scheme	EDDY with Vd +30%	EDDY with Vd -30%
S^1 (O_3 to NO_x) (ppb)	-3.97	-5.05	-4.23	-3.71
S^1 (O_3 to VOC) (ppb)	4.96	5.62	4.88	5.03

Note: averaged over 10am-5pm (local time)

Table 4.3: Effects of uncertainties on emission control (Bayland Park)

Emission Control	EDDY scheme	ACM2 scheme	EDDY with Vd +30%	EDDY with Vd -30%
S^1 (O_3 to NO_x) (ppb)	-3.4	-1.2	-3.72	-3.17
S^1 (O_3 to VOC) (ppb)	4.37	4.57	4.18	4.57

Note: averaged over 10am-5pm (local time)

The first order sensitivity coefficients of ozone to anthropogenic NO_x and

anthropogenic VOC used here can be considered as emission control factors. For example,

if the first order ozone sensitivity to anthropogenic NO_x equals to 12ppb, then 1.2ppb

ozone can be reduced by controlling 10% anthropogenic NO_x emission. Figure 4.19

indicates that the ANO_x and AVOC emission controls may vary significantly by using

different vertical diffusion schemes, especially from 10am to 5pm. At both sites, generally,

the ozone sensitivities calculated with the ACM2 scheme to anthropogenic NO_x and to

anthropogenic VOC are more sensitive than those using the EDDY scheme (Table 4.2, 4.3),

reflecting that at certain times, controlling the same amount of ANO_x and AVOC emissions

may have less effect on predicted ozone reductions when the EDDY scheme is used in the

model.

Figure 4.20 also indicates that the response of ozone to ANO_x and AVOC may vary

temporally due to the uncertainty in dry deposition velocity. The average values of

responses of ozone to ANO_x and AVOC with ±30% uncertainty in dry deposition velocity

showed in Table 4.2 and 4.3 indicate that, at the Bayland Park and Deer Park sites, the

effect of uncertainty in dry deposition velocity on AVOC emission control is smaller than

that on ANO_x emission control. The variation in ozone response to ANO_x could reach

approximately 14% at Deer Park, and 17% at Bayland Park, and the variation in ozone

response to AVOC could reach approximately 3% at Deer Park, and 9% at Bayland Park.

References

Cohan D.S., Hakami, A., Hu, YT., and Russell, A.G. (2005) Nonlinear response of ozone to emissions: Source apportionment and sensitivity analysis. *Environmental Science and Technology.* 39, 6739-6748.

Hakami, A., Odman, M.T., and Russell, A.G. (2003) High-order, direct sensitivity analysis of multidimensional air quality models. *Environmental Science and Technology.* 37, 2442-2452.

Hakami, A., Odman, M.T., and Russell, A.G. (2004) Nonlinearity in atmospheric response: A direct sensitivity analysis approach. *Journal of Geophysical Research.* 109, D15303.

Parrish, D.D., Allen, D.T., Bates, T.S., Estes, M., Fehsenfeld, F.C., Feingold, G., Ferrare, R., Hardesty, R.M., Meagher, J.F., Nielsen-Gammon, J.W., Pierce, R.B., Ryserson, T.B., Seinfeld, J.H. and Williams, E.J. (2009) Overview of the second Texas Air Quality Study (TexAQS II) and the Gulf of Mexico Atmosphere Composition and Climate Study (GoMACCS). *Journal of Geophysical Research.* 114, D00F13.

Pleim, J.E. (2006) A new combined local and non-local PBL model for meteorology and air quality modeling. CMAS conference paper. North Carolina.

Rappengluck, B., Perna, R., Zhong, S., and Morris, G.A. (2008) An analysis of the vertical structure of the atmosphere and the upper-level meteorology and their impact on surface ozone levels in Houston, Texas. *Journal of Geophysical Research.* 113, D17315.

TCEQ. *Houston-Galveston-Brazoria Ozone Nonattainment Area.*

(http://www.tceq.state.tx.us/implementation/air/sip/hgb.html#project Accessed on October 1st, 2009)

TCEQ. *Proposed HGB Attainment Demonstration SIP Revision for the 1997 Eight-Hour Ozone Standard.*

(http://www.tceq.state.tx.us/implementation/air/sip/hgb.html#project Accessed on November 23rd, 2009)

Wesely, M.L. and Hicks, B.B. (2000) A review of the current status of knowledge on dry deposition. *Atmospheric Environment.* 34, 2261-2282.

CHAPTER 5

Conclusions and Recommendations

A study on the influence of uncertainties in vertical mixing algorithms on photochemical air quality model was carried out in this thesis. It includes three major parts: model development, model evaluation, and model application. In the model development part, the first and second order of dry deposition velocity and eddy diffusivity sensitivities were implemented into CMAQ-DDM for both EDDY and ACM2 vertical diffusion schemes. In the model evaluation part, the performance of two vertical diffusion schemes was evaluated by comparing with field campaign measurement data. In the model application part, the sensitivity and uncertainty analysis by using the newly implemented code were conducted.

5.1 Conclusions

Seven main conclusions could be drawn from this study:

1. DDM was successfully implemented into ACM2 scheme in CMAQ.

2. The first and second order dry deposition velocity and eddy diffusivity sensitivities were implemented into DDM for both EDDY and ACM2 schemes in CMAQ successfully. Comparison with Brute Force approximation approach shows that the results from two methods are in very good agreement. The cross sensitivity term in ACM2 scheme was not reliable and needs further investigation.

3. Comparisons between modeling results from two schemes indicated that the ACM2 scheme tends to predict larger concentrations of secondary pollutants and smaller concentrations of primary pollutants at the surface compared to the EDDY scheme; the ACM2 scheme has a more well-mixed profile under the PBL, and the EDDY scheme has a deeper mixing depth.

4. Based on comparisons between modeled and observed data, both schemes performed well in simulating surface ozone concentration but performed poorly in simulating surface NO_x and CO concentrations. They both are capable of capturing the qualitative features of vertical profiles measured by ozonesonde and aircraft. However, at the surface level, the model performed weakly in simulating the very large and very small pollutant concentrations in this case. The discrepancies between modeled and observed data are much more significant than the differences of predicted concentrations between the two vertical mixing schemes. Hence, the discrepancy between modeled and observed data cannot be explained by changing the vertical mixing schemes. It is also not possible to determine which scheme is better on the basis of comparing modeled and observed data.

5. Sensitivity analysis results show that the chemical processes dominate the nonlinearity in the ozone responsiveness and that the largest nonlinear responsiveness of ozone was produced by anthropogenic NO_x. The responsiveness of ozone to dry deposition velocity and to anthropogenic VOC is less nonlinear than that to the anthropogenic

NO_x emission.

6. The effect of uncertainty in dry deposition velocities on ozone simulation results is small compared to the discrepancy between modeled and observed O_3 concentrations in this case. It may have significant impact on the modeling of pollutants with large dry deposition velocity, such as HNO_3 and SO_2.

7. The uncertainty in dry deposition velocity may cause as large as 60% variation in responsiveness of ozone to emission control. Different vertical diffusion schemes could have even more impact on emission control strategy.

5.2 Recommendations for future work

A few recommendations are suggested for future work.

1. As mentioned in Chapter Four, the newly implemented DDM code for calculating dry deposition velocity and eddy diffusivity sensitivities only had accurate results in fine resolution model grids (less than 8km) with convective cloud process turned off. Hence, the convective cloud process in the CMAQ-DDM model needs to be improved for better accuracy in DDM calculation of dry deposition velocity and eddy diffusivity sensitivities.

2. Further investigations and evaluations are needed for the second order sensitivity coefficients of dry deposition velocity calculations in the ACM2 scheme. The second order term for eddy diffusivity also needs to be tested and evaluated.

3. As mentioned in Chapter Three, the uncertainty analysis in eddy diffusivity was not

   performed in this study because a model inconsistency error between MM5 and CMAQ

   may occur in the simulation. Therefore, the sensitivity code also may need to be

   implemented into the meteorological model in order to investigate the effect of

   uncertainty in eddy diffusivity on model performance more realistically.

4. The evaluations of the uncertainty in choosing different vertical diffusion schemes and

   in dry deposition velocity on emission controls were only performed for two sites and

   the results are different. Hence, more evaluations need to be conducted. For example,

   more sites under different control regions can be investigated, including considering

   the effect on 8-hr ozone control strategy.

5. The results from this study showed that the uncertainties in dry deposition velocity and

   eddy diffusivity in the simulations cannot be ignored. Hence, the inverse modeling

   technique could be used in the future work to adjust the dry deposition velocity and

   eddy diffusivity in the simulation. For example, we can use the calculated sensitivity

   coefficients of dry deposition velocity and eddy diffusivity by DDM in the inverse

   modeling framework to minimize the difference between modeled and observed data,

   and therefore to optimize the input dry deposition velocity and eddy diffusivity values.