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IMPLEMENTING THE DECOUPLED DIRECT METHOD (DDM) AND PROCESS ANALYSIS (PA) FOR PARTICULATE MATTER IN CAMx

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Implementing the Decoupled Direct Method (DDM) and Process Analysis (PA) for Particulate Matter in CAMx

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	in contrast to Figure 6-3

EXECUTIVE SUMMARY

Implementing the Decoupled Direct Method in CAMx PM chemistry

The Decoupled Direct Method (DDM) is an efficient and accurate way of performing sensitivity analysis to model inputs. Traditionally, the brute-force (BF) method has been widely used to study the model responses to various system parameters. While the BF method is easy to apply and interpretation of the result is straightforward, it is computationally demanding and susceptible to numerical uncertainty. The DDM offers an alternative to the traditional brute-force (BF) method by directly solving sensitivity equations derived from the governing equations of the model.

CRC Project A-51a has extended the DDM probing tool in CAMx version 4.20 to include PM chemistry. CAMx PM chemistry consists of three processes: Inorganic aerosol thermodynamics by ISORROPIA, secondary organic aerosol partitioning by SOAP, and aqueous-phase chemistry by RADM-AQ. DDM algorithms were designed and implemented for these three PM modules. Stand-alone model tests for each PM module showed correct implementation and fairly good agreement between the DDM and brute force (BF) methods for 10% input changes.

The completed DDM codes were incorporated into CAMx version 4.20 and tested using a 2-day summer episode for the Eastern US. In most cases, the DDM first-order sensitivities closely follow those estimated by the BF method. Sensitivities of the organic species involved in SOAP are more linear and agree better between DDM and BF than sensitivities for species involved in ISORROPIA and RADM-AQ (e.g., particulate sulfate, nitrate, ammonium, etc.). Overall DDM performance is in an acceptable range for all species tested.

One of the main advantages of the DDM over the BF method is computational efficiency. As the number of input parameters to which the model sensitivity is calculated increases, the efficiency of calculating the DDM sensitivities becomes higher. When sensitivities are calculated together for 8 input parameters, the DDM is about 1.6 times faster than the BF method.

Implementing Process Analysis in CAMx PM chemistry

The CAMx Process Analysis (PA) tools make possible detailed model performance evaluation by tracking the contributions from individual physical and chemical processes governing the fate of the atmospheric pollutants. Using PA, one can more fully understand the complex interactions between the different processes, explain simulation results within the context of the model formulation, and improve the design of control strategies.

CRC Project A-51b has extended the Process Analysis probing tool in CAMx version 4.20 to provide information for the three PM chemistry processes: inorganic aerosol chemistry, organic aerosol chemistry, and aqueous chemistry. The updated PA implementation was tested and found to be accurate. The existing post-processing tools were also updated for the new PA implementation. The tools produce three bar charts for each species with different degrees of process aggregation to help interpret the process analysis results.

Recommendations

Although the DDM implementation in the CAMx PM modules shows reasonably good agreement with the BF method, the evaluation performed was limited to a 2 day test-case. Also, tests revealed an interaction between the chemistry and deposition calculations that degraded agreement between DDM and BF sensitivities. More thorough testing and evaluation is recommended to investigate whether the DDM performance can be improved, and to better assess any limitations in the applicability of DDM for PM species.

The CAMx PA implementation has three components of which one (Integrated Process Rates) was updated in this study. The two other PA components are Integrated Reaction Rates (IRR) and Chemical Process Analysis (CPA). The IRR formulation is rather specific to gas-phase chemistry and not applicable to PM modules that make equilibrium assumptions, namely ISORROPIA and RADM-AQ. The CPA formulation is more flexible than IRR and could be extended to provide valuable insights to the complex chemical processes for the PM species. A list of potential CPA improvements has been developed.

1. INTRODUCTION

1.1. Background

The Coordinating Research Council (CRC) funded the implementation of the Decoupled Direct Method (DDM) in version 3 of the Comprehensive Air Quality Model with Extensions (CAMx) for gas-phase species under CRC Project A-29. Dr. Alan Dunker and Mr. Jerome Ortmann at General Motors (GM) collaborated with ENVIRON (Dr. Greg Yarwood and Mr. Gary Wilson) in the project and the results were published (Dunker et al., 2002ab). Since then, new science modules for particulate matter (PM) have been developed and incorporated into CAMx. The current PM modules in CAMx perform the following three processes:

- Aqueous-phase SO₂ oxidation reactions in resolved cloud water using the Regional Acid Deposition Model (RADM-AQ) aqueous chemistry algorithm (Chang et al., 1987).
- Partitioning of organic condensable gases (CG1-CG5) to secondary organic aerosols (SOA1-SOA5) to form a condensed "organic solution phase" using a semi-volatile, equilibrium scheme called SOAP (Strader et al., 1998, 1999).
- Partitioning of inorganic aerosol constituents (sulfate, nitrate, ammonium, sodium, and chloride) between the gas and particle phases using the ISORROPIA thermodynamic module (Nenes et al., 1998, 1999).

Hence there was a need to extend the DDM to the PM modules in CAMx.

Process Analysis (PA) was originally implemented in CAMx version 3 and has been maintained through the current version 4.20 of CAMx. The current PA implementation provides only one parameter to report all information about chemical change due to the new PM processes. To provide more useful analysis, the PA module needed to be extended to report chremical change due to individual PM chemistry modules.

CRC sponsored Projects A-51a and A-51b to extend the DDM and PA probing tools to PM in CAMx version 4.20 (ENVIRON, 2005).

1.2. Decoupled Direct Method (DDM)

The simplest approach to sensitivity analysis, often referred to as the brute-force (BF) method, involves changing a model input parameter, rerunning the model, and then evaluating the change in model output. The change in output is quantified from the difference between the sensitivity case and base case. This approach requires a separate simulation for each parameter investigated, thus is computationally demanding. Also, the BF method tends to suffer from numerical noise if changes in the input parameters are small.

An alternative methodology for evaluating model sensitivity was developed by Dunker (1980 and 1981) called the decoupled direct method. The DDM can be used to calculate the same type of sensitivity coefficient as are available from the BF method. The difference is that with DDM, sensitivity coefficients are calculated explicitly by specialized algorithms implemented in the



host model. The implementation of the DDM for ozone in CAMx has been described elsewhere (Dunker et al., 2002a).

The DDM implementation developed for CAMx version 3 is working in version 4.20 for PM for all processes except chemistry and wet deposition. The DDM implementation for wet deposition needed revising because the host model algorithm was updated between CAMx versions 3 and 4.20 (Kemball-Cook, Emery and Yarwood, 2004). However, the PM chemistry updates had much greater impact on the DDM implementation than the wet deposition updates and so this report focuses mainly on implementing the DDM in the PM chemistry.

Of the two options for PM chemistry in the CAMx v4.20, the DDM is implemented for the Coarse/Fine (CF) 2-mode size scheme. The schematic diagram of the CF aerosol module is as follows:



In applying the DDM to the aerosol modules in CAMx, we are concerned primarily with the first-order sensitivity coefficients (S), which represent the change in concentration (Y) with respect to some input parameter (p), evaluated relative to the base case ($p = p_0$):

$$S = \frac{\partial Y}{\partial p}\Big|_{p_0} = \frac{\partial Y}{\partial p}\Big|_{p_0;SOAP} + \frac{\partial Y}{\partial p}\Big|_{p_0;RADM-AQ} + \frac{\partial Y}{\partial p}\Big|_{p_0;ISORROPIA}$$
(1.1)

CAMx uses an operator-splitting algorithm to improve efficiency in solving species concentrations. Therefore, analogous to the procedure for species concentrations, we operator-split the three PM chemistry processes and propagate the sensitivities sequentially through SOAP, then RADM-AQ, and finally ISORROPIA. I.e.,

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$$S(t_{0}) \xrightarrow{SOAP} S'(t_{1})$$

$$S'(t_{1}) \xrightarrow{RADM-AQ} S''(t_{1}) \qquad (1.2)$$

$$S''(t_{1}) \xrightarrow{ISORROPIA} S(t_{1})$$

1.3. Process Analysis (PA)

In general, the standard approach to evaluating air quality model results consists of examining the predicted concentrations, comparing predicted concentrations with observed concentrations, and calculating model performance statistics. While such comparisons are valuable and necessary, sometimes they can be misleading because complex interactions among various processes in the model and the model inputs can result in a prediction that accurately agrees with limited observations but for the wrong reasons. PA can help avoid such misinterpretations by providing detailed information on underlying individual physical and chemical processes.

There are three types of PA implemented in CAMx (ENVIRON, 2005):

- Integrated Processes Rate (IPR) analysis
- Integrated Reaction Rate (IRR) analysis
- Chemical Process Analysis (CPA)

An overview of each method is given below.

Integrated Processes Rate (IPR) Analysis. The IPR method provides detailed process rate information for each physical process in CAMx (i.e., advection, diffusion, deposition, emissions, chemistry, etc.) for selected grid cells and selected species (Wang, Langstaff and Jeffries, 1995). The IPR outputs can be analyzed to determine what processes governed the model-predicted concentrations at any time and place. IPR information has often been plotted as a time series of process contributions for specific cells or groups of cells. IPR outputs have also been used to check the mass balance in the host model, i.e., to determine whether model concentrations are fully explained by the diagnosed process information or whether unexpected artifacts are occurring. The IPR data are relatively easy to interpret and can be analyzed using simple tools such as spreadsheets.

Integrated Reaction Rate (IRR) Analysis. The IRR method provides detailed reaction rate information for all reactions in the chemical mechanism for selected grid cells (Jeffries and Tonnesen, 1994). The IRR data can be analyzed to determine how the chemical changes occurring in the model are related to the chemical mechanism. For example, by analyzing rate information over groups of reactions, it is possible to quantify chemically meaningful attributes such as radical initiation rates, radical propagation efficiencies, chain lengths, etc. Since these analyses tend to be complex, IRR data generally require post-processing to be useful.

Chemical Process Analysis (CPA). CPA is closely related to the IRR method but is designed to be more user-friendly and accessible. As mentioned above, IRR data are generally only useful after the data have been post-processed into chemically meaningful parameters. With CPA, a

selection of useful parameters is calculated within CAMx and then output to gridded files (Tonnesen and Dennis, 2000). The gridded CPA files are in the same format as the gridded concentration outputs and can be visualized using standard post-processing tools.

Project A-51b extended the IPR component of PA to individually track the process rates from all three PM modules (ISORROPIA, RADM-AQ and SOAP) for each chemical species.

1.4. Report Organization

Sections 2, 3, and 4 describe the algorithms of the ISORROPIA, RADM-AQ, and SOAP modules, respectively, discuss development of the DDM algorithm for each of the PM modules, and present results of stand-alone module testing. Full 3-D testing of the DDM implementation in CAMx v4.20 is presented in Section 5. The implementation of the PA IPR component for the individual PM modules is discussed in Section 6. Section 7 presents the study conclusions and recommendations.

2. IMPLEMENTING THE DDM IN ISORROPIA

The inorganic aerosol module ISORROPIA (Nenes et al., 1998, 1999) partitions inorganic aerosol constituents (sulfate, nitrate, ammonium, sodium, and chloride) between the gas and particle phases by assuming the constituents are in thermodynamic equilibrium. The ISORROPIA code was analyzed to develop equations defining the sensitivities of species output concentrations to input concentrations. These sensitivity equations were implemented and tested.

2.1. Interface Between CAMx and ISORROPIA

ISORROPIA has its own internal species that are mapped to CAMx species by an interface module. A corresponding interface module is required for sensitivity coefficients.

ISORROPIA takes molar concentrations of 5 inorganic species (sodium, sulfate, ammonium, nitrate, and chloride) as well as ambient temperature and relative humidity as inputs. The units for ISORROPIA input species are mol/m³ of air while CAMx species are in either ppm (gas) or μ g/m³ of air (aerosol). The following formulas represent the conversion between CAMx species (right-hand side) and ISORROPIA inputs (left-hand side):

Y ₀ (tNa)	$= (Y_0(cNa) / Mw) * 10^{-6}$	
$Y_0(tSO_4)$	$= (Y_0(cH_2SO_4) * P_{atm} / RT + Y_0(cSO_4) / Mw) * 10^{-6}$	
$Y_0(tNH_4)$	= $(Y_0(cNH_3) * P_{atm} / RT + Y_0(cNH_4) / Mw) * 10^{-6}$	(2.1)
$Y_0(tNO_3)$	= $(Y_0(cHNO_3) * P_{atm} / RT + Y_0(cNO_3) / Mw) * 10^{-6}$	
Y ₀ (tCl)	= $(Y_0(cHCl) * P_{atm} / RT + Y_0(cCl) / Mw) * 10^{-6}$	

where "t" and "c" that prefix the species name indicate total (gas and aerosol) concentration and CAMx species, respectively. Y_0 denotes the concentration before equilibrium is established in ISORROPIA. Mw is the appropriate molecular weight for the species, and P_{atm} is the atmospheric pressure. If Na and Cl are not active modeled species in CAMx, $Y_0(tNa) = Y_0(tCl) = (C(NaCl) / Mw) * 10^{-6}$ where C(NaCl) represents a background (constant) sea salt concentration.

While ISORROPIA internally determines equilibrium concentrations of a total of 20 species, CAMx takes results for only four of them and determines other CAMx species concentrations in a mass conserving manner. The following formulas represent the conversion between ISORROPIA outputs (right-hand side) and CAMx species (left-hand side):

CAMx gas species in ppm

$Y_1(cH_2SO_4)$	= 0
$Y_1(cNH_3)$	$= Y_1(NH_3) * 10^6 * RT / P_{atm}$
$Y_1(cHNO_3)$	$= Y_1(HNO_3) * 10^6 * RT / P_{atm}$
Y ₁ (cHCl)	$= Y_1(HCl) * 10^6 * RT / P_{atm}$

(2.2a)

CAM _x aerosol	l species	in $\mu g/m^3$	of air

Y ₁ (cNa)	$= Y_0(cNa)$
$Y_1(cSO_4)$	$= Y_0(tSO_4) * Mw * 10^6$
$Y_1(cNH_4)$	$= (Y_0(tNH_4) - Y_1(NH_3)) * Mw * 10^6$
$Y_1(cNO_3)$	$= (Y_0(tNO_3) - Y_1(HNO_3)) * Mw * 10^6$
$Y_1(cCl)$	$= (Y_0(tCl) - Y_1(HCl)) * Mw * 10^6$
$Y_1(cH_2O)$	$= Y_1(W) * 10^9$

(2.2b)

 Y_1 denotes the concentration after equilibrium is established. All the ISORROPIA internal species are in mol/m³ of air except aerosol water content $Y_1(W)$, which is in kg/m³ of air.

Differentiating Eq. (2.1) with respect to a parameter p gives S_0 (ISORROPIA species) as a function of S_0 (CAMx species). Differentiating Eq. (2.2) with respect to p gives S_1 (CAMx species) as a function of S_1 (ISORROPIA species). $S = \partial Y / \partial p$, and S_0 and S_1 are, respectively, the sensitivities before and after equilibrium is established by ISORROPIA's calculations.

Even though the sensitivities of only four ISORROPIA species are required in Eqs. (2.2) to determine the sensitivities of the CAMx species, we must calculate the sensitivities of all the ISORROPIA species because they are coupled together via equilibrium chemical reactions. The sensitivities of the other ISORROPIA species not needed for CAMx do provide additional useful information. For example, $S_1(H^+)$ is essentially the sensitivity of the aerosol pH.

There are 20 ISORROPIA species: 7 ions, 9 solids, 3 gases, and aerosol water. To define the concentrations of the species, there must be 20 equations relating the concentrations of the species. The 13 chemical equilibria considered by ISORROPIA define 13 equilibrium equations. The ZSR relationship for the aerosol water concentration and the electro-neutrality equation are two more equations. Lastly, there are 5 mass balance equations for sulfate, nitrate, chloride, ammonia and sodium.

2.2. Gas-Aerosol Phase Equilibria

If a liquid aerosol phase exists, gas-liquid-solid phase equilibrium is determined by the following equations:

Equilibrium reactions

$$HSO_{4}^{-} \leftrightarrow H^{+} + SO_{4}^{2-} \qquad K_{1} = \frac{[H^{+}][SO_{4}^{2-}]\gamma_{H^{+}}\gamma_{SO_{4}^{2-}}}{[HSO_{4}^{-}]\gamma_{HSO_{4}^{-}}} \qquad (2.3a)$$

$$NH_{3}(g) + H_{2}O(aq) \leftrightarrow NH_{4}^{+} + OH^{-} \qquad K_{2} = \frac{[NH_{4}^{+}][OH^{-}]\gamma_{NH_{4}^{+}}\gamma_{OH^{-}}}{P_{NH_{3}}a_{w}} \qquad (2.3b)$$

$$K_{w} = \frac{[H^{+}][OH^{-}]\gamma_{H^{+}}\gamma_{OH^{-}}}{a_{w}} \Rightarrow \qquad = \frac{[NH_{4}^{+}]\gamma_{NH_{4}^{+}}}{P_{NH_{3}}[H^{+}]\gamma_{H^{+}}}K_{w} \qquad (2.3b)$$

$$HCl(g) \leftrightarrow H^{+} + Cl^{-} \qquad K_{3} = \frac{[H^{+}][Cl^{-}]\gamma_{H^{+}}\gamma_{Cl^{-}}}{P_{HCl}} \qquad (2.3c)$$

$$HNO_{3}(g) \leftrightarrow H^{+} + NO_{3}^{-} \qquad K_{4} = \frac{[H^{+}][NO_{3}^{-}]\gamma_{H^{+}}\gamma_{NO_{3}^{-}}}{P_{HNO_{3}}} \qquad (2.3d)$$

$$Na_{2}SO_{4}(s) \leftrightarrow 2Na^{+} + SO_{4}^{2^{-}} \qquad K_{5} = [Na^{+}]^{2}[SO_{4}^{2^{-}}]\gamma_{Na^{+}}^{2}\gamma_{SO_{4}^{2^{-}}} \qquad (2.3e)$$

$$NH_{4}Cl(s) \leftrightarrow NH_{3}(g) + HCl(g) \qquad K_{6} = P_{NH_{3}}P_{HCl} \qquad (2.3f)$$

$$(NH_{4})_{2}SO_{4}(s) \leftrightarrow 2NH_{4}^{+} + SO_{4}^{2^{-}} \qquad K_{7} = [NH_{4}^{+}]^{2}[SO_{4}^{2^{-}}]\gamma_{NH_{4}^{+}}^{2}\gamma_{SO_{4}^{2^{-}}} \qquad (2.3g)$$

$$NaCl(s) \leftrightarrow Na^{+} + Cl^{-} \qquad K_{8} = [Na^{+}][Cl^{-}]\gamma_{Na^{+}}\gamma_{Cl^{-}} \qquad (2.3h)$$

$$NaNO_{3}(s) \leftrightarrow Na^{+} + NO_{3}^{-} \qquad K_{9} = [Na^{+}][NO_{3}^{-}]\gamma_{Na^{+}}\gamma_{NO_{3}^{-}} \qquad (2.3i)$$

$$NH_{4}NO_{3}(s) \leftrightarrow NH_{3}(g) + HNO_{3}(g) \qquad K_{10} = P_{NH_{3}}P_{HNO_{3}} \qquad (2.3j)$$

$$NaHSO_{4}(s) \leftrightarrow NH_{4}^{+} + HSO_{4}^{-} \qquad K_{12} = [NH_{4}^{+}]^{3}[HSO_{4}^{-}]\gamma_{NH_{4}^{+}}\gamma_{HSO_{4}} \qquad (2.3l)$$

$$(NH_{4})_{3}H(SO_{4})_{2}(s) \leftrightarrow 3NH_{4}^{+} + HSO_{4}^{-} \qquad K_{13} = [NH_{4}^{+}]^{3}[HSO_{4}^{-}][SO_{4}^{2^{-}}]\gamma_{NH_{4}^{+}}^{3}\gamma_{HSO_{4}} \gamma_{SO_{4}^{-}} \qquad (2.3m)$$

where γ_A , [A], and P_A are the activity coefficient, molality, and partial pressure of the species A, respectively.

Unit conversion:
$$[A] = Y_1(A) / Y_1(W); P_A = Y_1(A) * RT$$

Differentiating Eqs. (2.3) with respect to p gives 13 equations for sensitivities. For example, let's consider the first equilibrium reaction:

$$K_{1} = \frac{[H^{+}][SO_{4}^{2-}]\gamma_{H^{+}}\gamma_{SO_{4}^{2-}}}{[HSO_{4}^{-}]\gamma_{HSO_{4}^{-}}} = \frac{Y_{1}(H^{+})Y_{1}(SO_{4}^{2-})\gamma_{H_{2}SO_{4}}^{3}}{Y_{1}(HSO_{4}^{-})Y_{1}(W)\gamma_{H-HSO_{4}}^{2}}$$
(2.4)

Note that ISORROPIA calculates activity coefficients for ion pairs, not individual ions. By definition,

$$\gamma^{3}_{H_{2}SO_{4}} = \gamma^{2}_{H^{+}}\gamma_{SO_{4}^{2-}} \text{ and } \gamma^{2}_{H^{-}HSO_{4}} = \gamma_{H^{+}}\gamma_{HSO_{4}^{-}}$$

Differentiating Eq. (2.4) with respect to p gives the following equation:

$$\frac{Y_{1}(SO_{4}^{2-})}{Y_{1}(HSO_{4}^{-})Y_{1}(W)}\Gamma S_{1}(H^{+}) + \frac{Y_{1}(H^{+})}{Y_{1}(HSO_{4}^{-})Y_{1}(W)}\Gamma S_{1}(SO_{4}^{2-})
- \frac{Y_{1}(H^{+})Y_{1}(SO_{4}^{2-})}{Y_{1}(W)[Y_{1}(HSO_{4}^{-})]^{2}}\Gamma S_{1}(HSO_{4}^{-}) - \frac{Y_{1}(H^{+})Y_{1}(SO_{4}^{2-})}{Y_{1}(HSO_{4}^{-})[Y_{1}(W)]^{2}}\Gamma S_{1}(W)
+ 3\frac{\gamma_{H_{2}SO_{4}}^{2}}{\gamma_{H_{-}HSO_{4}}^{2}}C\sum_{j=1}^{J}\frac{\partial\gamma_{H_{2}SO_{4}}}{\partial Y_{1}(A_{j})}S_{1}(A_{j}) - 2\frac{\gamma_{H_{2}SO_{4}}^{3}}{\gamma_{H_{-}HSO_{4}}^{3}}C\sum_{j=1}^{J}\frac{\partial\gamma_{H_{-}HSO_{4}}}{\partial Y_{1}(A_{j})}S_{1}(A_{j}) = \frac{\partial K_{1}}{\partial p} = 0$$
(2.5)

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where J is the number of species in ISORROPIA that are involved in calculating the activity coefficients,

$$C = \frac{Y_1(H^+)Y_1(SO_4^{2-})}{Y_1(HSO_4^-)Y_1(W)} \text{ and } \Gamma = \frac{\gamma_{H_2SO_4}^3}{\gamma_{H_2HSO_4}^2}$$

Nine of the ISORROPIA reactions represent the dissolution or precipitation of solids. If the solid involved in a particular reaction R is absent at equilibrium, then we omit the sensitivity equation derived from the equilibrium constant for reaction R. I.e., the total number of sensitivity equations that we must solve is reduced by one for every solid that is absent at equilibrium. Eliminating the sensitivity equation also eliminates one unknown sensitivity because each solid appears in only one reaction. Thus, the number of equations remains equal to the number of unknown sensitivities regardless of how many solids are present at equilibrium. The presence or absence of solids can be diagnosed from the ISORROPIA output. If a solid species A_j is absent at equilibrium, then the sensitivity is set to zero, $S_1(A_j) = 0$.

For a sufficiently large perturbation to parameter p, the solid A_j may form. However, the sensitivity coefficient, which is identically zero, cannot predict the formation of the solid when the parameter is varied. This is a limitation of local sensitivity methods and other methods that use information from only one simulation of the atmosphere (one set of values for the parameters of interest). The consequences of this limitation may be mitigated by the fact that the concentrations of some CAMx aerosol species are calculated as the difference between the total (gas+aerosol) and equilibrium gas concentrations of the species. For example, the concentration of cNO₃ corresponds to the difference between the concentration of tNO₃ and the equilibrium concentration of HNO₃. Then, the sensitivity of cNO₃ is the difference between the sensitivities of the total nitrate and nitric acid at equilibrium, which likely will not be highly dependent on whether the aerosol nitrate is in aqueous solution or in a solid.

Mass balance equations

$$\begin{split} Y_{0}(tNa) &= Y_{1}(Na^{+}) + Y_{1}(NaCl) + 2Y_{1}(Na_{2}SO_{4}) + Y_{1}(NaNO_{3}) + Y_{1}(NaHSO_{4}) \\ Y_{0}(tSO_{4}) &= Y_{1}(SO_{4}^{2^{-}}) + Y_{1}(HSO_{4}^{-}) + Y_{1}((NH_{4})_{2}SO_{4}) + Y_{1}(NH_{4}HSO_{4}) + Y_{1}(Na_{2}SO_{4}) \\ &+ Y_{1}(NaHSO_{4}) + 2Y_{1}((NH_{4})_{3}H(SO_{4})_{2}) \\ Y_{0}(tNH_{4}) &= Y_{1}(NH_{3}) + Y_{1}(NH_{4}^{+}) + 2Y_{1}((NH_{4})_{2}SO_{4}) + Y_{1}(NH_{4}HSO_{4}) + Y_{1}(NH_{4}NO_{3}) \\ &+ Y_{1}(NH_{4}Cl) + 3Y_{1}((NH_{4})_{3}H(SO_{4})_{2}) \\ Y_{0}(tNO_{3}) &= Y_{1}(HNO_{3}) + Y_{1}(NO_{3}^{-}) + Y_{1}(NaNO_{3}) + Y_{1}(NH_{4}NO_{3}) \\ Y_{0}(tCl) &= Y_{1}(HCl) + Y_{1}(Cl^{-}) + Y_{1}(NaCl) + Y_{1}(NH_{4}Cl) \end{split}$$
(2.6)

Differentiating Eqs. (2.6) with respect to p gives 5 more sensitivity equations.

Charge balance equation

$$Y_{1}(H^{+}) + Y_{1}(Na^{+}) + Y_{1}(NH_{4}^{+}) = 2Y_{1}(SO_{4}^{2-}) + Y_{1}(HSO_{4}^{-}) + Y_{1}(NO_{3}^{-}) + Y_{1}(Cl^{-}) + \frac{K_{w}a_{w}Y_{1}(W)^{2}}{Y_{1}(H^{+})}$$

(2.7)

Here $\gamma_{H^+}\gamma_{OH^-}$ is assumed to be 1. Again, differentiating Eq. (2.7) with respect to p gives another sensitivity equation.

ZSR relationship

The Zdanovskii-Stokes-Robinson (ZSR) relationship (Stokes and Robinson, 1966) is used to calculate the water content of the aerosols:

$$Y_1(W) = \sum_{i} \frac{E_i}{m_{0i}(a_w)}$$
(2.8)

where E_i is the molar concentration of the i-th electrolyte in the multicomponent solution and $m_{0i}(a_w)$ is the molality of an aqueous solution of the i-th electrolyte with the same water activity as the multicomponent solution. The water activity a_w is equal to the ambient relative humidity expressed on a fractional (0-1) scale. Given temperature and relative humidity, m_{0i} is constant. There are 10 electrolytes that are present in solution: NaCl, Na₂SO₄, NaNO₃, (NH₄)₂SO₄, NH₄NO₃, NH₄Cl, NH₄HSO₄, NaHSO₄, (NH₄)₃H(SO₄)₂, and H₂SO₄. ISORROPIA determines the concentrations E_i by considering a variety of cases that are described in the Appendix A.

Differentiating Eq. (2.8) with respect to p yields the last sensitivity equation:

$$S_{1}(W) = \sum_{i} \left[\frac{1}{m_{0i}(a_{w})} \sum_{j=1}^{J} \frac{\partial E_{i}}{\partial Y_{1}(A_{j})} S_{1}(A_{j}) \right]$$
(2.9)

To obtain $\partial E_i / \partial Y_1(A_j)$, we differentiate the equations in the Appendix A with respect to the concentrations of the species, $Y_1(A_j)$.

Activity coefficients

The multicomponent activity coefficients in ISORROPIA are calculated using Bromley's formula (Bromley, 1973):

$$\log \gamma_{12} = -A_{\gamma} \frac{z_1 z_2 I^{1/2}}{1 + I^{1/2}} + \frac{z_1 z_2}{z_1 + z_2} \left[\frac{F_1}{z_1} + \frac{F_2}{z_2} \right]$$
(2.10a)

where γ_{12} is the activity coefficient of Cation 1 and Anion 2, A_{γ} is the Debye-Huckel constant, which has a value of 0.511 kg^{1/2}mol^{1/2} at 298.15 K, and,

$$F_{1} = Y_{21} \log \gamma_{12}^{0} + Y_{41} \log \gamma_{14}^{0} + Y_{61} \log \gamma_{16}^{0} + \dots + \frac{A_{\gamma} I^{1/2}}{1 + I^{1/2}} (z_{1} z_{2} Y_{21} + z_{1} z_{4} Y_{41} + z_{1} z_{6} Y_{61} + \dots)$$

$$F_{2} = X_{12} \log \gamma_{21}^{0} + X_{32} \log \gamma_{23}^{0} + Y_{52} \log \gamma_{25}^{0} + \dots + \frac{A_{\gamma} I^{1/2}}{1 + I^{1/2}} (z_{1} z_{2} X_{12} + z_{3} z_{2} X_{32} + z_{5} z_{2} X_{52} + \dots)$$

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$$Y_{21} = \left(\frac{z_1 + z_2}{2}\right)^2 \frac{[A_2]}{I}$$

$$X_{12} = \left(\frac{z_1 + z_2}{2}\right)^2 \frac{[A_1]}{I}$$
Ionic strength, $I = \frac{1}{2} \sum_i [A_i] z_i^2$
(2.1)

where $[A_i]$ and z_i are the molality and the absolute charge, respectively, of ionic species i, and γ_{ij}^{0} is the mean ionic activity coefficient of the binary pair i-j for a solution that contains only i-j ions at the ionic strength of the multicomponent solution. In Eqs. (2.10), odd subscripts refer to cations and even subscripts refer to anions.

The binary activity coefficients needed in Eqs. (2.10b) are calculated using the Kusik and Meissner method (Kusik and Meissner, 1978):

$$\log \gamma_{12}^{0} = z_{1}z_{2}(\log \beta + \chi)$$

$$\beta = 1 + B(1 + 0.1I)^{q} - B$$

$$B = 0.75 - 0.065q$$

$$\chi = \frac{-0.5107I^{1/2}}{1 + CI^{1/2}}$$

$$C = 1 + 0.055q \exp(-0.023I^{3})$$

(2.11)

where q is a parameter specific for each salt.

Differentiating the activity coefficient equation with respect to $Y_1(A_j)$ gives the following:

$$\begin{aligned} \frac{1}{\gamma_{12}\ln 10} \frac{\partial \gamma_{12}}{\partial Y_{1}(A_{j})} &= -\frac{A_{\gamma} z_{1} z_{2}}{2} \frac{I^{-1/2}}{(1+I^{1/2})^{2}} \frac{\partial I}{\partial Y_{1}(A_{j})} + \frac{z_{1} z_{2}}{z_{1}+z_{2}} \left[\frac{1}{z_{1}} \frac{\partial F_{1}}{\partial Y_{1}(A_{j})} + \frac{1}{z_{2}} \frac{\partial F_{2}}{\partial Y_{1}(A_{j})} \right] \quad (2.12) \\ \frac{\partial F_{1}}{\partial Y_{1}(A_{j})} &= \log \gamma_{12}^{0} \frac{\partial Y_{21}}{\partial Y_{1}(A_{j})} + Y_{21} \frac{\partial \log \gamma_{12}^{0}}{\partial Y_{1}(A_{j})} + \log \gamma_{14}^{0} \frac{\partial Y_{41}}{\partial Y_{1}(A_{j})} + Y_{41} \frac{\partial \log \gamma_{14}^{0}}{\partial Y_{1}(A_{j})} + \cdots \\ &+ \frac{A_{\gamma}}{2} \frac{I^{-1/2}}{(1+I^{1/2})^{2}} (z_{1} z_{2} Y_{21} + z_{1} z_{4} Y_{41} + \cdots) \frac{\partial I}{\partial Y_{1}(A_{j})} + \frac{A_{\gamma} I^{1/2}}{1+I^{1/2}} (z_{1} z_{2} \frac{\partial Y_{21}}{\partial Y_{1}(A_{j})} + z_{1} z_{4} \frac{\partial Y_{41}}{\partial Y_{1}(A_{j})} + \cdots) \\ &\frac{\partial F_{2}}{\partial Y_{1}(A_{j})} &= \log \gamma_{21}^{0} \frac{\partial X_{12}}{\partial Y_{1}(A_{j})} + X_{12} \frac{\partial \log \gamma_{21}^{0}}{\partial Y_{1}(A_{j})} + \log \gamma_{23}^{0} \frac{\partial X_{32}}{\partial Y_{1}(A_{j})} + X_{32} \frac{\partial \log \gamma_{23}^{0}}{\partial Y_{1}(A_{j})} + \cdots \\ &+ \frac{A_{\gamma}}{2} \frac{I^{-1/2}}{(1+I^{1/2})^{2}} (z_{1} z_{2} X_{12} + z_{3} z_{2} X_{32} + \cdots) \frac{\partial I}{\partial Y_{1}(A_{j})} + \frac{A_{\gamma} I^{1/2}}{1+I^{1/2}} (z_{1} z_{2} \frac{\partial X_{12}}{\partial Y_{1}(A_{j})} + z_{3} z_{2} \frac{\partial X_{32}}{\partial Y_{1}(A_{j})} + \cdots \\ &+ \frac{A_{\gamma}}{2} \frac{I^{-1/2}}{(1+I^{1/2})^{2}} (z_{1} z_{2} X_{12} + z_{3} z_{2} X_{32} + \cdots) \frac{\partial I}{\partial Y_{1}(A_{j})} + \frac{A_{\gamma} I^{1/2}}{1+I^{1/2}} (z_{1} z_{2} \frac{\partial X_{12}}{\partial Y_{1}(A_{j})} + z_{3} z_{2} \frac{\partial X_{32}}{\partial Y_{1}(A_{j})} + \cdots) \\ &\frac{\partial F_{2}}{\partial Y_{1}(A_{j})} &= \left(\frac{z_{1}+z_{i}}{2}\right)^{2} \left[\frac{1}{Y_{1}(W)I} \frac{\partial Y_{1}(A_{i})}{\partial Y_{1}(A_{j})} - \frac{Y_{1}(A_{i})}{Y_{1}(W)I^{2}} \frac{\partial I}{\partial Y_{1}(A_{j})}\right] \qquad \text{if } A_{j} \neq W \\ &= \left(\frac{z_{1}+z_{i}}{2}\right)^{2} \left[-\frac{Y_{1}(A_{i})}{Y_{1}(W)I} - \frac{Y_{1}(A_{i})}{Y_{1}(W)I^{2}} \frac{\partial I}{\partial Y_{1}(W)}\right] \qquad \text{if } A_{j} = W$$

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(2.10b)

$$\begin{aligned} \frac{\partial X_{i2}}{\partial Y_1(A_j)} &= \left(\frac{z_i + z_2}{2}\right)^2 \left[\frac{1}{Y_1(W)I} \frac{\partial Y_1(A_i)}{\partial Y_1(A_j)} - \frac{Y_1(A_i)}{Y_1(W)I^2} \frac{\partial I}{\partial Y_1(A_j)}\right] & \text{if } A_j \neq W \\ &= \left(\frac{z_i + z_2}{2}\right)^2 \left[-\frac{Y_1(A_i)}{Y_1(W)^2 I} - \frac{Y_1(A_i)}{Y_1(W)I^2} \frac{\partial I}{\partial Y_1(W)}\right] & \text{if } A_j = W \\ \frac{\partial \log \gamma_{12}^0}{\partial Y_1(A_j)} &= z_1 z_2 \left[\frac{0.1Bq(1 + 0.1I)^{q-1}}{\beta \ln 10} - 0.5107 \frac{\frac{1}{2}I^{-1/2} + 0.003795qI^3 \exp(-0.023I^3)}{(1 + CI^{1/2})^2}\right] \frac{\partial I}{\partial Y_1(A_j)} \\ \frac{\partial I}{\partial Y_1(A_j)} &= \frac{z_j^2}{2Y_1(W)} & \text{if } A_j = H^+, Na^+, NH_4^+, SO_4^{-2}, HSO_4^-, NO3^-, \text{ or } CI^- \\ &= -\frac{1}{2Y_1(W)^2} \sum_i Y_1(A_i) z_i^2 & \text{if } A_j = W \\ &= 0 & \text{if } A_j \neq \text{ ions or water} \end{aligned}$$

While ISORROPIA has an option to use pre-calculated tables of binary activity coefficients to enhance the speed, we decided not to tabulate the derivatives of the binary activity coefficients. Tables of the derivatives of the binary activity coefficients would require extra coding and memory for no significant computational advantage because the set of sensitivity equations are linear and can be solved without iteration.

2.3. Dry (Solid-phase Only) Aerosols

If only solids are present, the equilibrium reactions of the gas-aerosol equilibria do not apply nor does the ZSR equation for the water content of the aerosol. Furthermore, the chemical formulas for the solids force charge balance so that the electro-neutrality equation is automatically satisfied. Consequently, ISORROPIA uses only the mass balance equations (and some chemical assumptions) to determine the concentrations of the solid species. There are seven dry cases considered in ISORROPIA. These cases are solved case-by-case using mass balances of the solid species that are possible in the given system. For example, we consider sub-case I1A, which is a sulfate rich, sodium-ammonium-nitrate-sulfate-chloride system with a sufficiently low relative humidity that no water is present. All of the sodium reacts with sulfate to produce Na₂SO₄ and NaHSO₄. The remaining sulfate reacts with ammonia to form (NH₄)₂SO₄, (NH₄)₃H(SO₄)₂ and/or NH₄HSO₄. HCl and HNO₃ remain in the gas phase.

Solid species

a)
$$Y_0(tNH_4) / 3 \le (Y_0(tSO_4) - 0.5 Y_0(cNa)) / 2$$

i) $Y_0(tSO_4) - 0.5 Y_0(cNa) - 2 Y_0(tNH_4) / 3 \le Y_0(tNH_4) / 3$
 $Y_1(Na_2SO_4) = 0.5 Y_0(cNa)$
 $Y_1(NH_4HSO_4) = 3 (Y_0(tSO_4) - 0.5 Y_0(cNa)) - 2 Y_0(tNH_4)$
 $Y_1((NH_4)_3H(SO_4)_2) = Y_0(tNH_4) - (Y_0(tSO_4) - 0.5 Y_0(cNa))$
 $Y_1(NaHSO_4) = 0$
(2.13a)

$$\begin{split} Y_{1}((NH_{4})_{2}SO_{4}) &= 0 \\ \\ \text{ii)} \ Y_{0}(tSO_{4}) &= 0.5 \ Y_{0}(cNa) - 2 \ Y_{0}(tNH_{4}) \ / \ 3 > Y_{0}(tNH_{4}) \ / \ 3 \\ & Y_{1}(NH_{4}HSO_{4}) = Y_{0}(tNH_{4}) \\ Y_{1}((NH_{4})_{3}H(SO_{4})_{2}) &= 0 \\ Y_{1}(NaHSO_{4}) &= 2 \ Y_{0}(tSO_{4}) - Y_{0}(cNa) - 2 \ Y_{0}(tNH_{4}) \\ Y_{1}(Na_{2}SO_{4}) &= Y_{0}(cNa) - Y_{0}(tSO_{4}) + Y_{0}(tNH_{4}) \\ Y_{1}((NH_{4})_{2}SO_{4}) &= 0 \end{split}$$
(2.13b)
b) $Y_{0}(tNH_{4}) \ / \ 3 > (Y_{0}(tSO_{4}) - 0.5 \ Y_{0}(cNa)) \ / \ 2 \\ Y_{1}(Na_{2}SO_{4}) &= 0.5 \ Y_{0}(cNa) \\ Y_{1}((NH_{4})_{3}H(SO_{4})_{2}) &= 2 \ (Y_{0}(tSO_{4}) - 0.5 \ Y_{0}(cNa)) - Y_{0}(tNH_{4}) \\ Y_{1}((NH_{4})_{3}H(SO_{4})_{2}) &= 2 \ (Y_{0}(tSO_{4}) - 0.5 \ Y_{0}(cNa)) - Y_{0}(tNH_{4}) \\ Y_{1}((NH_{4})_{2}SO_{4}) &= 2 \ Y_{0}(tNH_{4}) - 3 \ (Y_{0}(tSO_{4}) - 0.5 \ Y_{0}(cNa)) \\ Y_{1}(NH_{4}HSO_{4}) &= 0 \\ Y_{1}(NaHSO_{4}) &= 0 \end{aligned}$ (2.13c)

Gas species

$$Y_{1}(HNO_{3}) = Y_{0}(tNO_{3})$$

$$Y_{1}(HCl) = Y_{0}(tCl)$$

$$Y_{1}(NH_{3}) = 0$$
(2.13d)

Differentiating Eqs. (2.13) with respect to p gives the sensitivities of the solid and gas species. The sensitivities of the ions are identically zero.

2.4. Mutual Deliquescence Region (MDR)

A special situation arises when the relative humidity (RH) is in a MDR. A system is said to be in a MDR when the RH is

$$MDRH(salt_1,...,salt_n) \le RH \le MIN(DRH(salt_1),...,DRH(salt_n))$$
(2.14)

Here, DRH is the deliquescence RH (RH at which a salt is completely dissolved into a solution) and MDRH is the mutual DRH (minimum DRH of the salt mixture).

When RH is in the MDR, ISORROPIA assumes the solution to be the sum of two weighted solutions: the "dry" solution (solid-only case) and the "wet" solution (the case where the salt with the lowest DRH is completely dissolved). The weighting factor is defined as

$$c = \frac{RH - RH_{wet}}{MDRH - RH_{wet}}$$
(2.15)

For example, the concentration of any solid salt or gaseous species is

$$Y_1(A_i) = cY_1(A_i, RH_{dry}) + (1 - c)Y_1(A_i, RH_{wet})$$
(2.16)

where $RH_{dry} < MDRH$. By differentiating Eq. (2.16) with respect to p, we obtain the equation for the sensitivities:

$$S_1(A_i) = cS_1(A_i, RH_{drv}) + (1 - c)S_1(A_i, RH_{wet})$$
(2.17)

Because ISORROPIA must solve two cases, the wet and dry states, approximately twice as much work is necessary to determine both the concentrations and the sensitivities when the RH is in a MDR.

2.5. Solution Procedure for Sensitivities

There are a total of (up to) 20 independent equations for the concentrations, equal to the 20 chemical species. Differentiating each of the equations with respect to a parameter p_q leads to 20 independent linear equations for the sensitivities $S_1(A_j)$, j = 1, ..., 20, with the form

$$\underline{\underline{G}} \ \underline{\underline{S}}_{1q} = \underline{\underline{b}}_{\underline{q}} \tag{2.18}$$

Here, \underline{G} is a matrix of coefficients from the equations for the sensitivities, and \underline{b}_q is a vector whose elements are the constants from the equations. \underline{S}_{1q} is a vector with elements $S_{1q}(A_j)$ that are the sensitivities with respect to parameter p_q . The dimensions of \underline{G} , \underline{S}_{1q} , and \underline{b}_q are $N_+ \times N_+$, $N_+ \times 1$ and $N_+ \times 1$, respectively, where N_+ is the number of ISORROPIA species with nonzero concentrations (e.g., $N_+ = 19$ if one solid is not present). Matrix \underline{G} can be triangularized once, and then Eq. (2.18) can be solved multiple times for different sets of sensitivities corresponding to different parameters p_q , q = 1, 2, ... After solving Eq. (2.18), we take the sensitivities $S_{1q}(HNO_3)$, $S_{1q}(HCl)$, $S_{1q}(NH_3)$, and $S_{1q}(W)$ and use them to obtain the sensitivities of the CAMx species after equilibrium is achieved.

2.6. Stand-Alone Testing – Liquid-Only

The DDM algorithm described above was implemented in ISORROPIA and the code was tested in a stand-alone model. The model responses to the input changes of total (gas and aerosol phases) sulfate, nitrate, and ammonium predicted by brute force (BF) method and DDM were compared. The input change is formulated as follows:

$$Y_{0}(tA)\Big|_{p} = Y_{0}(tA)\Big|_{p=0} + p \times Y_{0}(tA)\Big|_{p=0}$$
(2.19)

where $Y_0(tA)$ is the input concentration of species A (gas+aerosol) and p is the scalar parameter to which the DDM calculates sensitivities of model species. Then, the response of a model species with respect to the parameter p is predicted as follows:

$$Y_{1}(A)\Big|_{p} = Y_{1}(A)\Big|_{p=0} + p \times S_{1}(A)$$
(2.20)

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where $S_1(A)$ is the sensitivity of species A predicted by the DDM.

Four types of aerosols were considered for this stand-alone testing as described below:

Sulfate poor, sodium poor aerosol system

$$\frac{Y_0(tNa) + Y_0(tNH_4)}{Y_0(tSO_4)} \ge 2 \quad \& \quad \frac{Y_0(tNa)}{Y_0(tSO_4)} < 2$$

There is enough ammonia and sodium to fully neutralize the sulfate, but sodium is not enough to neutralize sulfate by itself. In this case, excess ammonia can react with the other gaseous species, HNO_3 and/or HCl, to form volatile salts which may dissolve in the liquid phase if RH is sufficiently high. The test case inputs are:

Y ₀ (tNa)	$= 1.5 \times 10^{-7} \text{ mol/m}^3$
$Y_0(tSO_4)$	$= 1.0 \times 10^{-7} \text{ mol/m}^3$
$Y_0(tNH_4)$	$= 1.5 \times 10^{-7} \text{ mol/m}^3$
$Y_0(tNO_3)$	$= 1.0 \times 10^{-7} \text{ mol/m}^3$
Y ₀ (tCl)	$= 1.0 \times 10^{-7} \text{ mol/m}^3$

Sulfate poor, sodium rich aerosol system

$$\frac{Y_0(tNa) + Y_0(tNH_4)}{Y_0(tSO_4)} \ge 2 \quad \& \quad \frac{Y_0(tNa)}{Y_0(tSO_4)} \ge 2$$

There is enough sodium to fully neutralize the sulfates. In this case, ammonia and excess sodium can react with the other species, HNO_3 and/or HCl, to form salts, while no ammonium sulfate is formed. The test case inputs are:

Y ₀ (tNa)	$= 2.5 \times 10^{-7} \text{ mol/m}^3$
$Y_0(tSO_4)$	$= 1.0 \times 10^{-7} \text{ mol/m}^3$
Y ₀ (tNH ₄)	$= 1.0 \times 10^{-7} \text{ mol/m}^3$
$Y_0(tNO_3)$	$= 1.0 \times 10^{-7} \text{ mol/m}^3$
$Y_0(tCl)$	$= 1.0 \times 10^{-7} \text{ mol/m}^3$

Sulfate rich, no free acid aerosol system

$$1 \le \frac{Y_0(tNa) + Y_0(tNH_4)}{Y_0(tSO_4)} < 2$$

There is enough ammonia and sodium to partially (but not fully) neutralize the sulfates. The sulfates exist as a mixture of bisulfates and sulfates. The test case inputs are:

Y ₀ (tNa)	$= 0.5 \times 10^{-7} \text{ mol/m}^3$
$Y_0(tSO_4)$	$= 1.0 \times 10^{-7} \text{ mol/m}^3$
$Y_0(tNH_4)$	$= 1.0 \times 10^{-7} \text{ mol/m}^3$

$Y_0(tNO_3)$	$= 1.0 \times 10^{-7} \text{ mol/m}^3$
Y ₀ (tCl)	$= 1.0 \times 10^{-7} \text{ mol/m}^3$

Sulfate rich, free acid aerosol system

$$\frac{Y_0(tNa) + Y_0(tNH_4)}{Y_0(tSO_4)} < 1$$

The sulfates are in abundance and part of it is in the form of free sulfuric acid. The test case inputs are:

Y ₀ (tNa)	$= 0.3 \times 10^{-7} \text{ mol/m}^3$
$Y_0(tSO_4)$	$= 1.0 \times 10^{-7} \text{ mol/m}^3$
$Y_0(tNH_4)$	$= 0.3 \times 10^{-7} \text{ mol/m}^3$
$Y_0(tNO_3)$	$= 1.0 \times 10^{-7} \text{ mol/m}^3$
Y ₀ (tCl)	$= 1.0 \times 10^{-7} \text{ mol/m}^3$

In this testing, only liquid-only phases were examined by giving sufficiently high relative humidity (RH = 0.95; T = 298 K).

2.7. Test Results – Liquid-Only

The results of stand-alone tests are shown in Figures 2-1 to 2-12. The responses for three gas species and aerosol water are shown here since they are directly related to CAMx species. Additionally, the responses of hydrogen ion are shown as this can be used for the sensitivity of the aerosol pH. In most cases, the model responses predicted by DDM closely follow those by the BF method for up to 10% change in total input species concentrations (i.e., -0.1).Cases beyond 10% input change where the BF responses of ISORROPIA start to become nonlinear indicate cases where the higher-order sensitivities are important. Although it is known that predictions based on first-order sensitivities are valid over a limited range, the 3-D averaging in CAMx may smooth out a lot of chemical non-linearity. Only the sub-case of sulfate rich, no free sulfuric acid seems to show noticeable errors (Figures 2-7 to 2-9). It should be noted, however, that the sensitivities of those gas species to the input changes are almost negligible except for the response of nitric acid to the change of total nitrate. In this sub-case (sulfate rich, no free acid), ISORROPIA assumes that ammonia in the gas phase is a minor species. Also the dissolution of nitric acid and hydrogen chloride is assumed to be minor. Therefore, ISORROPIA first establishes aerosol phase equilibrium without considering ammonia, nitric acid and hydrogen chloride in the gas phase, whose equilibria between gas and liquid phases are subsequently calculated assuming this does not significantly affect the already-established equilibrium point. Since DDM equations were derived from the full set of equilibrium reactions, it may be possible that the responses by ISORROPIA and DDM calculations slightly disagree. Although the same assumption is made by ISORROPIA for the sub-case of sulfate rich, free sulfuric acid, the aerosol phase is significantly more acidic and thus ammonia in the gas phase and dissolution of nitric acid and hydrogen chloride are even more negligible. In this case, DDM and brute force method indeed agree well (Figures 2-10 to 2-12).

There are also some indications (H^+ in Figures 2-1 and 2-4, NH₃ in Figure 2-7, water in Figure 2-8, and HNO₃ and HCl in Figure 2-10) that ISORROPIA may be switching between cases or

solution procedures as p is varied from -0.3 to 0.3, resulting in a discontinuity in the derivative of the BF results with respect to p. No method for calculating local first- and higher-order derivatives can reproduce such discontinuities.



Figure 2-1. Response of a sulfate poor, sodium poor aerosol system to the change of total sulfate concentration by brute force method (BF) and DDM; the unit of concentrations is mol/m³ of air except for water which is in kg/m³ of air.



Figure 2-2. Response of a sulfate poor, sodium poor aerosol system to the change of total ammonium concentration by brute force method (BF) and DDM; the unit of concentrations is mol/m³ of air except for water which is in kg/m³ of air.



Figure 2-3. Response of a sulfate poor, sodium poor aerosol system to the change of total nitrate concentration by brute force method (BF) and DDM; the unit of concentrations is mol/m³ of air except for water which is in kg/m³ of air.



Figure 2-4. Response of a sulfate poor, sodium rich aerosol system to the change of total sulfate concentration by brute force method (BF) and DDM; the unit of concentrations is mol/m³ of air except for water which is in kg/m³ of air.



Figure 2-5. Response of a sulfate poor, sodium rich aerosol system to the change of total ammonium concentration by brute force method (BF) and DDM; the unit of concentrations is mol/m³ of air except for water which is in kg/m³ of air.



Figure 2-6. Response of a sulfate poor, sodium rich aerosol system to the change of total nitrate concentration by brute force method (BF) and DDM; the unit of concentrations is mol/m³ of air except for water which is in kg/m³ of air.



Figure 2-7. Response of a sulfate rich, no free acid aerosol system to the change of total sulfate concentration by brute force method (BF) and DDM; the unit of concentrations is mol/m³ of air except for water which is in kg/m³ of air.



Figure 2-8. Response of a sulfate rich, no free acid aerosol system to the change of total ammonium concentration by brute force method (BF) and DDM; the unit of concentrations is mol/m³ of air except for water which is in kg/m³ of air.



Figure 2-9. Response of a sulfate rich, no free acid aerosol system to the change of total nitrate concentration by brute force method (BF) and DDM; the unit of concentrations is mol/m³ of air except for water which is in kg/m³ of air.



Figure 2-10. Response of a sulfate rich, free acid aerosol system to the change of total sulfate concentration by brute force method (BF) and DDM; the unit of concentrations is mol/m³ of air except for water which is in kg/m³ of air.


Figure 2-11. Response of a sulfate rich, free acid aerosol system to the change of total ammonium concentration by brute force method (BF) and DDM; the unit of concentrations is mol/m³ of air except for water which is in kg/m³ of air.



Figure 2-12. Response of a sulfate rich, free acid aerosol system to the change of total nitrate concentration by brute force method (BF) and DDM; the unit of concentrations is mol/m³ of air except for water which is in kg/m³ of air.

2.8. Stand-Alone Testing – Comprehensive

When a solution phase exists in ISORROPIA, the solution regime is divided into many sub-cases with different sets of possible solid and ion species, which reduces the complexity of the system for ISORROPIA to solve. The sub-cases are divided by the sulfate ratio (the ratio of total ammonium and sodium to total sulfate) and the relative humidity (RH). In this comprehensive test, three possible aerosol types were tested with RH range of 25% to 95% (with increments of 5%). Temperature was set to 298 °K.

Sulfate poor (sulfate ratio greater than 2)

$= 1.0 \times 10^{-9} \text{ mol/m}^3$
$= 1.0 \times 10^{-7} \text{ mol/m}^3$
$= 2.5 \times 10^{-7} \text{ mol/m}^3$
$= 2.0 \times 10^{-7} \text{ mol/m}^3$
$= 1.0 \times 10^{-9} \text{ mol/m}^3$

Sulfate rich, no free acid (sulfate ratio between 1 and 2)

Y ₀ (tNa)	$= 1.0 \times 10^{-9} \text{ mol/m}^3$
$Y_0(tSO_4)$	$= 1.0 \times 10^{-7} \text{ mol/m}^3$
$Y_0(tNH_4)$	$= 1.7 \times 10^{-7} \text{ mol/m}^3$
$Y_0(tNO_3)$	$= 2.0 \times 10^{-7} \text{ mol/m}^3$
Y ₀ (tCl)	$= 1.0 \times 10^{-9} \text{ mol/m}^3$

Sulfate rich, free acid (sulfate ratio less than 1)

Y ₀ (tNa)	$= 1.0 \times 10^{-9} \text{ mol/m}^3$
$Y_0(tSO_4)$	$= 2.0 \times 10^{-7} \text{ mol/m}^3$
$Y_0(tNH_4)$	$= 1.7 \times 10^{-7} \text{ mol/m}^3$
$Y_0(tNO_3)$	$= 2.0 \times 10^{-7} \text{ mol/m}^3$
Y ₀ (tCl)	$= 1.0 \times 10^{-9} \text{ mol/m}^3$

2.9. Test Results – Comprehensive

Figures 2-13 to 2-15 show the sensitivity coefficients predicted by the BF method and DDM. The sensitivity coefficient, s, is estimated by the BF method as follows:

$$s = \frac{\partial Y_1(A)}{\partial p}\Big|_{p=0} \cong \frac{Y_1(A)\Big|_{p=0.1} - Y_1(A)\Big|_{p=-0.1}}{0.2}$$
(2.21)

In most cases, the DDM agrees well with the BF method. For the sulfate poor system, however, there are two RH's (65% and 70%) where the DDM and BF don't agree well (indicated by red and blue arrows in Figure 2-13). For both these RH's, the systems at p = -0.1 and p = 0.1 fall into different sub-cases in ISORROPIA (Table 2-1). The NH₃, HNO₃, and water concentrations as a function of p apparently change slope between p = -0.1 and p = 0.1, and consequently the

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sensitivity coefficient predicted by the DDM at p = 0 does not agree well with that estimated by the BF method using Eq. (2.21). The change in slope of the concentrations as a function of p between the two sub-cases could reflect actual abrupt changes in the equilibrium concentrations or could reflect limitations in the assumptions used in ISORROPIA to define and solve the different sub-cases.

Input Change	RH (%)	Sub-cases		
		p = -0.1	p = 0.1	
Total SO4	65	G2S1 (solid & liquid possible)	G2S2 (solid only)	
Total NH4	65	G2S2 (solid only)	G2S1 (solid & liquid possible)	
	70	G2S2 (solid only)	G2S1 (solid & liquid possible)	
Total NO3	65	G2S1 (solid & liquid possible)	G2S2 (solid only)	

|--|

For the sulfate rich, no free acid system, the sensitivity coefficients of HNO₃ predicted by the DDM and BF differ at RH =95% (indicated by red arrows in Figure 2-14). This is due to ISORROPIA's assumption that the dissolution of HNO₃ in this regime is minor. This discrepancy has been explained in Section 2.7. Normally this assumption holds and the DDM and BF agree well, but at high relative humidity, the discrepancy might be more noticeable as happens here at RH =95%.



Figure 2-13. Sensitivity coefficients of a sulfate poor system to the change of total SO4 (a), total NH3 (b), and total NO3 (c) predicted by BF and DDM; the units are μ mol/m³ except for water which is in mg/m³; the red and blue arrows indicate RH = 65% and 70%, respectively.



Figure 2-14. Sensitivity coefficients of a sulfate rich, no free acid system to the change of total SO4 (a), total NH3 (b), and total NO3 (c) predicted by BF and DDM; the units are μ mol/m³ except for water which is in mg/m³; the red arrows indicate RH = 95%.



Figure 2-15. Sensitivity coefficients of a sulfate rich, free acid system to the change of total SO4 (a), total NH3 (b), and total NO3 (c) predicted by BF and DDM; the units are μ mol/m³ except for water which is in mg/m³.

3. IMPLEMENTING THE DDM IN RADM-AQ

The aqueous phase chemistry module RADM-AQ (Chang et al., 1987) models SO_2 oxidation reactions in cloud water. The RADM-AQ code was analyzed to develop equations defining the sensitivities of species output concentrations to input concentrations. These sensitivity equations were implemented and tested.

3.1. Interface between CAMx and RADM-AQ

RADM-AQ has its own internal species that are mapped to CAMx species by an interface module. A corresponding interface module is required for sensitivity coefficients.

RADM-AQ has 24 internal species: 11 gas species represented as partial pressure in atmospheres (atm) and 13 aerosol species represented as molarity (M). RADM-AQ also takes ambient temperature, pressure and cloud water content as inputs. The input concentrations of RADM-AQ species (left-hand side) are related to CAMx species (right-hand side) as follows:

RADM-AQ gas species in atm

$Y_0(SO_2)$	$= Y_0(cSO_2) * 10^{-6} * P_{atm}$	
$Y_0(HNO_3)$	$= Y_0(cHNO_3) * 10^{-6} * P_{atm}$	
$Y_0(N_2O_5)$	$= 0.5 * Y_0(cN_xO_y) * 10^{-6} * P_{atm}$	
$Y_0(CO_2)$	$= C(CO_2) * 10^{-6} * P_{atm}$	
$Y_0(NH_3)$	$= Y_0(cNH_3) * 10^{-6} * P_{atm}$	
$Y_0(H_2O_2)$	$= Y_0(cH_2O_2) * 10^{-6} * P_{atm}$	(3.1a)
$Y_0(O_3)$	$= Y_0(cO_3) * 10^{-6} * P_{atm}$	
Y ₀ (FOA)	$= C(FOA) * 10^{-6} * P_{atm}$	
$Y_0(MHP)$	$= C(MHP) * 10^{-6} * P_{atm}$	
$Y_0(PAA)$	$= C(PAA) * 10^{-6} * P_{atm}$	
$Y_0(H_2SO_4)$	$= Y_0(cH_2SO_4) * 10^{-6} * P_{atm}$	

RADM-AQ aerosol species in M (mol of solute/liter of solution)

$Y_0(SO_4)$ $Y_0(NH_4)$ $Y_0(NO_2)$	$= [(Y_0(cSO_4) / Mw) / w_L] * 10^{-9}$ = [(Y_0(cNH_4) / Mw) / w_L] * 10^{-9} = [(Y_0(cNO_2) / Mw) / w_L] * 10^{-9}	
$Y_0(Ca)$	$= [(C(CaCO_3) / Mw) / w_L] * 10^{-9}$ = [(C(CaCO_3) / Mw) / w_L] * 10^{-9}	
$Y_0(Mg)$ $Y_0(CO_3)$	$= [(C(MgCO_3) / Mw) / w_L] * 10^{9}$ = [(C(CaCO_3) / Mw + C(MgCO_3) / Mw) / w_L] * 10^{9}	
$Y_0(Na)$	= $[(C(NaCl) / Mw) / w_L] * 10^{-9}$	(3.1b)
$Y_0(K)$ $Y_0(Cl)$	$= [(C(PotCl) / Mw) / w_L] * 10^{-9}$ = [(C(NaCl) / Mw + C(KCl) / Mw) / w_L] * 10^{-9}	
$Y_0(Fe)$	$= [(C(A_3Fe) / Mw) / w_L] * 10^9$	
$Y_0(Mn)$	$= [(C(B_2Mn) / Mw) / w_L] * 10^{-9}$	
$Y_0(A)$	$= 3 * [(C(A_3Fe) / Mw) / w_L] * 10^{-9}]$	
$Y_0(B)$	$= 2 * [(C(B_2Mn) / Mw) / w_L] * 10^{-9}$	

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where w_L is the liquid water mixing ratio (volume water/volume air) and C represents a background (constant) concentration. FOA is formic acid, MHP is methyl hydroperoxide, and PAA is peroxyacetic acid. A and B are arbitrary counter ions to Fe(III) and Mn(II), respectively. If Na and Cl are modeled species, $C(NaCl) = MIN(Y_0(Na), Y_0(Cl))$.

The final concentrations of the internal species determined by RADM-AQ (right-hand side) are mapped back to CAMx species (left-hand side) by the following formulas:

CAMx gas species in ppm

$Y_1(cSO_2)$	$= (Y_1(SO_2) + Y_1(S(IV)) * w_LRT) * 10^6 / P_{atm}$	
$Y_1(cH_2O_2)$	$= (Y_1(H_2O_2) + Y_1(H_2O_2(aq)) * w_LRT) * 10^6 / P_{atm}$	
$Y_1(cO_3)$	$= (Y_1(O_3) + Y_1(O_3(aq)) * w_LRT) * 10^6 / P_{atm}$	
$Y_1(cNH_3)$	$= Y_1(NH_3) * 10^6 / P_{atm}$	(3.2a)
$Y_1(cHNO_3)$	$= Y_1(HNO_3) * 10^6 / P_{atm}$	
$Y1(cN_xO_y)$	= 0	
$Y1(cH_2SO_4)$	= 0	

CAMx aerosol species in $\mu g/m^3$ of air

$Y_1(cSO_4)$	$= (Y_1(HSO_4^{-}) + Y_1(SO_4^{2-})) * 10^9 * w_L * Mw$	
$Y_1(cNH_4)$	$= (Y_1(NH_4^+) + Y_1(NH_3(aq))) * 10^9 * w_L * Mw$	(3.2b)
$Y_1(cNO_3)$	$= (Y_1(NO_3^-) + Y_1(HNO_3(aq))) * 10^9 * w_L * Mw$	

Differentiating Eq. (3.1) with respect to a parameter p gives $S_0(RADM-AQ$ species) as a function of $S_0(CAMx$ species). Differentiating Eq. (3.2) with respect to p gives $S_1(CAMx$ species) as a function of $S_1(RADM-AQ$ species). $S = \partial Y/\partial p$.

Note that S_0 is zero for species with constant initial concentrations. Furthermore, S_1 is always zero for species that have constant concentrations throughout the RADM-AQ step. The concentrations of K, Fe, Mn, A, B, Na, and Cl are constant throughout the RADM-AQ step.

3.2. Gas-Aqueous Partitioning with Dissociation

The gas-aqueous phase equilibrium equations consist of dissolution equations and dissociation (ionization) equations:

Sulfur dioxide

$$SO_2(g) \leftrightarrow SO_2(aq)$$
 $H_{SO_2} = \frac{Y_1(SO_2(aq))}{Y_1(SO_2)}$ (3.3a)

$$SO_{2}(aq) \leftrightarrow H^{+} + HSO_{3}^{-}$$
 $K_{s1} = \frac{Y_{1}(H^{+})Y_{1}(HSO_{3}^{-})\gamma_{H^{+}}\gamma_{HSO_{3}^{-}}}{Y_{1}(SO_{2}(aq))}$ (3.3b)

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$$HSO_{3}^{-} \leftrightarrow H^{+} + SO_{3}^{2-} \qquad \qquad K_{s2} = \frac{Y_{1}(H^{+})Y_{1}(SO_{3}^{2-})\gamma_{H^{+}}\gamma_{SO_{3}^{2-}}}{Y_{1}(HSO_{3}^{-})\gamma_{HSO_{3}^{-}}}$$
$$= \frac{Y_{1}(H^{+})Y_{1}(SO_{3}^{2-})\gamma_{SO_{3}^{2-}}}{Y_{1}(HSO_{3}^{-})} \qquad (3.3c)$$

Activity coefficients for un-dissociated molecules are usually assumed to be 1. RADM-AQ uses the Davies equation where activity coefficients for ions with the same absolute charge are assumed to be identical.

Carbon dioxide

$$CO_2(g) \leftrightarrow CO_2(aq)$$
 $H_{CO_2} = \frac{Y_1(CO_2(aq))}{Y_1(CO_2)}$ (3.3d)

$$CO_2(aq) \leftrightarrow H^+ + HCO_3^ K_{c1} = \frac{Y_1(H^+)Y_1(HCO_3^-)\gamma_{H^+}\gamma_{HCO_3^-}}{Y_1(CO_2(aq))}$$
 (3.3e)

$$HCO_{3}^{-} \leftrightarrow H^{+} + CO_{3}^{2-} \qquad \qquad K_{c2} = \frac{Y_{1}(H^{+})Y_{1}(CO_{3}^{2-})\gamma_{H^{+}}\gamma_{CO_{3}^{2-}}}{Y_{1}(HCO_{3}^{-})\gamma_{HCO_{3}^{-}}}$$
$$= \frac{Y_{1}(H^{+})Y_{1}(CO_{3}^{2-})\gamma_{CO_{3}^{2-}}}{Y_{1}(HCO_{3}^{-})} \qquad (3.3f)$$

Nitric acid

$$HNO_{3}(g) \leftrightarrow HNO_{3}(aq) \qquad \qquad H_{HNO_{3}} = \frac{Y_{1}(HNO_{3}(aq))}{Y_{1}(HNO_{3})}$$
(3.3g)

$$HNO_{3}(aq) \leftrightarrow H^{+} + NO_{3}^{-}$$
 $K_{n} = \frac{Y_{1}(H^{+})Y_{1}(NO_{3}^{-})\gamma_{H^{+}}\gamma_{NO_{3}^{-}}}{Y_{1}(HNO_{3}(aq))}$ (3.3h)

Ammonia

$$NH_{3}(g) \leftrightarrow NH_{3}(aq) \qquad H_{NH_{3}} = \frac{Y_{1}(NH_{3}(aq))}{Y_{1}(NH_{3})}$$
(3.3i)

$$NH_{3}(aq) \leftrightarrow NH_{4}^{+} + OH^{-} \qquad K_{a} = \frac{Y_{1}(NH_{4}^{+})Y_{1}(OH^{-})\gamma_{NH_{4}^{+}}\gamma_{OH^{-}}}{Y_{1}(NH_{3}(aq))}$$

$$K_{w} = Y_{1}(H^{+})Y_{1}(OH^{-})\gamma_{H^{+}}\gamma_{OH^{-}} \implies = \frac{Y_{1}(NH_{4}^{+})\gamma_{NH_{4}^{+}}K_{w}}{Y_{1}(NH_{3}(aq))Y_{1}(H^{+})\gamma_{H^{+}}}$$

$$= \frac{Y_{1}(NH_{4}^{+})K_{w}}{Y_{1}(NH_{3}(aq))Y_{1}(H^{+})}$$
(3.3j)



Formic acid (FOA)

$$HCOOH(g) \leftrightarrow HCOOH(aq) \qquad H_{FOA} = \frac{Y_1(FOA(aq))}{Y_1(FOA)}$$
(3.3k)
$$HCOOH(aq) \leftrightarrow H^+ + HCOO^- \qquad K_f = \frac{Y_1(H^+)Y_1(HCO_2^-)\gamma_{H^+}\gamma_{HCO_2^-}}{Y_1(FOA(aq))}$$
(3.3l)

Sulfate and bisulfate (S(VI))

$$HSO_{4}^{-} \leftrightarrow H^{+} + SO_{4}^{2-} \qquad K_{s3} = \frac{Y_{1}(H^{+})Y_{1}(SO_{4}^{2-})\gamma_{H^{+}}\gamma_{SO_{4}^{2-}}}{Y_{1}(HSO_{4}^{-})\gamma_{HSO_{4}^{-}}}$$
$$= \frac{Y_{1}(H^{+})Y_{1}(SO_{4}^{2-})\gamma_{SO_{4}^{2-}}}{Y_{1}(HSO_{4}^{-})} \qquad (3.3m)$$

Mass balance equations

$$\begin{aligned} Y_{0}(SO_{2}) + dY(S(IV))w_{L}RT &= Y_{1}(SO_{2}) + \left[Y_{1}(SO_{2}(aq)) + Y_{1}(HSO_{3}^{-}) + Y_{1}(SO_{3}^{2-})\right]w_{L}RT \\ Y_{0}(CO_{2}) + Y_{0}(CO_{3})w_{L}RT &= Y_{1}(CO_{2}) + \left[Y_{1}(CO_{2}(aq)) + Y_{1}(HCO_{3}^{-}) + Y_{1}(CO_{3}^{2-})\right]w_{L}RT \\ Y_{0}(HNO_{3}) + 2Y_{0}(N_{2}O_{5}) + Y_{0}(NO_{3})w_{L}RT &= Y_{1}(HNO_{3}) + \left[Y_{1}(HNO_{3}(aq)) + Y_{1}(NO_{3}^{-})\right]w_{L}RT \\ Y_{0}(NH_{3}) + Y_{0}(NH_{4})w_{L}RT &= Y_{1}(NH_{3}) + \left[Y_{1}(NH_{3}(aq)) + Y_{1}(NH_{4}^{+})\right]w_{L}RT \\ Y_{0}(FOA) &= Y_{1}(FOA) + \left[Y_{1}(FOA(aq)) + Y_{1}(HCO_{2}^{-})\right]w_{L}RT \end{aligned}$$
(3.4)

dY(S(IV)) is determined by the oxidation reactions described in Section 3.4, below. Initially, dY(S(IV)) is set to 0.

Charge balance equation

$$Y_{1}(H^{+}) + Y_{1}(NH_{4}^{+}) + 2Y_{0}(Ca) + 2Y_{0}(Mg) = 2Y_{1}(CO_{3}^{2-}) + 2Y_{1}(SO_{3}^{2-}) + 2Y_{1}(SO_{4}^{2-}) + Y_{1}(HCO_{3}^{-}) + Y_{1}(HSO_{3}^{-}) + Y_{1}(NO_{3}^{-}) + Y_{1}(HSO_{4}^{-}) + Y_{1}(HCO_{2}^{-}) + \frac{K_{w}}{Y_{1}(H^{+})\gamma_{H^{+}}\gamma_{OH^{-}}}$$
(3.5)

Na, K, Cl, Fe, Mn, A, and B are not included in the charge balance equation since they always cancel each other out: $Y_0(Na)+Y_0(K) = Y_0(Cl)$; $3Y_0(Fe) = Y_0(A)$; $2Y_0(Mn) = Y_0(B)$.

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Activity coefficients (Davies equation)

$$\log \gamma_{i} = -0.509 z_{i}^{2} \left(\frac{\sqrt{I}}{1 + \sqrt{I}} + 0.2I \right)$$

$$I = \frac{1}{2} \sum_{i} Y_{1}(A_{i}) z_{i}^{2}$$

$$= \frac{1}{2} \left[Y_{1}(H^{+}) + \frac{K_{w}}{Y_{1}(H^{+})\gamma_{H^{+}}\gamma_{OH^{-}}} + Y_{1}(NH_{4}^{+}) + Y_{1}(NO_{3}^{-}) + Y_{1}(HCO_{3}^{-}) + Y_{1}(HSO_{3}^{-}) + Y_{1}(HSO_{4}^{-}) + Y_{1}(HCO_{2}^{-}) + Y_{0}(Na) + Y_{0}(K) + Y_{0}(Cl) + Y_{0}(A) + Y_{0}(B) + 9Y_{0}(Fe) + 4 \left(Y_{1}(CO_{3}^{2-}) + Y_{1}(SO_{3}^{2-}) + Y_{1}(SO_{4}^{2-}) + Y_{0}(Ca) + Y_{0}(Mg) + Y_{0}(Mn) \right) \right]$$
(3.6)

Now there are 20 unknowns ($Y_1(SO_2)$, $Y_1(SO_2(aq))$, $Y_1(HSO_3^-)$, $Y_1(SO_3^{2^-})$, $Y_1(CO_2)$, $Y_1(CO_2(aq))$, $Y_1(HCO_3^-)$, $Y_1(CO_3^{2^-})$, $Y_1(HNO_3)$, $Y_1(HNO_3(aq))$, $Y_1(NO_3^-)$, $Y_1(NH_3)$, $Y_1(NH_3(aq))$, $Y_1(NH_4^+)$, $Y_1(FOA)$, $Y_1(FOA(aq))$, $Y_1(HCO_2^-)$, $Y_1(HSO_4^-)$, $Y_1(SO_4^{2^-})$, and $Y_1(H^+)$) and 20 equations ((3.3a) through (3.3m), (3.4), and (3.5)) in the equations of this section, which are solved by a double-bisection method. Eq. (3.6) is used to replace the γ_i 's in Eqs. (3.3) and (3.5) with the unknown quantities.

Differentiating Eqs. (3.3), (3.4) and (3.5) with respect to p leads to 20 linear equations involving S_1 's and $\partial \gamma_i / \partial p$'s. The $\partial \gamma_i / \partial p$'s are replaced with functions of the S_1 's by differentiating Eq. (3.6) with respect to p.

3.3. Gas-Aqueous Partitioning without Dissociation

The following species are assumed not to dissociate in the aqueous phase are thus solved independently using Henry's Law.

Hydrogen peroxide

 $Y_1(H_2O_2(aq)) = H_{H_2O_2}Y_1(H_2O_2)$ (3.7a)

$$Y_1(H_2O_2) = \frac{Y_0(H_2O_2) + R_1dt \ w_LRT}{1 + H_{H_2O_2}w_LRT}$$
(3.7b)

Ozone

$$Y_1(O_3(aq)) = H_{O_3}Y_1(O_3)$$
(3.7c)

$$Y_1(O_3) = \frac{Y_0(O_3) + R_2 dt \ w_L RT}{1 + H_{O_3} w_L RT}$$
(3.7d)

Methyl hydroxyperoxide (CH₃OOH)

$$Y_1(MHP(aq)) = H_{MHP}Y_1(MHP)$$
(3.7e)

$$Y_{1}(MHP) = \frac{Y_{0}(MHP) + R_{4}dt \ w_{L}RT}{1 + H_{MHP}w_{L}RT}$$
(3.7f)

Peroxyacetic acid (CH₃C(O)OOH)

$$Y_1(PAA(aq)) = H_{PAA}Y_1(PAA)$$

$$(3.7g)$$

$$Y_{1}(PAA) = \frac{Y_{0}(PAA) + R_{5}dt \ w_{L}RT}{1 + H_{PAA}w_{L}RT}$$
(3.7h)

R_idt is given by the individual oxidation reaction described in Section 3.4. Initially dt is set to 0.

Differentiating Eqs. (3.7) with respect to p gives S_1 's for H_2O_2 , $H_2O_2(aq)$, O_3 , $O_3(aq)$, MHP, MHP(aq), PAA, and PAA(aq).

3.4. Aqueous Reactions

RADM-AQ considers 5 oxidation reactions for S(IV):

S(IV) Oxidation by Hydrogen Peroxide

$$R_{1} = -k_{H_{2}O_{2}} \frac{Y_{1}(H_{2}O_{2}(aq))Y_{1}(SO_{2}(aq))}{0.1 + Y_{1}(H^{+})}$$
(3.8a)

S(IV) Oxidation by Dissolved Ozone

$$R_{2} = -4.19 \times 10^{5} \left(1 + \frac{2.39 \times 10^{-4}}{Y_{1}(H^{+})} \right) Y_{1}(O_{3}(aq)) Y_{1}(S(IV)) \qquad \text{pH} \ge 2.7$$
(3.8b)

$$R_{2} = -1.9 \times 10^{4} \frac{Y_{1}(O_{3}(aq))Y_{1}(S(IV))}{\sqrt{Y_{1}(H^{+})}} \qquad \text{pH} < 2.7 \qquad (3.8c)$$

S(IV) Oxidation by O₂ Catalyzed by Iron and Manganese

i) pH ≥ 4

$$R_{3} = -5.0 \times 10^{3} Y_{0}(Mn) Y_{1}(HSO_{3}^{-}) \qquad Y_{1}(S(IV)) \le 10^{-5} \qquad (3.8d)$$

$$R_{3} = -\left(\frac{4.7Y_{0}(Mn)^{2}}{Y_{1}(H^{+})} + 10^{7}Y_{0}(Fe)Y_{1}(S(IV))^{2}\right) \qquad Y_{1}(S(IV)) > 10^{-5} \qquad (3.8e)$$

ii) pH < 4

$$R_{3} = -3\left(5.0 \times 10^{3} Y_{0}(Mn)Y_{1}(HSO_{3}^{-}) + 0.82Y_{0}(Fe)\frac{Y_{1}(S(IV))}{Y_{1}(H^{+})}\right) \qquad Y_{1}(S(IV)) \le 10^{-5}$$
(3.8f)

$$R_{3} = -\left(\frac{4.7Y_{0}(Mn)^{2}}{Y_{1}(H^{+})} + 0.82Y_{0}(Fe)\frac{Y_{1}(S(IV))}{Y_{1}(H^{+})}\left(1 + 1.7 \times 10^{3}\frac{Y_{0}(Mn)^{1.5}}{6.3 \times 10^{-6} + Y_{0}(Fe)}\right)\right)$$
(3.8g)
$$Y_{1}(S(IV)) > 10^{-5}$$

S(IV) Oxidation by MHP

$$R_4 = -k_{MHP}Y_1(H^+)Y_1(MHP(aq))Y_1(HSO_3^-)$$
(3.8h)

S(IV) Oxidation by PAA

$$R_{5} = -k_{PAA} \left(1.65 \times 10^{-5} + Y_{1}(H^{+}) \right) Y_{1}(PAA(aq)) Y_{1}(HSO_{3}^{-})$$
(3.8i)

$$Y_1(S(IV)) = Y_1(SO_2(aq)) + Y_1(HSO_3^-) + Y_1(SO_3^{2-})$$
(3.8j)

$$dY(S(IV)) = (R_1 + R_2 + R_3 + R_4 + R_5)dt$$
(3.8k)

The integration time step (dt) is selected so that the limiting reactants will be decreased not more than 5-10% during dt. The gas-aqueous equilibria and aqueous reactions calculations are updated and repeated until the end time is reached (Figure 3-1).

Differentiating Eqs. (3.8) with respect to p gives dS(S(IV)) as well as $\partial R_i/\partial p$, which are then used in Sections 3.2 and 3.3. We use the same time step to solve for the sensitivities and the concentrations, which keeps the solutions for the concentrations and the sensitivities consistent. (This is also the same approach previously used to implement DDM for the gas-phase chemistry.)



Figure 3-1. Diagram of RADM-AQ solution procedure.

3.5. Stand-Alone Testing

The DDM algorithm described above was implemented in the RADM-AQ code and tested in a stand-alone model. The inputs for the test case are as follows:

Temp	= 298 K	Press	= 1 atm
Cloud water	$= 0.2 \text{ g/m}^3$	Δt	= 360 sec
SO_2	= 10 ppb	H_2O_2	= 1 ppb
O ₃	= 50 ppb		
TS $(H_2SO_4 + I)$	PSO ₄)	= 1 ppb	
$TN (N_xO_y + H)$	$INO_3 + PNO_3$)	= 2 ppb	
$TA (NH_3 + PI)$	NH ₄)	= 5 ppb (case 1) and 2 ppb	(case 2)
CO_2	= 330 ppm	FOA	= 1 ppt
MHP	= 1 ppt	PAA	= 1 ppt
NaCl	$= 0.05 \ \mu g/m^3$	KCl	$= 0.0 \ \mu g/m^3$
CaCO ₃	$= 0.0 \ \mu g/m^3$	MgCO ₃	$= 0.0 \ \mu g/m^3$
Fe(III)	$= 0.01 \ \mu g/m^3$	Mn(II)	$= 0.005 \ \mu g/m^3$

In CAMx, constant background concentrations are used for CO₂, FOA, MHP, PAA, KCl, CaCO₃, MgCO₃, Fe(III) and Mn(II). NaCl is also given a constant background concentration if Na and Cl are not modeling species.

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Since the aqueous-phase reactions are sensitive to pH, two test cases with different pH ranges were prepared. Figure 3-2 shows the hydrogen ion concentrations during the time step for the two test cases.



Figure 3-2. Changes in the hydrogen ion concentration for the test cases 1 and 2.

3.6. Test Results

Like ISORROPIA, RADM-AQ calculates concentrations for numerous species including many dissolved ions. Of those species, however, CAMx carries only SO₂, H₂O₂, O₃, H₂SO₄ and PSO₄ (while RADM-AQ also solves NH₃, HNO₃, NH₄⁺ and NO₃⁻, the changes of these species are always overridden in CAMx by ISORROPIA which re-partitions these species right after RADM-AQ). Furthermore, all H₂SO₄ is assumed to exist in the particle phase (PSO₄) by RADM-AQ, thus the sensitivity coefficient of H₂SO₄ is always zero after RADM-AQ. Therefore, test results are shown only for SO₂, H₂O₂, O₃, and PSO₄. Up to ±30% input changes were applied for SO₂, H₂O₂, O₃, and total sulfate (H₂SO₄ and PSO₄) using Eq. (2.19). Figures 3-3 to 3-10 show that the model responses predicted by the DDM agree well with those of the BF method as long as the responses are linear.



Figure 3-3. Output concentration responses to changing the SO₂ input concentration (p) predicted by BF and DDM for test case 1; the concentrations are in ppb except for PSO₄ which is in $\mu g/m^3$ of air.



Figure 3-4. Output concentration responses to changing the H_2O_2 input concentration (p) predicted by BF and DDM for test case 1; the concentrations are in ppb except for PSO₄ which is in $\mu g/m^3$ of air.



Figure 3-5. Output concentration responses to changing the O_3 input concentration (p) predicted by BF and DDM for test case 1; the concentrations are in ppb except for PSO₄ which is in $\mu g/m^3$ of air.



Figure 3-6. Output concentration responses to changing the total sulfate input concentration (p) predicted by BF and DDM for test case 1; the concentrations are in ppb except for PSO_4 which is in $\mu g/m^3$ of air.



Figure 3-7. Output concentration responses to changing the SO₂ input concentration (p) predicted by BF and DDM for test case 2; the concentrations are in ppb except for PSO₄ which is in $\mu g/m^3$ of air.



Figure 3-8. Output concentration responses to changing the H_2O_2 input concentration (p) predicted by BF and DDM for test case 2; the concentrations are in ppb except for PSO₄ which is in $\mu g/m^3$ of air.



Figure 3-9. Output concentration responses to changing the O_3 input concentration (p) predicted by BF and DDM for test case 2; the concentrations are in ppb except for PSO₄ which is in $\mu g/m^3$ of air.



Figure 3-10. Output concentration responses to changing the total sulfate input concentration (p) predicted by BF and DDM for test case 2; the concentrations are in ppb except for PSO₄ which is in μ g/m³ of air.

4. IMPLEMENTING THE DDM IN SOAP

The secondary organic aerosol (SOA) module SOAP (Strader et al., 1998, 1999) takes the total (gas plus aerosol) concentrations of CAMx SOA species in $\mu g/m^3$ of air and determines the equilibrium concentrations in the gas and aerosol phases. SOAP assumes that semi-volatile organics form a liquid aerosol phase that can be described as a pseudo-ideal solution. SOAP also requires ambient temperature and primary organic aerosol (POA) concentration (in $\mu g/m^3$ of air) as additional inputs.

4.1. Organic Pseudo-Ideal Solution

We consider the partitioning of N condensable organic species (products of the photo-oxidation of hydrocarbon precursors) between gas and aerosol phases. Each product satisfies the mass balance:

$$Y_1(A_i) + Y_1(G_i) = Y_0(A_i) + Y_0(G_i)$$
(4.1)

where G_i and A_i represent species i in gas and aerosol phases, respectively.

Assuming that the organic compounds form a pseudo-ideal solution when they condense, a set of N equations is obtained:

$$Y_{1}(A_{i}) + x_{i}C_{i} = Y_{0}(A_{i}) + Y_{0}(G_{i})$$

$$x_{i} = \frac{Y_{1}(A_{i})}{\sum_{j} Y_{1}(A_{j}) + Y_{0}(POA)}$$
(4.2)

where C_i is effective saturation concentration of species i. POA is assumed to exist only in the aerosol phase.

Differentiating Eq. (4.2) with respect to input parameter p gives:

$$S_{1}(A_{i}) + C_{i} \left[\frac{S_{1}(A_{i})}{\sum_{j} Y_{1}(A_{j}) + Y_{0}(POA)} - Y_{1}(A_{i}) \frac{\sum_{j} S_{1}(A_{j}) + S_{0}(POA)}{\left(\sum_{j} Y_{1}(A_{j}) + Y_{0}(POA)\right)^{2}} \right] = S_{0}(A_{i}) + S_{0}(G_{i}) \quad (4.3)$$

$$i = 1, ..., N$$

where $S_1 = \partial Y_1 / \partial p$ and $S_0 = \partial Y_0 / \partial p$. Solving the set of Eqs. (4.3) gives the $S_1(A_i)$'s.

For the gas-phase species,

$$S_1(G_i) = S_0(A_i) + S_0(G_i) - S_1(A_i)$$
(4.4)

4.2. Stand-Alone Testing

The sensitivity equations derived in the previous section were implemented in the SOAP code and tested in a stand-alone model. CAMx version 4.20 includes 5 SOA species formed from oxidation of organic gases: low-volatile products from aromatics (SOA1), high-volatile products from aromatics (SOA2), products from alkanes (SOA3), products from terpenes (SOA4), and products from cresols (SOA5). The physical properties of the SOA species are shown in Table 4-1.

Condensable Precursor Saturation Heat of Molecular **Gas Species** Concentration vaporization Weight (µg m⁻³ at 298 K) (kJ mole⁻¹) (g mole⁻¹) SOA1 Aromatics 1.9 156.25 150 156.25 150 SOA2 Aromatics 56 SOA3 Alkanes 0.007 150 0 SOA4 Terpenes 800.0 0 180 0 150 SOA5 Cresols 0.007

Table 4-1. Properties of secondary organic aerosol species SOA1 - SOA5.

The inputs for the test case are as follows:

Temp = 298 KtSOA1 = 0.15 ppb = 0.92 μ g/m³ tSOA2 = 0.55 ppb = 3.4 μ g/m³ tSOA3 = 0.02 ppb = 0.12 μ g/m³ tSOA4 = 0.50 ppb = 3.7 μ g/m³ tSOA5 = 0.05 ppb = 0.31 μ g/m³ POA = 5 μ g/m³

where tSOA represents total (gas and aerosol) SOA concentration. The sensitivities to input parameter p in Eq. (2.19) were calculated by the DDM and BF method.

4.3. Test Results

Figures 4-1 to 4-4 show the model responses to the changes in tSOA1, tSOA2, tSOA4, and POA predicted by the BF method and DDM. The model responses are mostly linear within the tested range of the input changes (-30% to +30%) and the DDM agrees almost perfectly with the BF method. The results for changes in tSOA3 and tSOA5 are similar to others and are not shown here.



Figure 4-1. Responses of aerosol SOA species concentraions (μ g/m³) to changing the total SOA1 concentration predicted by BF and DDM.

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Figure 4-2. Responses of aerosol SOA species concentraions (μ g/m³) to changing the total SOA2 concentration predicted by BF and DDM.



Figure 4-3. Responses of aerosol SOA species concentraions (μ g/m³) to changing the total SOA4 concentration predicted by BF and DDM.



Figure 4-4. Model responses of SOA species to the change of POA concentration predicted by BF and DDM; the concentrations are in μ g/m³ of air.

5. TESTING THE DDM WITH FULL 3-D CAMx

The DDM implementations developed for three PM modules (see Sections 2-4) were incorporated into CAMx version 4.20 (ENVIRON, 2005). The complete model was then applied for a 2-day test case for June 2002 and the Eastern US, and sensitivities computed by the DDM were compared to the brute-force (BF) method.

5.1. CAMx 3-D Test Case

The test case used here is the June 13-14 2002 simulation for the Midwest Regional Planning Organization $(MRPO)^1$ with a 36 km grid covering the Eastern US. There are 97 × 90 cells in the horizontal grid and 14 vertical layers. The sensitivities to the emissions of NOx, VOC (anthropogenic and biogenic), SO₂, NH₃, primary particulate sulfate (PSO₄), primary particulate nitrate (PNO₃) and primary organic (POA) aerosols were tested. To calculate the brute-force sensitivity coefficients, the standard model was run repeatedly with emissions increased and decreased by 10% and the following equation was used:

$$S_{ij}(BF) = \frac{C_i(1.1 \times E_j) - C_i(0.9 \times E_j)}{0.2}$$
(5.1)

where $S_{ij}(BF)$ is the brute-force sensitivity of species *i* to the emissions of species *j* and $C_i(E_j)$ is the predicted concentration of species *i* by the simulation with the emissions of species *j* changed. The changes in emissions are assigned uniformly in time and space.

5.2. Results – No Deposition

Deposition processes were turned off in the first test to focus on evaluating the performance of the newly developed DDM implementations for PM chemistry.

Ozone sensitivity

Figures 5-1 and 5-2 show the 24-hr average sensitivities of ozone in the surface layer to emissions of NO_x and VOC, respectively. The agreement between the DDM and BF method for the spatial distribution of the sensitivities is very good. The average absolute difference between the DDM and BF sensitivities is less than 0.4 ppb in all cases (Table 5-1), which is similar to the result of the previous study of the DDM implementation for ozone in CAMx (Dunker et al., 2002). It is unlikely that the PM chemistry in CAMx significantly affects ozone concentrations since there are only a few feedbacks from the PM-related species to ozone chemistry (e.g., HNO₃ + OH \rightarrow NO₃; SO₂ + OH \rightarrow H₂SO₄ + HO₂). Indeed, the sensitivities of ozone to SO₂, NH₃, PSO₄, PNO₃, and POA emissions are relatively small.

¹ http://www.ladco.org/mrpo.html

PM sensitivity

Figures 5-3 to 5-17 show the 24-hr average sensitivities of PM species in the surface layer to the emissions of several species. The agreement between the DDM and BF method is quite good considering the inherent non-linearity in the PM modules (e.g., the assumption of the sub-cases in ISORROPIA discussed in Section 2). The average absolute difference between the DDM and BF sensitivities is less than $0.2 \ \mu g/m^3$ in most cases (Table 5-1).

Emission	Average absolute value of difference ^a				
perturbed	Ozone (ppb)	PSO₄ (µg/m³)	PNO ₃ (μg/m ³)	PNH₄ (µg/m³)	SOA (μg/m³)
NOx	0.32 (30.0)	0.054 (1.4)	0.42 (7.6)	0.082 (1.5)	0.005 (0.41)
VOC	0.13 (17.0)	0.021 (0.64)	0.19 (2.1)	0.037 (0.47)	0.003 (1.8)
SO2	0.013 (0.51)	0.058 (3.0)	0.26 (1.5)	0.053 (0.53)	0.0001 (0.002)
NH3	0.033 (0.32)	0.092 (0.84)	0.73 (7.6)	0.16 (2.7)	0.0001 (0.001)
PSO4	0.0008 (0.002)	0.003 (0.11)	0.050 (0.068)	0.010 (0.024)	6.e-6 (9.e-6)
PNO3	0.0004 (0.001)	0.0004 (0.001)	0.006 (0.010)	0.001 (0.002)	3.e-6 (7.e-6)
POA	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	3.e-5 (0.033)

^a averaged over those grid cells in the surface layer and hours with ozone concentrations above 80 ppb or individual PM species concentrations above 1 μ g/m³; the average absolute value of the DDM sensitivity is given in parentheses.

The sensitivity of nitrate aerosol shows the largest differences. For cases with average absolute DDM sensitivity above $0.1 \ \mu g/m^3$, the average absolute difference is less than 10% of the average absolute DDM sensitivity except for the sensitivity of PSO₄ to NH₃ emissions (11%) and the sensitivity of PNO₃ to SO₂ emissions (17%).

The DDM sensitivities of SOA (SOA1+SOA2+SOA3+SOA4+SOA5) agree with the BF sensitivities more closely than those of PSO_4 , PNO_3 and PNH_4 , which is expected because the SOAP module displayed less non-linearity in stand-alone testing than either ISORROPIA or RADM-AQ. For SOA, the average absolute difference is less than 2% of the average absolute DDM sensitivity in all cases with average absolute DDM sensitivity above 0.01 μ g/m³.

The sensitivities of PSO₄, PNO₃, and PNH₄ to the changes in primary sulfate and nitrate particle emissions are small as they are mostly secondary, and their sensitivities to the changes in primary organic aerosols are zero. The sensitivities of SOA to the changes in SO₂, NH₃, and primary sulfate and nitrate particle emissions are also negligible.

Computational Efficiency

Table 5-2 shows the CPU times for DDM runs with different numbers of sensitivities as well as the standard CAMx run on a Linux PC with a 2.2 GHz processor. Interestingly, DDM shows slightly better efficiency than in the previous study of the DDM implementation in CAMx (gasphase chemistry only) where the normalized time per sensitivity parameter was reported as 1.59, 1.04, and 0.70 for 1, 2, and 5 sensitivity parameters, respectively (Dunker et al., 2002a). The improved efficiency of DDM is probably because PM chemistry is the most time-consuming processes in CAMx offering the greatest potential for efficiency in DDM. In general, DDM is more efficient for the PM processes because the concentration algorithms require iterative solutions whereas the DDM algorithms do not require iteration. However, since a large number of PM sensitivities are added, the I/O burden for writing output files is increased by DDM.



No. of sensitivity	Total CPU time	Time per parameter ^b
parameters	(min/simulation-day)	
0 ^c	30.7	
1	73.6	1.40
2	89.5	0.96
4	118.1	0.71
8	179.2	0.60

Table 5-2. CPU time for CAMx simulation without deposition and varying numbers of sensitivities determined by the DDM^a.

^a Based on a Linux PC with a 2.2 GHz processor ^b Normalized to time required for standard CAMx:

$$\frac{T_n - T_0}{nT_0}$$

where T_n is the total CPU time to calculate the concentrations and sensitivities for *n* parameters together and T_0 is the time for the concentrations only (standard CAMx run).

^c Standard CAMx run



Figure 5-1. 24-hr average sensitivity of O_3 to NO_x emissions on June 14, 2002 predicted by DDM and BF methods.





Figure 5-3. 24-hr average sensitivity of PSO_4 to NO_x emissions on June 14, 2002 predicted by DDM and BF methods.





Figure 5-5. 24-hr average sensitivity of PSO_4 to SO_2 emissions on June 14, 2002 predicted by DDM and BF methods.





Figure 5-7. 24-hr average sensitivity of PNO_3 to NO_x emissions on June 14, 2002 predicted by DDM and BF methods.

Figure 5-8. 24-hr average sensitivity of PNO_3 to VOC emissions on June 14, 2002 predicted by DDM and BF methods.



Figure 5-9. 24-hr average sensitivity of PNO_3 to SO_2 emissions on June 14, 2002 predicted by DDM and BF methods.





 PNH_4 to NO_x emissions on June 14, 2002 predicted by DDM and BF methods.

Figure 5-12. 24-hr average sensitivity of PNH_4 to VOC emissions on June 14, 2002 predicted by DDM and BF methods.



PNH₄ to SO₂ emissions on June 14, 2002 predicted by DDM and BF methods.

Figure 5-14. 24-hr average sensitivity of PNH₄ to NH₃ emissions on June 14, 2002 predicted by DDM and BF methods.


Figure 5-15. 24-hr average sensitivity of SOA to NO_x emissions on June 14, 2002 predicted by DDM and BF methods.

Figure 5-16. 24-hr average sensitivity of SOA to VOC emissions on June 14, 2002 predicted by DDM and BF methods.



5.3. Results – Full CAMx

The DDM algorithms for wet and dry deposition were updated for PM species and then full CAMx testing was performed. Tests that included deposition but not chemistry found good agreement between DDM and BF sensitivities. The test case is the same as described in Section 5.1.

DDM vs. BF sensitivities

Figures 5-18 to 5-34 show the 24-hr average sensitivities of ozone and fine PM species in the surface layer to various emissions. Figures 5-18 to 5-34 are the same as Figures 5-1 to 5-17 except that this time they show the results of full CAMx testing. The agreement between the DDM and BF method for the spatial distribution of the sensitivities is similar to that of the "no-deposition" testing.

The average absolute difference between the DDM and BF sensitivities is shown in Table 5-3. Since tests that included deposition but not chemistry found good agreement between DDM and BF sensitivities, the poorer agreement for PM species is not due to simple errors in the implementations of DDM for deposition. The differences between the DDM and BF sensitivities with deposition become larger than for the no-deposition testing when average sensitivity is small. This may indicate a non-trivial impact of particle size on the deposition velocity, i.e., there are interactions between chemistry changing particle sizes and deposition rates. The particle dry deposition velocity and wet scavenging rate depend on particle size as well as environmental factors. If a particle absorbs significant amount of water, it will change particle density and diameter, which in turn affect deposition velocity (or scavenging rate if wet deposition). However, the current DDM code assumes that the particle size impact is negligible, which simplifies the implementation of the DDM in the wet/dry deposition modules because the sensitivity equations then take the same form as the concentration equations. Further tests are needed to clearly understand this issue.

Another series of plots presented in Appendix B show scatter plots for the DDM vs. BF method for CAMx runs with and without deposition. The scatter plots show the 24-hr average sensitivities for all grid cells in the surface layer. It should be noted that although the degree of agreement between the DDM and BF method is slightly worse with deposition included, the agreement between the two methods is still in a reasonable range.

Emission	Average absolute value of difference ^a				
perturbed	Ozone (ppb)	PSO4 (μg/m ³)	PNO3 (μg/m ³)	PNH4 (μg/m ³)	SOA (μg/m³)
NOx	0.19 (31.)	0.067 (0.90)	0.69 (6.0)	0.15 (1.1)	0.007 (0.40)
VOC	0.17 (20.)	0.034 (0.42)	0.30 (1.6)	0.067 (0.37)	0.005 (1.6)
SO2	0.012 (0.19)	0.082 (2.0)	0.31 (0.88)	0.085 (0.62)	9.e-4 (0.002)
NH3	0.008 (0.027)	0.10 (0.59)	1.1 (6.0)	0.25 (1.9)	0.001 (4.e-4)
PSO4	2.e-4 (4.e-4)	0.003 (0.12)	0.046 (0.057)	0.010 (0.040)	2.e-4 (5.e-6)
PNO3	1.e-4 (3.e-4)	6.e-4 (7.e-4)	0.007 (0.010)	0.001 (0.002)	5.e-6 (3.e-6)
POA	1.e-4 (0.0)	8.e-4 (0.0)	0.002 (0.0)	8.e-4 (0.0)	6.e-4 (0.026)

 Table 5-3. Difference between DDM and BF sensitivities on June 14, 2002 for full 3-D tests.

^a averaged over those grid cells in the surface layer and hours with ozone concentrations above 80 ppb or individual PM species concentrations above 1 μ g/m³; the average absolute value of the DDM sensitivity is given in parentheses.

Computational Efficiency

Table 5-4 gives the CPU times for the DDM runs with different numbers of sensitivities as well as the standard CAMx run on a Linux PC with a 2.1 GHz processor. This time the CAMx tests were performed with the deposition modules turned on. As expected, the result is almost the same as that of the previous testing.

Table 5-4. CPU time for fu	III CAMx simulation	(including deposition)	and varying numbers of
sensitivities determined by	[,] the DDM ^a .		

No. of sensitivity	Total CPU time	Time per parameter ^b	
parameters	(min/simulation-day)		
0 ^c	32.3		
1	78.8	1.44	
2	93.6	0.95	
4	124.3	0.71	
8	194.5	0.63	

^a Based on a Linux PC with a 2.1 GHz processor ^b Normalized to time required for standard CAMx:

$$\frac{T_n - T_0}{nT_0}$$

where T_n is the total CPU time to calculate the concentrations and sensitivities for *n* parameters together and T_0 is the time for the concentrations only (standard CAMx run). ^c Standard CAMx run

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Figure 5-18. 24-hr average sensitivity of O3 to NOx emissions on June 14, 2002 predicted by DDM and BF methods.

Figure 5-19. 24-hr average sensitivity of O3 to VOC emissions on June 14, 2002 predicted by DDM and BF methods.



PSO4 to NOx emissions on June 14, 2002 predicted by DDM and BF methods.

Figure 5-21. 24-hr average sensitivity of PSO4 to VOC emissions on June 14, 2002 predicted by DDM and BF methods.



PSO4 to SO2 emissions on June 14, 2002 predicted by DDM and BF methods.

Figure 5-23. 24-hr average sensitivity of PSO4 to NH3 emissions on June 14, 2002 predicted by DDM and BF methods.



PNO3 to NOx emissions on June 14, 2002 predicted by DDM and BF methods.

Figure 5-25. 24-hr average sensitivity of PNO3 to VOC emissions on June 14, 2002 predicted by DDM and BF methods.



PNO3 to SO2 emissions on June 14, 2002 predicted by DDM and BF methods.

Figure 5-27. 24-hr average sensitivity of PNO3 to NH3 emissions on June 14, 2002 predicted by DDM and BF methods.



PNH4 to NOx emissions on June 14, 2002 predicted by DDM and BF methods.

Figure 5-29. 24-hr average sensitivity of PNH4 to VOC emissions on June 14, 2002 predicted by DDM and BF methods.



PNH4 to SO2 emissions on June 14, 2002 predicted by DDM and BF methods.

Figure 5-31. 24-hr average sensitivity of PNH4 to NH3 emissions on June 14, 2002 predicted by DDM and BF methods.



Figure 5-32. 24-hr average sensitivity of SOA to NOx emissions on June 14, 2002 predicted by DDM and BF methods.

Figure 5-33. 24-hr average sensitivity of SOA to VOC emissions on June 14, 2002 predicted by DDM and BF methods.



6. IMPLEMENTING PROCESS ANALYSIS FOR PM IN CAMx

The Process Analysis (PA) implementation in CAMx version 4.20 (ENVIRON, 2005) was extended to report the chemical change occurring in individual PM chemistry modules by species and by grid cell.

6.1. Improving the IPR Method for PM

The integrated process rate (IPR) component of PA (Wang, Langstaff and Jeffries, 1995) reports how each major model processes (emissions, transport, diffusion, deposition, chemistry) changes the concentration of each species and, as such, IPR is not specifically tailored to either ozone or PM. The IPR information provided by CAMx version 4.20 is shown in Table 6-1.

IPR Parameter	Process Information	Units ^a	
1	Initial concentration	μmol/m³ (μg/m³)	
2	Gas-phase chemistry	μmol/m ³ (μg/m ³)	
3	Area emissions	μmol/m ³ (μg/m ³)	
4	Point source emissions	μmol/m ³ (μg/m ³)	
5	Plume-in-grid change	μmol/m³ (μg/m³)	
6	West boundary advection	μmol/m ³ (μg/m ³)	
7	East boundary advection	μmol/m³ (μg/m³)	
8	South boundary advection	μmol/m³ (μg/m³)	
9	North boundary advection	μmol/m³ (μg/m³)	
10	Bottom boundary advection	μmol/m ³ (μg/m ³)	
11	Top boundary advection	μmol/m ³ (μg/m ³)	
12	Dilution in the vertical	μmol/m³ (μg/m³)	
13	West boundary diffusion	μmol/m ³ (μg/m ³)	
14	East boundary diffusion	μmol/m ³ (μg/m ³)	
15	South boundary diffusion	μmol/m³ (μg/m³)	
16	North boundary diffusion	μmol/m³ (μg/m³)	
17	Bottom boundary diffusion	μmol/m³ (μg/m³)	
18	Top boundary diffusion	μmol/m³ (μg/m³)	
19	Dry deposition	μmol/m³ (μg/m³)	
20	Wet deposition	μmol/m³ (μg/m³)	
21	Heterogeneous chemistry	μmol/m ³ (μg/m ³)	
22	Final concentration	μmol/m ³ (μg/m ³)	
23	Unit conversion	ppm/µmol-m⁻³ (n/aʰ)	
24	Average cell volume	m ³	

 Table 6-1. Integrated Process Rate (IPR) information reported by CAMx v4.2.

^a Units in the parentheses are for PM species.

^b Unit conversion factor for PM species is always 1.

A total of 24 parameters are reported for each selected species and grid cell: the initial and final concentrations, 20 parameters reporting process changes and two parameters that are needed to combine results across grid cells (Table 6-1). However, the CAMx v4.2 IPR implementation



reports all information about chemical change due to PM chemistry in a single parameter "Heterogeneous Chemistry" that is number 21 in Table 6-1. This is because the IPR implementation predates several PM chemistry upgrades in CAMx.

Three new IPR parameters were added to CAMx to record chemical change due to the individual PM modules: inorganic aerosol chemistry (ISORROPIA), secondary organic aerosol partitioning (SOAP), and aqueous chemistry (RADM-AQ). This involved code development and testing, changes to output files and changes to post-processing tools. The improved IPR implementation is described in Table 6-2.

IPR Parameter	Process Information	Units ^a	
1	Initial concentration	μmol/m³ (μg/m³)	
2	Gas-phase chemistry	µmol/m³ (µg/m³)	
3	Area emissions	μmol/m³ (μg/m³)	
4	Point source emissions	μmol/m ³ (μg/m ³)	
5	Plume-in-grid change	µmol/m³ (µg/m³)	
6	West boundary advection	µmol/m³ (µg/m³)	
7	East boundary advection	μmol/m³ (μg/m³)	
8	South boundary advection	µmol/m³ (µg/m³)	
9	North boundary advection	µmol/m³ (µg/m³)	
10	Bottom boundary advection	μmol/m³ (μg/m³)	
11	Top boundary advection	μmol/m³ (μg/m³)	
12	Dilution in the vertical	μmol/m ³ (μg/m ³)	
13	West boundary diffusion	µmol/m³ (µg/m³)	
14	East boundary diffusion	µmol/m³ (µg/m³)	
15	South boundary diffusion	μmol/m ³ (μg/m ³)	
16	North boundary diffusion	µmol/m³ (µg/m³)	
17	Bottom boundary diffusion	μmol/m³ (μg/m³)	
18	Top boundary diffusion	μmol/m³ (μg/m³)	
19	Dry deposition	µmol/m³ (µg/m³)	
20	Wet deposition	µmol/m³ (µg/m³)	
21	Inorganic aerosol chemistry	µmol/m³ (µg/m³)	
22	Organic aerosol chemistry	μmol/m ³ (μg/m ³)	
23	Aqueous-phase chemistry	µmol/m³ (µg/m³)	
24	Final concentration	µmol/m³ (µg/m³)	
25	Unit conversion	ppm/µmol-m ⁻³ (n/a ^b)	
26	Average cell volume	m ³	

Table 6-2.	Integrated Proc	cess Rate (IF	PR) informa	tion reporte	d by CAMx.
		`	,		

^a Units in the parentheses are for PM species.

^b Unit conversion factor for PM species is always 1.

The IPR post-processing tool extracts IPR data from the binary IPR output file and reformats the data to comma delimited ASCII format (CSV format) suitable for subsequent analysis using spreadsheets. The CAMx IPR post-processing tool was extended to work with IPR data from PM and ozone model simulations.

6.2. Test Case

The MRPO test case described in Section 5.1 was used to test the extended PA code. IPR data were output for just the Chicago area. The portion of the horizontal modeling domain for which process rate data were output consisted of a 10×10 block grid cells surrounding Chicago, IL (Figure 6-1) and the lowest five model layers above the surface.



Figure 6-1. CAMx test modeling domain and PM sub-domain (gray area).

6.3. Results

The accuracy of the IPR implementation was confirmed by comparing mass changes reported by IPR for specific PM modules to changes in total species mass. For example, among the three PM modules, only ISORROPIA affects the mass of particulate chloride (PCL). Therefore, the mass change of PCL due to the inorganic aerosol process (IAERO) must be equal to the final mass of PCL minus the mass changes due to all other processes except the PM processes (Final-Others). Figure 6-2 shows the mass changes for several species that are involved in only one of the three PM processes to verify that the PA implementation for the module observes mass conservation.

For PSO₄, PNO₃ and PNH₄, the mass changes due to inorganic aerosol chemistry and aqueous chemistry are compared with the final mass minus the mass changes due to all other processes because those species are involved in both ISORROPIA and RADM-AQ (Figure 6-3). Figures 6-2 and 6-3 show no noticeable discrepancy between the two time-series plots, which indicates that the PA IPR code was correctly implemented for the PM modules.



Figure 6-2. Mass changes of selected species due to inorganic aerosol chemistry (IAERO), aqueous chemistry (AQCHEM), organic aerosol chemistry (OAERO) along with the final mass minus mass changes due to all other processes (Final-Others).





The IPR post-processing tools were updated to accommodate expanding the number of IPR parameters from 24 to 26. Example charts are shown in Figures 6-4 to 6-6. These charts aggregate IPR data over all 500 grid cells $(10 \times 10 \times 5)$ included in the Chicago analysis area (Figure 6-1).

The bar charts in Figure 6-4 show the changes in particulate sulfate and nitrate (PSO4 and PNO3) due to all model processes averaged over June 13 and 14, 2002. The "gas-phase chemistry" process changes neither PSO4 nor PNO3 because it changes the corresponding precursors (H₂SO₄ and HNO₃) that consequently form aerosol in the "inorganic aerosol chemistry" process. Figure 6-4 shows more PSO4 formed in Chicago by "aqueous-phase chemistry" than "inorganic aerosol chemistry" whereas the converse is true for PNO3.

The bar charts in Figures 6-5 and 6-6 compare the impacts of chemistry, deposition and transport for PSO4 and PNO3 hour-by-hour. All chemistry processes are combined to a single term in Figures 6-5 and 6-6; the difference between the Figures is in the amount of detail shown for transport in and out of the Chicago area. Gas-phase and heterogeneous chemistry processes are separated in Figure 6-6. Figure 6-5 shows that chemistry is always a production term for PSO4 whereas PNO3 may either be produced or destroyed by chemistry depending upon hour of day. Chemical destruction of PNO3 would be evaporation to HNO₃ and this is consistent with negative chemical change for PNO3 occurring in the middle of the day (Figure 6-5).





Time-Averaged PSO4 Change from the Different Processes in Chicago Area. Run = postproc_test Grid cells used from grid number 1: (43, 47) to (52, 56) using layers 1 to 5

Time-Averaged PNO3 Change from the Different Processes in Chicago Area. Run = postproc_test Grid cells used from grid number 1: (43, 47) to (52, 56) using layers 1 to 5



Figure 6-4. Time-averaged IPR analysis for PSO4 and PNO3 on June 13 and 14, 2002; All the processes are plotted individually.





Hourly PSO4 Change from Different Processes in Chicago Area. Run = postproc_test Grid cells used from grid number 1: (43, 47) to (52, 56) using layers 1 to 5





Figure 6-5. IPR time series analysis for PSO4 and PNO3; Lateral boundary/Chemistry terms are aggregated to a single net term.





Hourly PSO4 Change from Different Processes in Chicago Area.





Figure 6-6. IPR time series analysis for PSO4 and PNO3; Lateral boundary/Chemistry terms are not aggregated, in contrast to Figure 6-5.

7. CONCLUSIONS AND RECOMENDATIONS

7.1. CONCLUSIONS

DDM Implementation

For project CRC A-51a, ENVIRON implemented the Decoupled Direct Method (DDM) for Particulate Matter (PM) in CAMx v4.20. In close collaboration with Dr. Alan Dunker at GM, detailed DDM equations/algorithms were constructed and implemented in each of the PM modules. The main PM modules in CAMx are:

- ISORROPIA for inorganic gas-aerosol partitioning
- RADM-AQ for aqueous phase sulfate formation
- SOAP for organic gas-aerosol partitioning

The DDM implementations were tested in stand-alone models over ranges of input conditions to verify the initial design and implementation. Excellent agreement between the DDM and brute force (BF) sensitivities for small input changes confirmed the DDM implementation.

When input changes exceed about 10%, ISORROPIA begins to show non-linearity for some species in some tests. Non-linearity is also introduced when input changes cause the system to cross over between sub-cases in ISORROPIA's solution algorithm. In most cases, however, the DDM sensitivities well reflect the model response to input changes up to 10%. RADM-AQ shows less non-linear responses than ISORROPIA does. When input changes exceed about 20%, the responses of RADM-AQ start to deviate from linear in some cases. The DDM agrees well with the brute-force (BF) method as long as the responses are linear. With SOAP, the model responses to input changes are mostly linear and the DDM sensitivities closely follow the BF sensitivities for input changes up to 30%.

The completed DDM codes were incorporated into CAMx v4.20 and tested using a 2-day summer episode test-case for the Eastern US. To evaluate the DDM performance, the BF method was used to estimate first-order sensitivities to various emissions, which were then compared with the DDM sensitivities. The DDM sensitivities follow those of the BF method closely in most cases. The spatial patterns in the sensitivities computed by the two methods are in good agreement. In general, the agreement between DDM and BF sensitivities of ozone to NO_x and VOC emissions are comparable to that of a previous study for gas-species only in CAMx (Dunker et al., 2002a). The DDM performed well for SOA species because there is less non-linearity in SOAP than the other PM modules. For ISORROPIA-related species (PSO₄, PNO₃, PNH₄, etc.), the DDM and BF sensitivities agree less well, but still are acceptable.

The test with CAMx was performed twice: first without deposition and then with deposition (full CAMx). Including deposition slightly degraded the agreement between the DDM and BF sensitivities. Tests that included deposition but not chemistry found good agreement between DDM and BF sensitivities. Determining how chemistry and deposition combine to degrade agreement between the DDM and BF methods will require further investigation.



One of the main advantages of the DDM over the BF method is computational efficiency. As the number sensitivities calculated is increased, the efficiency of the DDM significantly outgrows that of the BF method. When sensitivities are calculated together for 8 input parameters, the DDM is about 1.6 times faster than the BF method.

PA Implementation

For project CRC A-51b, the Process Analysis (PA) module in CAMx v4.20 was extended to calculate and explicitly report process rate information from three PM modules (ISORROPIA, RADM-AQ, and SOAP) using the Integrated Process Rate (IPR) component of PA. The revised IPR implementation was tested and found to be accurate. The CAMx IPR output file now includes three new parameters for inorganic aerosol chemistry, organic aerosol chemistry, and aqueous chemistry.

The post-processing tools that process the CAMx IPR output file for subsequent analysis were updated for the three new IPR parameters. The tools produce three bar charts for each species with different degree of process aggregation to help interpret the process analysis results.

7.2. RECOMENDATIONS

DDM Recommendations

Although the DDM implementation in the CAMx PM modules shows reasonably good agreement with the BF method, the evaluation performed was limited to a 2 day test-case. Also, tests revealed an interaction between the chemistry and deposition calculations that degraded agreement between DDM and BF sensitivities. More thorough testing and evaluation is recommended to investigate whether the DDM performance can be improved and better assess any limitations in the applicability of DDM for PM species.

PA Recommendations

In addition to the IPR component that was extended in this work, CAMx includes two other PA components: Integrated Reaction Rate (IRR) and Chemical Process Analysis (CPA). The IRR formulation is rather specific to the gas-phase chemistry and not applicable to PM modules that make equilibrium assumptions, namely ISORROPIA and RADM-AQ. The CPA formulation is more flexible than IRR and could be extended to provide valuable insights to the complex chemical processes for the PM species. CPA parameters that could be added are listed below:

Gas-Phase Chemistry

Add CPA parameters to track the production of inorganic and organic aerosol precursors:

- 1) SO₂ oxidation by OH
- 2) HNO₃ production from NO₂ oxidation by OH
- 3) HNO₃ production from N₂O₅ hydrolysis to HNO₃
- 4) Production of condensable organic gas (CG) species (treat each CG separately)
- 5) Production of HCl when optional gas-phase Cl-chemistry is included



RADM Aqueous Chemistry

Add CPA parameters to track the production of sulfate and nitric acid:

- 6) SO₂ oxidation by H_2O_2
- 7) SO₂ oxidation by dissolved O_3
- 8) SO₂ oxidation by dissolved O_2 catalyzed by Iron (Fe)
- 9) SO₂ oxidation by dissolved O₂ catalyzed by Manganese (Mn)
- 10) SO₂ oxidation by methyl hydroperoxide (MHP)
- 11) SO_2 oxidation by peroxyacetic acid (PAA)
- 12) HNO₃ production from N_2O_5 hydrolysis to HNO₃

Inorganic Equilibrium Chemistry

Add CPA variables to track condensation/evaporation of inorganic aerosol. Focus on the change in gas-phase species so that the same scheme will work for both the CF and CMU particle size schemes.

- 13) Condensation/evaporation of HNO₃
- 14) Condensation/evaporation of NH₃
- 15) Condensation of sulfuric acid vapor (SULF)
- 16) Condensation/evaporation of HCl

Secondary Organic Chemistry

Add CPA variables to report the calculated saturation vapor pressure (SVP) for each condensable gas. Comparing the CG concentrations to the local SVP reveals whether organic gases are condensing at or below their SVPs for the current conditions.

17) Saturation vapor pressure (SVP) for each CG species.

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Appendix A Calculating the Concentrations of Electrolytes (E) in ISORROPIA Sulfate-ammonium system $(Y_0(cNa) + Y_0(tCl) + Y_0(tNO_3) = 0)$

Case A ($Y_0(tNH_4) / Y_0(tSO_4) \ge 2.0$)

 $E[(NH_4)_2SO_4] = Y_1(SO_4^{2-}) + Y_1(HSO_4^{-})$

<u>Case B (1.0 \leq Y₀(tNH₄) / Y₀(tSO₄) < 2.0)</u>

 $i) \; Y_1(SO_4^{\; 2^{\text{-}}}) - Y_1(H^{\scriptscriptstyle +}) < Y_1(HSO_4^{\; -}) + Y_1(H^{\scriptscriptstyle +})$

$$\begin{split} E[(NH_4)_3H(SO_4)_2] &= Y_1(SO_4^{2-}) - Y_1(H^+) \\ E[NH_4HSO_4] &= Y_1(HSO_4^{-}) - Y_1(SO_4^{2-}) + 2 Y_1(H^+) \end{split}$$

ii) $Y_1(SO_4^{-2}) - Y_1(H^+) \ge Y_1(HSO_4^{-1}) + Y_1(H^+)$

$$\begin{split} E[(NH_4)_3H(SO_4)_2] &= Y_1(HSO_4^-) + Y_1(H^+) \\ E[(NH_4)_2SO_4] &= Y_1(SO_4^{2-}) - Y_1(HSO_4^-) - 2 \ Y_1(H^+) \end{split}$$

<u>Case C ($Y_0(tNH_4) / Y_0(tSO_4) < 1.0$)</u>

$$\begin{split} E[NH_4HSO_4] &= Y_1(NH_4^+) \\ E[2H-SO_4] &= Y_0(tSO_4) - Y_0(tNH_4) \end{split}$$

Sulfate-ammonium-nitrate system $(Y_0(cNa) + Y_0(tCl) = 0)$

<u>Case D ($Y_0(tNH_4) / Y_0(tSO_4) \ge 2.0$)</u>

 $E[(NH_4)_2SO_4] = Y_1(SO_4^{2-}) + Y_1(HSO_4^{-})$ $E[NH_4NO_3] = MIN(Y_1(NH_4^{+}) - 2 E[(NH_4)_2SO_4], Y_1(NO_3^{-}))$

<u>Case E (1.0 \leq Y₀(tNH₄) / Y₀(tSO₄) < 2.0)</u>

The same as the case B

<u>Case F ($Y_0(tNH_4) / Y_0(tSO_4) < 1.0$ </u>)

The same as the case C

Sulfate-ammonium-nitrate-chloride-sodium system

<u>Case G (($Y_0(cNa) + Y_0(tNH_4)$) / $Y_0(tSO_4) \ge 2.0 \& Y_0(cNa) / Y_0(tSO_4) < 2.0$)</u>

$$\begin{split} E[Na_2SO_4] &= 0.5 \ Y_1(Na^+) \\ E[(NH_4)_2SO_4] &= Y_1(SO_4^{-2-}) + Y_1(HSO_4^{--}) - 0.5 \ Y_1(Na^+) \\ E[NH_4NO_3] &= MIN(Y_1(NH_4^+) - 2 \ E[(NH_4)_2SO_4], \ Y_1(NO_3^{--})) \\ E[NH_4Cl] &= MIN(Y_1(NH_4^+) - 2 \ E[(NH_4)_2SO_4] - E[NH_4NO_3], \ Y_1(Cl^-)) \end{split}$$

<u>Case H (($Y_0(cNa) + Y_0(tNH_4)$) / $Y_0(tSO_4) \ge 2.0 \& Y_0(cNa) / Y_0(tSO_4) \ge 2.0$)</u>

$$\begin{split} & E[Na_2SO_4] = Y_0(tSO_4) - Y_1(Na_2SO_4) \\ & E[NaNO_3] = MIN(Y_0(cNa) - 2 Y_0(tSO_4), Y_0(tNO_3)) - Y_1(NaNO_3) \\ & E[NaCl] = MIN(MAX(Y_0(cNa) - 2 Y_0(tSO_4) - Y_0(tNO_3), 0), Y_0(tCl)) - Y_1(NaCl) \\ & E[NH_4NO_3] = MIN(Y_1(NO_3^-) - E[NaNO_3], Y_1(NH_4^+)) \\ & E[NH_4Cl] = MIN(Y_1(Cl^-) - E[NaCl], Y_1(NH_4^+) - E[NH_4NO_3]) \end{split}$$

<u>Case I (1.0 \leq (Y₀(cNa) + Y₀(tNH₄)) / Y₀(tSO₄) < 2.0)</u>

$$\begin{split} E[(NH_4)_2SO_4] &= D((NH_4)_2SO_4) - Y_1((NH_4)_2SO_4) \\ E[Na_2SO_4] &= D(Na_2SO_4) - Y_1(Na_2SO_4) \\ E[NH_4HSO_4] &= D(NH_4HSO_4) - Y_1(NH_4HSO_4) \\ E[NaHSO_4] &= D(NaHSO_4) - Y_1(NaHSO_4) \\ E[(NH_4)_3H(SO_4)_2] &= D((NH_4)_3H(SO_4)_2) - Y_1((NH_4)_3H(SO_4)_2) \end{split}$$

D's are the dry salt concentrations from the solid-only case I1A (a sub-case of Case I where the relative humidity is sufficiently low that no water is present).

<u>Case J (($Y_0(cNa) + Y_0(tNH_4)$) / $Y_0(tSO_4) < 1.0$)</u>

$$\begin{split} & E[NH_4HSO_4] = Y_1(NH_4^+) \\ & E[NaHSO_4] = Y_1(Na^+) \\ & E[2H\text{-}SO_4] = Y_1(SO_4^{-2^-}) + Y_1(HSO_4^-) - Y_1(NH_4^+) - Y_1(Na^+) \end{split}$$

Appendix B. Scatter plots of the DDM vs. BF sensitivities



Figure B-1. Comparison of 24-hr average DDM and BF sensitivities for all grid cells in the surface layer, June 14, 2002; Sensitivity of PSO_4 to NO_x emissions (squares) and 1:1 line (solid line); (a) and (b) represent no-deposition and full CAMx tests, respectively.



Figure B-2. Comparison of 24-hr average DDM and BF sensitivities for all grid cells in the surface layer, June 14, 2002; Sensitivity of PSO_4 to VOC emissions (squares) and 1:1 line (solid line); (a) and (b) represent no-deposition and full CAMx tests, respectively.



Figure B-3. Comparison of 24-hr average DDM and BF sensitivities for all grid cells in the surface layer, June 14, 2002; Sensitivity of PSO_4 to SO_2 emissions (squares) and 1:1 line (solid line); (a) and (b) represent no-deposition and full CAMx tests, respectively.



Figure B-4. Comparison of 24-hr average DDM and BF sensitivities for all grid cells in the surface layer, June 14, 2002; Sensitivity of PSO_4 to NH_3 emissions (squares) and 1:1 line (solid line); (a) and (b) represent no-deposition and full CAMx tests, respectively.



Figure B-5. Comparison of 24-hr average DDM and BF sensitivities for all grid cells in the surface layer, June 14, 2002; Sensitivity of PNO_3 to NO_x emissions (squares) and 1:1 line (solid line); (a) and (b) represent no-deposition and full CAMx tests, respectively.



Figure B-6. Comparison of 24-hr average DDM and BF sensitivities for all grid cells in the surface layer, June 14, 2002; Sensitivity of PNO_3 to VOC emissions (squares) and 1:1 line (solid line); (a) and (b) represent no-deposition and full CAMx tests, respectively.



Figure B-7. Comparison of 24-hr average DDM and BF sensitivities for all grid cells in the surface layer, June 14, 2002; Sensitivity of PNO_3 to SO_2 emissions (squares) and 1:1 line (solid line); (a) and (b) represent no-deposition and full CAMx tests, respectively.



Figure B-8. Comparison of 24-hr average DDM and BF sensitivities for all grid cells in the surface layer, June 14, 2002; Sensitivity of PNO₃ to NH₃ emissions (squares) and 1:1 line (solid line); (a) and (b) represent no-deposition and full CAMx tests, respectively.



Figure B-9. Comparison of 24-hr average DDM and BF sensitivities for all grid cells in the surface layer, June 14, 2002; Sensitivity of PNH_4 to NO_x emissions (squares) and 1:1 line (solid line); (a) and (b) represent no-deposition and full CAMx tests, respectively.



Figure B-10. Comparison of 24-hr average DDM and BF sensitivities for all grid cells in the surface layer, June 14, 2002; Sensitivity of PNH_4 to VOC emissions (squares) and 1:1 line (solid line); (a) and (b) represent no-deposition and full CAMx tests, respectively.


Figure B-11. Comparison of 24-hr average DDM and BF sensitivities for all grid cells in the surface layer, June 14, 2002; Sensitivity of PNH_4 to SO_2 emissions (squares) and 1:1 line (solid line); (a) and (b) represent no-deposition and full CAMx tests, respectively.



Figure B-12. Comparison of 24-hr average DDM and BF sensitivities for all grid cells in the surface layer, June 14, 2002; Sensitivity of PNH_4 to NH_3 emissions (squares) and 1:1 line (solid line); (a) and (b) represent no-deposition and full CAMx tests, respectively.



Figure B-13. Comparison of 24-hr average DDM and BF sensitivities for all grid cells in the surface layer, June 14, 2002; Sensitivity of SOA to NO_x emissions (squares) and 1:1 line (solid line); (a) and (b) represent no-deposition and full CAMx tests, respectively.



Figure B-14. Comparison of 24-hr average DDM and BF sensitivities for all grid cells in the surface layer, June 14, 2002; Sensitivity of SOA to VOC emissions (squares) and 1:1 line (solid line); (a) and (b) represent no-deposition and full CAMx tests, respectively.