# **CRC Report No. A-64**

# Evaluation of CAMx Probing Tools for Particulate Matter

**Final Report** 

**March 2009** 



**COORDINATING RESEARCH COUNCIL, INC.** 3650 MANSELL ROAD SUITE 140 ALPHARETTA, GA 30022

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## Foreword

Under CRC Project A-64 "Evaluation of CAMx Probing Tools for Particulate Matter," ENVIRON International Corporation conducted research to evaluate and compare two CAMx probing tools that provide information on the source-receptor relationship for particulate matter pollutants. Based on the research results, a draft journal manuscript entitled "Comparison of Source Apportionment and Sensitivity Analysis in a Particulate Matter Air Quality Model" was produced. It will be submitted to Environmental Science and Technology for publication.

The draft manuscript is included in this report along with an Executive Summary and additional supporting material not presented in the journal article.



#### **Final Report**

#### **CRC PROJECT A-64**

#### **Evaluation of CAMx Probing Tools for Particulate Matter**

Prepared for

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# **Executive Summary**

The Comprehensive Air-quality Model with Extensions (CAMx) includes several probing tools (extensions) that run simultaneously with the regular model and provide various in-depth analyses to help users better understand the simulation results. The goal of CRC Project A-64 is to compare two of the probing tools for particulate matter (PM), the Particulate Source Apportionment Technology (PSAT) and the Decoupled Direct Method (DDM), and determine their advantages and limitations.

PSAT is a tagged species method that apportions concentrations of PM components to their respective primary precursors. Traditionally, the brute-force method (BFM) has been used for source contributions, which involves repeating a model simulation with and without perturbed emissions and comparing the two simulation results. Therefore, the number of simulations to run increases linearly with the number of perturbations to examine. PSAT was developed as an efficient alternative to the BFM for PM source apportionment and has been implemented in CAMx.

DDM is an efficient and accurate alternative to the BFM for sensitivity analysis. It directly solves sensitivity equations derived from the governing equations of the atmospheric processes modeled in the host model. DDM was originally implemented for gas-phase species in CAMx (CRC Project A-29) and later extended to PM species (CRC Project A-51). Currently, the DDM implementation for PM in CAMx is limited to the first-order sensitivity. Under CRC Project A-64, we updated the previous DDM implementation in CAMx v4.2 for the latest version of CAMx (version 4.5). The updates include:

- Implementing DDM in a new CAMx gas-phase chemistry solver based on the Euler Backward Iterative (EBI) method
- Updating the DDM code for the latest version (v1.7) of ISORROPIA inorganic aerosol thermodynamic model
- Revising the DDM code for the updated CAMx secondary organic aerosol (SOA) module

The updated CAMx DDM code was applied to a two-day PM modeling episode for the Eastern US which is essentially the same test case used for the previous CRC study (CRC Project A-51). In most cases, the results from the current study show similar or better agreement between the DDM and BFM sensitivities to those from the previous study.

The updated DDM was then compared with PSAT using two month-long (February and July 2002) episodes from the St. Louis  $36/12 \text{ km} 2002 \text{ PM}_{2.5}$  State Implementation Plan (SIP) modeling database. Source apportionments and source sensitivities for domain-wide emissions of SO<sub>2</sub> (point), NO<sub>x</sub> (area/point), anthropogenic/biogenic VOC (area), NH3 (area), and total emissions from on-road mobile sources were examined. Brute force emission reductions of 100% (zero-out) and 20% were also simulated for comparison with PSAT and DDM.

The results demonstrated that source sensitivity and source apportionment are equivalent for pollutants that are linearly related to emissions but otherwise differ because of non-linearity and/or indirect effects which represent influences from emissions of non-primary precursors.

In our sensitivity simulations, the first-order DDM sensitivities adequately predicted the model responses of inorganic secondary aerosols to 20% emission changes. For SOA and primary aerosols, DDM agreed reasonably well with BFM up to 100% emission reductions. The DDM also gave reasonably good predictions for the impact of removing 100% of on-road mobile source emissions (all VOC,  $NO_x$ , and particulate emissions) because the DDM incorporates the indirect effects. However, as the size of model input changes increases beyond 20%, higher-order sensitivities become more important in general, and first-order sensitivity alone may not be enough to describe the model response.

Source apportionment by PSAT successfully approximated the zero-out contributions for primary aerosols. Results for ammonium demonstrate that PSAT source apportionment and zero-out are nearly equivalent in a case where the emissions-concentration relationship is highly non-linear, but there is no indirect effect. Results for sulfate demonstrate that indirect effects (in this case oxidant-limited sulfate formation) can limit the ability of zero-out to provide source apportionment and, therefore, that PSAT and zero-out may disagree when there are indirect effects.

Emissions from auto and oil industries tend to include more than one pollutant and therefore indirect effects will likely contribute to the air-quality impacts of these emissions. Consequently, multiple methods (DDM, PSAT, and zero-out) should be applied for quantifying the impacts of entire source sectors such as the auto and oil industries.

**Draft Journal Manuscript** 

# Comparison of Source Apportionment and Sensitivity Analysis in a Particulate Matter Air Quality Model

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#### Abstract

Two efficient methods to study relationships between particulate matter (PM) concentrations and emission sources are compared in the CAMx three-dimensional air quality model. The Particulate Source Apportionment Technology (PSAT) is a tagged-species method that apportions concentrations of PM components to their respective primary precursors, e.g., sulfate is apportioned to  $SO_x$ , nitrate to  $NO_x$ , etc. The Decoupled Direct Method (DDM) calculates first-order sensitivities of PM concentrations to model inputs. Both tools were applied to two month long (February and July) PM modeling episodes and evaluated against changes in PM concentrations due to various emission reductions. The results show that source contributions calculated by PSAT start to deviate from the actual model responses as indirect effects from limiting reactants or non-primary precursor emissions become important. The DDM first-order sensitivity is useful for determining source contributions only if the model response to input changes is reasonably linear. For secondary inorganic PM, the range of linear response is limited to emission changes of 20%. The model response for secondary organic aerosols and primary PM remains nearly linear up to 100% emission reductions.

#### Introduction

Particulate matter (PM) is an important atmospheric pollutant that can be directly emitted into the atmosphere (primary PM) or produced via chemical reactions of precursors (secondary PM). Understanding relationships between emissions from various sources and ambient PM concentrations is often vital in establishing effective control strategies.

Two different approaches to quantifying source-receptor relationships for PM are investigated here. Source apportionment assumes that clear mass-continuity relationships exist between emissions and concentrations (e.g., between SO<sub>2</sub> and sulfate) and uses them to determine contributions from different sources to pollutant concentrations at receptor locations. On the other hand, sensitivity analysis measures how pollutant concentrations at receptors respond to perturbations at sources. In many cases, these quantities cannot be directly measured, thus air quality models have been widely used. The most straightforward sensitivity method (the brute-force method or BFM) is to run a model simulation, repeat it with perturbed emissions, and compare the two simulation results. The BFM is not always practical because computational cost increases linearly with the number of perturbations to examine and the smaller concentration changes between the simulations may be strongly influenced by numerical errors.

The Particulate Source Apportionment Technology (PSAT) was developed as an efficient alternative to the BFM for PM source apportionment (Yarwood et al., 2004; Wagstrom et al., 2008). PSAT uses tagged species (also called reactive tracers) to apportion PM components to different source types and locations. Computational efficiency results from using computed changes in bulk species concentrations to determine the changes for tagged species within individual atmospheric processes (advection, chemistry, etc.). PSAT has been implemented in the Comprehensive Air-quality Model with extensions (CAMx). Similar source apportionment tools include the Tagged Species Source Apportionment (TSSA) developed by Tonnesen and Wang (2004) and implemented in the Community Multiscale Air Quality (CMAQ) model. Unlike PSAT, TSSA adopts an "on-line" approach and explicitly solves tagged species using the same algorithms as the host model for physical atmospheric processes like advection and diffusion. Wagstrom et al. (2008) implemented an on-line approach and the "off-line" PSAT approach in PMCAMx and showed that the computationally more efficient off-line method agreed well with the on-line method for source apportionment of PM sulfate. Kleeman et al. (1997) took a more rigorous approach and their Source-Oriented External Mixture (SOEM) model simulates each tagged species separately through every modeled atmospheric process (physical and chemical). The SOEM is potentially the most accurate tagged species method but is computationally very demanding. With these and other methods, it is important to recognize that there is no unique apportionment of ambient concentrations to sources when nonlinear chemistry is present. Different methods will inherently give different results, and there is no "true" apportionment to which all methods can be compared.

The Decoupled Direct Method (DDM) is an efficient and accurate alternative to the BFM for sensitivity analysis (Dunker, 1980; 1981). DDM directly solves sensitivity equations derived from the governing equations of the atmospheric processes modeled in the host model. Yang et al. (1997) introduced a variant of DDM called DDM-3D that uses different, less rigorous numerical algorithms to solve time-evolution of the chemistry sensitivity equations than used to solve concentrations. This improves numerical efficiency at the expense of potential inconsistencies between the sensitivities and concentrations (Koo et al., 2009). DDM was originally implemented for gas-phase species in CAMx (Dunker et al., 2002b) and later extended to PM species (Koo et al., 2007a). The DDM-3D implementation in CMAQ has also been extended to PM (Napelenok et al., 2006). While higher-order DDM has been implemented for gas-phase species (Hakami et al., 2003; Cohan et al., 2005; Koo et al., 2007b; 2008), DDM for PM species is currently limited to first-order sensitivity.

There have been a few attempts to compare source apportionment and sensitivity analysis for ozone. Dunker et al. (2002a) compared source impacts on ozone estimated using Ozone Source Apportionment Technology (OSAT) and first-order DDM sensitivities. Cohan et al. (2005) approximated the zero-out contribution (change in the pollutant concentration that would occur if a source is removed) using the first- and second-order DDM sensitivities of ozone to NO<sub>x</sub> and VOC emissions. In this paper, the model responses of atmospheric PM components to various emission reductions calculated by PSAT and first-order DDM sensitivities are compared with those by the BFM and the differences between their results are discussed.

#### Methods

Both PSAT and DDM are implemented in CAMx and they can be compared using the same modeling framework. The details of the PSAT and DDM implementation in CAMx are given in the references mentioned above. Two month long (February and July) episodes from the St. Louis 36/12 km 2002 PM<sub>2.5</sub> State Implementation Plan modeling database were selected for evaluating PSAT and DDM with 10 spin-up days before each month. The Pennsylvania State University/National Center for Atmospheric Research (PSU/NCAR) Mesoscale Model (MM5) and the Sparse Matrix Operator Kernel Emissions (SMOKE) were used to prepare meteorological fields and emissions inputs, respectively. On-road mobile source emissions were processed by MOBILE6, and biogenic emissions were generated by Model of Emissions of Gases and Aerosols from Nature (MEGAN). Figure 1 shows the modeling domain that consists of a master grid with 36 km resolution and a 12 km nested grid. 16 vertical layers extend up to about 15 km. We selected 8 receptor locations that cover both urban (2 receptors) and rural (6 receptors) conditions for the analysis.

Brute force emission reductions of 100% (zero-out) and 20% were simulated for the following anthropogenic emissions:  $SO_2$  and  $NO_x$  from point sources;  $NO_x$ , VOC, and  $NH_3$  from area sources; all emission species from on-road mobile sources (see Table S1 for average daily emissions from each source category). BFM contributions were calculated by subtracting the PM concentrations of the emission reduction case from those of the base case. Both the PSAT source contributions and the first-order DDM sensitivities are computed in concentration units and may be directly compared with the BFM response to 100% emissions reduction. Both quantities were linearly scaled for comparison with the 20% reduction BFM results. However, non-linear model response affects both the PSAT and DDM results, but in different ways. As illustrated in Figure 2, in a strongly non-linear system, the first-order DDM sensitivity is useful only for relatively small input changes while good agreement between PSAT and BFM is expected only near 100% emission reduction.

The BFM inherently accounts for non-linear model response but may suffer limitations as a source apportionment method when the model response includes an indirect effect resulting from influence by chemicals other than the direct precursor. For example, consider an oxidant-limiting case of sulfate formation where oxidation of  $SO_2$  is limited by availability of  $H_2O_2$  or  $O_3$ . Removing an  $SO_2$  source in an oxidant-limited case makes more oxidant available to convert  $SO_2$  from other sources, resulting in a smaller zero-out contribution for the source than in an oxidant-abundant case. Furthermore, the sum of the zero-out contributions calculated separately for each source will likely not add up to the total sulfate concentration in the base case. Indirect effects also can influence PSAT contributions for multi-pollutant sources where emissions of non-direct precursors have significant impact on the PM component of interest.

#### Results

#### Sulfate

Monthly averaged contributions of point source SO<sub>2</sub> emissions to PM<sub>2.5</sub> sulfate concentrations are compared in Figure 3 for the zero-out, PSAT, and DDM runs. Close to large SO<sub>2</sub> sources,

PSAT shows higher source contributions than those estimated by BFM. This is a consequence of sulfate formation being limited by availability of oxidants (see the description of oxidant-limiting case in the previous section). By design, PSAT does not take such indirect effects into account. This effect is less noticeable in July when the oxidant concentrations are higher. DDM mostly under-estimates the sulfate changes calculated by the zero-out method. This difference results from the non-linear response of sulfate concentrations to large changes in SO<sub>2</sub> emissions. As noted earlier, the current DDM implementation for PM in CAMx is limited to first-order sensitivities which cannot capture such non-linearities. First-order DDM sensitivities compare well with 20% BFM emission changes, as discussed below.

Scatter plots comparing the PSAT (or DDM) and BFM results are shown in Figure 4 for the 8 receptor sites selected (hereafter we will focus on the analyses at the receptor locations). With 100% reduction in the point source SO<sub>2</sub> emissions, PSAT shows excellent agreement with the BFM in July while exhibiting slight over-estimation in February when oxidant-limiting effects are more important. With smaller (20%) reduction in point source SO<sub>2</sub> emissions, the oxidant-limiting effect has greater impact because a greater fraction of the freed oxidant can oxidize SO<sub>2</sub> from non-point sources (this happens because point sources dominate the SO<sub>2</sub> emissions, Table S1). This results in more difference between PSAT and BFM for 20% than 100% SO<sub>2</sub> reduction. On the other hand, DDM and BFM agree better with 20% reduction than 100% as the model response becomes more linear with smaller input changes.

Scatter plots for sulfate changes due to reduced emissions of all species from mobile sources illustrate another indirect effect that is not accounted by PSAT (Figure 5). Under winter condition (low temperature), more nitric acid can dissolve into water. Therefore, reducing mobile source NO<sub>x</sub> emissions decreases the acidity of the aqueous phase, which in turn increases sulfate concentrations as more SO<sub>2</sub> dissolves and then is oxidized in the aqueous phase. In summer, reducing NO<sub>x</sub> emissions means less oxidant available to oxidize SO<sub>2</sub>, which decreases sulfate formation beyond reductions attributable to SO<sub>2</sub> emissions reductions alone. However, because PSAT is designed to apportion PM to its primary precursor (in this case, sulfate is apportioned to SO<sub>x</sub> emissions and the indirect effect of reduced NO<sub>x</sub> emissions is ignored), the changes in sulfate estimated by PSAT are much smaller than those estimated using zero-out BFM in summer and even opposite direction in winter. The zero-out BFM is a sensitivity method and it is debatable whether the zero-out result can be considered a source apportionment in this case. DDM agrees much better with the zero-out result in this case because DDM can calculate sensitivity to multiple inputs and account for indirect effects.

#### Ammonium

Figure 6 presents a clear example of the limitations of PSAT and DDM. With 100% reduction of  $NH_3$  emissions from area sources, the changes in  $PM_{2.5}$  ammonium concentrations by PSAT are in excellent agreement with those by BFM while the DDM performance is impaired by non-linearity in the gas-aerosol thermodynamic equilibrium for  $NH_3$  and ammonium. The same non-linearity also weakens agreement between PSAT and BFM in the case of 20% emission reduction. Small emission changes can also emphasize any existing indirect effects (e.g., ammonium formation limited by sulfate or nitric acid). As seen in the above cases, the first-order DDM sensitivity performs well in describing model response to the smaller emission

change. Comparison of PSAT and BFM for the changes in ammonium concentrations due to reduced mobile source emissions also shows the influence of indirect effects (Figure S1).

#### <u>Nitrate</u>

Scatter plots shown in Figure 7 compare  $PM_{2.5}$  nitrate changes due to reductions in area  $NO_x$  emissions. PSAT slightly over-estimates nitrate changes by zero-out BFM because availability of ammonia can limit nitrate partitioning into particle phase (similar to the effect of oxidant-limiting sulfate formation, discussed above). The differences between PSAT and BFM become larger for smaller emissions reduction due to the non-linear system. DDM again performs better with smaller change in  $NO_x$  emissions. Similar behaviors were observed in the case with reductions in point source  $NO_x$  emissions (Figure S2). Figure 8 shows the case with all species from on-road mobile source emissions reduced. Since  $NO_x$  is the dominant component of mobile emissions (see Table S1), there is much less indirect effect due to other emission species. This explains relatively good agreement between PSAT and BFM in this case.

### Secondary Organic Aerosol (SOA)

Both PSAT and DDM perform well in predicting the BFM responses of SOA concentrations to reductions in anthropogenic VOC emissions from area sources (Figure 9). DDM shows good performance even with 100% emission reduction demonstrating that the SOA module in CAMx responded linearly to this emission change. PSAT also shows reasonable agreement with BFM for both 100% and 20% reductions probably because enough oxidant is available to convert VOC precursors to SOA and there are minimal indirect effects (although a hint of the oxidant-limiting effect can be seen in February). However, reducing NO<sub>x</sub> as part of mobile source emission reductions can significantly alter ambient oxidant levels, which changes SOA formation from not only anthropogenic but also biogenic VOC precursors. Source apportionment by PSAT excludes this kind of indirect effect, and thus significantly underestimates the model response by BFM in summer when mobile source NO<sub>x</sub> emissions influence oxidants strongly (Figure 10).

#### Primary PM

Since the source-receptor relationship for primary PM is essentially linear and not affected by any indirect effects, it is expected that both PSAT and DDM should accurately predict the model response of primary PM species to their emissions. Excellent agreement was found between PSAT (or DDM) and BFM for changes in primary PM<sub>2.5</sub> concentrations from mobile sources (Figure S3).

#### Discussion

PSAT and DDM were applied in the same regional modeling framework to estimate the model responses to various BFM emission reductions by 100% and 20%. The results demonstrate that source sensitivity and source apportionment are equivalent for pollutants that are linearly related to emissions but otherwise differ because of non-linearity and/or indirect effects.

Based on the simulations conducted in this study, the first-order DDM sensitivities can adequately predict the model responses of inorganic secondary aerosols to 20% emission changes. For SOA and primary aerosols, DDM agreed reasonably well with BFM up to 100% emission reductions. The DDM also gave reasonably good predictions for the impact of removing 100% of on-road mobile source emissions (all VOC, NO<sub>x</sub>, and particulate emissions) because the DDM accounts for indirect effects. However, as the size of model input changes increases beyond 20%, higher-order sensitivities become more important in general, and first-order sensitivity alone may not be enough to describe the model response.

Source apportionment by PSAT could successfully approximate the zero-out contributions for primary aerosols. Results for ammonium demonstrate that PSAT source apportionment and zero-out are nearly equivalent in a case (reduction in area source NH<sub>3</sub> emissions) where the emissions-concentration relationship is highly non-linear, but there is no indirect effect. Results for sulfate demonstrate that indirect effects (i.e., oxidant-limited sulfate formation) can limit the ability of zero-out to provide source apportionment and, therefore, that PSAT and zero-out may disagree when there are indirect effects. Indirect effects tend to be more likely when multiple precursors are changed simultaneously suggesting that multiple methods (DDM, PSAT, and zero-out) should be applied for quantifying the impacts of entire source sectors (e.g., on-road mobile sources).

#### Acknowledgment

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#### **Supporting Information**

Summary table showing emissions from each source sector; Scatter plots for nitrate changes at the receptors due to reductions in point source  $NO_x$  emissions; Scatter plots for ammonium changes at the receptors due to reductions in on-road mobile source emissions; Scatter plots for primary PM changes at the receptors due to reductions in on-road mobile source emissions.

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### Figures



**Figure 1.** Modeling domain with locations of the 8 receptors selected: Chicago PM<sub>2.5</sub> nonattainment area (CNAA), St. Louis PM<sub>2.5</sub> nonattainment area (SNAA), Mingo wilderness area (MING), Hercules-Glades wilderness area (HEGL), Upper Buffalo wilderness area (UPBU), Caney Creek wilderness area (CACR), Mammoth Cave national park (MACA), and Sipsey wilderness area (SIPS).



**Figure 2.** Non-linear responses of pollutant concentration to emission reductions:  $\Delta C_1$  and  $\Delta C_2$  represent the changes in the pollutant concentration due to 100% reduction in the emission (from  $E_0$  to 0) estimated using zero-out BFM and first-order DDM sensitivity, respectively; if there exist no indirect effects, PSAT gives the same answer ( $\Delta C_1$ ) as the BFM;  $\Delta C_3$ ,  $\Delta C_4$ , and  $\Delta C_5$  represent the model responses due to a smaller emission change (from  $E_0$  to  $E_1$ ) estimated by BFM, DDM, and PSAT, respectively.



Monthly Average - July Min= 0.00 at (1,1), Max= 9.67 at (75,61) Figure 3. Monthly averaged contributions of domain-wide point source emissions of SO<sub>2</sub> to surface concentrations of PM<sub>2.5</sub> sulfate calculated by the zero-out, PSAT, and DDM simulations for February (top) and July (bottom).



**Figure 4.** Comparison of the  $PM_{2.5}$  sulfate changes ( $\mu g/m^3$ ) due to reductions in point source SO<sub>2</sub> emissions calculated by PSAT/DDM and BFM; each point represents the change in 24-hr average sulfate concentration due to the emission reduction at one receptor on one day. (A positive number means a decrease in ambient sulfate with the decrease in emissions).



**Figure 5.** Comparison of the  $PM_{2.5}$  sulfate changes ( $\mu g/m^3$ ) due to reductions in on-road mobile source emissions calculated by PSAT/DDM and BFM; each point represents the change in 24-hr average sulfate concentration due to the emission reduction at one receptor on one day. (A positive number means a decrease in ambient sulfate with the decrease in emissions and a negative number an increase).



**Figure 6.** Comparison of the  $PM_{2.5}$  ammonium changes ( $\mu g/m^3$ ) due to reductions in area source anthropogenic NH<sub>3</sub> emissions calculated by PSAT/DDM and BFM; each point represents the change in 24-hr average ammonium concentration due to the emission reduction at one receptor on one day.



**Figure 7.** Comparison of the  $PM_{2.5}$  nitrate changes ( $\mu g/m^3$ ) due to reductions in area source anthropogenic NO<sub>x</sub> emissions calculated by PSAT/DDM and BFM; each point represents the change in 24-hr average nitrate concentration due to the emission reduction at one receptor on one day.



**Figure 8.** Comparison of the  $PM_{2.5}$  nitrate changes ( $\mu g/m^3$ ) due to reductions in on-road mobile source emissions calculated by PSAT/DDM and BFM; each point represents the change in 24-hr average nitrate concentration due to the emission reduction at one receptor on one day.



**Figure 9.** Comparison of the  $PM_{2.5}$  SOA changes ( $\mu$ g/m<sup>3</sup>) due to reductions in area source anthropogenic VOC emissions calculated by PSAT/DDM and BFM; each point represents the change in 24-hr average SOA concentration due to the emission reduction at one receptor on one day.



**Figure 10.** Comparison of the  $PM_{2.5}$  SOA changes ( $\mu g/m^3$ ) due to reductions in on-road mobile source emissions calculated by PSAT/DDM and BFM; each point represents the change in 24-hr average SOA concentration due to the emission reduction at one receptor on one day.

## **Supporting Information**

	Average dail	y total emissic	ons (tons/day)	– February	
			On-road		
Species	Point	Area*	mobile	Biogenic	Total
NO <sub>x</sub>	16009	26055	15056	143	42207
	(37.9%)	(61.7%)	(35.7%)	(0.3%)	
VOC	3545	31756	9243	6649	41949
	(8.4%)	(75.7%)	(22.0%)	(15.8%)	
$SO_2$	30135	3768	495	0	33903
	(88.9%)	(11.1%)	(1.5%)	(0.0%)	
NH <sub>3</sub>	202	3571	429	0	3774
	(5.4%)	(94.6%)	(11.4%)	(0.0%)	
Primary	1903	6024	259	0	7927
PM <sub>2.5</sub>	(24.0%)	(76.0%)	(3.3%)	(0.0%)	
	Average dail	y total emissic	ons (tons/day)	– July	
			On-road		
Species	Point	Area <sup>*</sup>	mobile	Biogenic	Total
NO <sub>x</sub>	17018	25143	14007	2872	45034
	(37.8%)	(55.8%)	(31.1%)	(6.4%)	
VOC	3193	26373	9409	193663	223230
	(1.4%)	(11.8%)	(4.2%)	(86.8%)	
$SO_2$	31585	3382	550	0	34967
	(90.3%)	(9.7%)	(1.6%)	(0.0%)	
NH <sub>3</sub>	162	10632	501	0	10794
	(1.5%)	(98.5%)	(4.6%)	(0.0%)	
Primary	12/0	5278	270	0	6527
	1249	5278	270	0	0527

Table S1. Average daily total emissions from point, area, on-road mobile and biogenic sources.

\*Area source emissions include on-road mobile source emissions.



**Figure S1.** Comparison of the  $PM_{2.5}$  ammonium changes ( $\mu g/m^3$ ) due to reductions in on-road mobile source emissions calculated by PSAT/DDM and BFM; each point represents the change in 24-hr average ammonium concentration due to the emission reduction at one receptor on one day.



**Figure S2.** Comparison of the  $PM_{2.5}$  nitrate changes ( $\mu g/m^3$ ) due to reductions in point source anthropogenic NO<sub>x</sub> emissions calculated by PSAT/DDM and BFM; each point represents the change in 24-hr average nitrate concentration due to the emission reduction at one receptor on one day.



**Figure S3.** Comparison of the primary  $PM_{2.5}$  changes ( $\mu g/m^3$ ) due to reductions in on-road mobile source emissions calculated by PSAT/DDM and BFM; each point represents the change in 24-hr average primary  $PM_{2.5}$  concentration due to the emission reduction at one receptor on one day.

# Appendix A

#### **Supporting Material**

Spatial plots showing monthly average contributions of anthropogenic point  $NO_x$ , area  $NO_x$ , area  $NH_3$ , and area VOC emissions estimated by the zero-out, PSAT, and DDM simulations; Scatter plots for SOA changes at the receptors due to 20% reductions in area source biogenic VOC emissions.



**Figure A-1.** Monthly averaged contributions of domain-wide point source emissions of NO<sub>x</sub> to surface concentrations of PM<sub>2.5</sub> nitrate calculated by the zero-out, PSAT, and DDM simulations for February (top) and July (bottom).



**Figure A-2.** Monthly averaged contributions of domain-wide area source emissions of  $NO_x$  to surface concentrations of  $PM_{2.5}$  nitrate calculated by the zero-out, PSAT, and DDM simulations for February (top) and July (bottom).



**Figure A-3.** Monthly averaged contributions of domain-wide area source emissions of  $NH_3$  to surface concentrations of  $PM_{2.5}$  ammonium calculated by the zero-out, PSAT, and DDM simulations for February (top) and July (bottom).



Min= 0.000 at (1,1). Max= 0.040 at (71,95) Min= 0.000 at (1,1). Max= 0.034 at (71,95) Min= 0.000 at (1,1). Max= 0.040 at (71,95) Min= 0.000 at (71,95) Min= 0.000



**Figure A-5.** Comparison of the  $PM_{2.5}$  SOA changes ( $\mu g/m^3$ ) due to 20% reduction in area source biogenic VOC emissions calculated by PSAT/DDM and BFM; each point represents the change in 24-hr average SOA concentration due to the emission reduction at one receptor on one day.

# **Appendix B**

## **Progress Report**

Updating the DDM implementation for the latest version of CAMx

### 1. Background

The Coordinating Research Council (CRC) has previously funded several different studies related to the CAMx Probing Tools as follows:

<u>CRC Project A-29</u>: This project first implemented the Decoupled Direct Method (DDM) for sensitivity analysis in CAMx for ozone. The project was a collaboration between ENVIRON and General Motors (GM) and resulted in two publications: one describing the DDM implementation (Dunker et al., 2002a) and the second comparing DDM and OSAT (Dunker et al., 2002b).

<u>CRC Project A-37</u>: This project involving AER, ENVIRON, and UC Riverside compared DDM, OSAT and process analysis in CAMx for ozone. Project participants disagreed on the methods chosen by AER to compare DDM and OSAT. The project highlighted that source sensitivity and source apportionment are different when pollutants are formed by non-linear chemical processes. Project A-37 resulted in one publication (Zhang et al., 2005).

<u>CRC Project A-51</u>: This project extended the CAMx DDM implementation from ozone to particulate matter (PM). A major effort was developing rigorous sensitivity equations for inorganic aerosol (sulfate/nitrate/ammonium/sea-salt) as solved by the ISORROPIA algorithm (Nenes et al., 1998). ENVIRON and GM collaborated on the DDM implementation for PM which was then tested in a full 3D simulation to ensure proper implementation. The project resulted in one publication (Koo et al., 2007).

The objective of the current project (CRC Project A-64) is to determine the advantages and limitations of the Probing Tools for PM (DDM and PSAT) in three-dimensional photochemical grid models.

This Progress Report documents the efforts made to update the current DDM implementation for the latest version of CAMx and testing results to confirm that the porting was successful.

## 2. Porting Current DDM Implementation in CAMx

Since the DDM was originally implemented in CAMx v3.0 for gas-phase species like ozone and later extended for PM in CAMx v4.2, there have been several public releases of the CAMx model with the latest one being version 4.5. Some of the updates made in the newer versions of CAMx have impacts on the existing DDM implementation, thus requires it to be updated.

## 2.1. Implementing DDM in EBI Chemistry Solver

The DDM implementation in the CAMx gas-phase chemistry was originally developed for the CMC chemistry solver and closely follows solution algorithm of the solver. With CAMx v4.3, a change was made to the solution algorithm for NO3 and N2O5 in the CMC solver to improve accuracy under cold conditions, thus breaking the DDM implementation. The original plan of the CRC project was to update the DDM implementation for the modified CMC solver.

However, it has recently been decided that the CMC chemistry solver in CAMx is to be replaced by the Euler Backward Iterative (EBI) solver (Hertel et al., 1993), which provides similar (during the day) or better (at night) accuracy with similar numerical efficiency to the CMC solver. CRC agreed to change the plan to implement the DDM for the EBI solver instead of updating it for the CMC solver.

The updated CAMx model was applied for a June 2005 ozone modeling episode with a 36 km grid covering the Eastern US. First, we compared accuracy of different chemistry solvers implemented in CAMx: LSODE, IEH, CMC, and EBI solvers. The LSODE, IEH, and CMC solvers are described in CAMx User's Guide (ENVIRON, 2008). Note that the CMC solver tested here was the original version without the modified algorithm for NO3/N2O5 radicals. LSODE is based on Gear's method, and regarded as the most accurate among the chemistry solvers in CAMx, thus serves as a reference for the comparison. Figure B-1 shows that the EBI solver provides better agreement with LSODE than the CMC solver while IEH is slightly better than EBI. The numerical efficiency of the EBI solver is comparable to that of the CMC solver (Figure B-4).

To test the DDM implementation in the EBI solver, 8-hour average ozone sensitivities to the domain-wide emissions of NOx or VOC were calculated by the brute-force method (BFM) and the DDM. Figures B-2 and B-3 show normalized mean bias (NMB) and error (NME) and coefficient of determination ( $r^2$ ) from linear regression. The NMB and NME are defined as follows:

$$NMB = \frac{\sum (S(DDM) - S(BFM))}{\sum S(BFM)}$$
$$NME = \frac{\sum |S(DDM) - S(BFM)|}{\sum S(BFM)}$$

where S(DDM) and S(BFM) are sensitivities calculated by the DDM and BFM, respectively. The BFM sensitivities were calculated by running the standard model twice with small input changes:

$$S(BFM) = \frac{C(+10\%) - C(-10\%)}{0.2}$$

where C(+10%) is the ozone concentration from the model run with 10% increase in NOx or VOC emissions and C(-10%) with 10% decrease in the emissions.

We have included in the plots results from the DDM-3D which was recently implemented in CAMx. The DDM-3D is a DDM variant developed by Georgia Tech (Yang et al., 1997) and uses a different (usually larger) time step to integrate time progression of sensitivities than concentrations. This approach helps to improve the computational efficiency, but may introduce inconsistencies between the sensitivities and concentrations.

On our testing, the DDM provided better agreement with the BFM than the DDM-3D did. It appears that the DDM-3D approach does not work well with the CMC chemistry solver. The DDM implementation in the EBI solver shows similar level of accuracy to the previous DDM implementation in the CMC solver.

Figure B-4 compares computational efficiency. The CPU times for the DDM and DDM-3D are shown as the time required for solving sensitivities only and defined as follows:

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

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). It is shown that the DDM with the EBI solver is less efficient than the DDM with CMC. Efficiency of the DDM-3D is little affected by the chemistry solver used as the DDM-3D does not follow the solution algorithm of individual chemistry solver.



**Figure B-1.** Daily average differences in 8-hr average ozone concentrations in the surface layer between LSODE and other chemistry solvers (IEH, CMC, and EBI).



**Figure B-2.** Comparison between 8-hour average ozone sensitivities to the domain-wide emissions of NOx by the BFM and DDM.



**Figure B-3.** Comparison between 8-hour average ozone sensitivities to the domain-wide emissions of VOC by the BFM and DDM.



**Figure B-4.** Average CPU time per simulation day for different chemistry solvers; Plotted for DDM-3D and DDM runs are the CPU time required to calculate sensitivities per sensitivity parameters (from the runs with 4 sensitivity parameters); based on OMP runs with four 2.8 GHz processors.

### 2.1. ISORROPIA v1.7

ISORROPIA, the thermodynamic equilibrium model for inorganic particles, was recently updated to v1.7. The main changes from the previous version are as follows (Fountoukis et al., 2006):

- The water activity database was updated using the output from the AIM model.
- A bug in the subroutine calculating temperature dependence of Kusik-Meissner binary activity coefficients was fixed and the tabulated binary activity coefficients were recomputed.
- Upper limit in ionic strength was increased to smooth out the solution for low relative humidity (RH).
- The deliquescence RH (DRH) of NH4NO3 is strongly dependent on temperature. Under low temperature conditions (T<270K), this changes the order (starting from low to high RH) with which salts deliquesce. For these cases the DRH of NH4NO3 is assumed to not "cross over" the DRH of the other salts present in the solution, especially since thermodynamic data for supercooled NH4NO3 solutions are not known. The same is assumed for NH4Cl and NaNO3 which exhibit similar behavior with NH4NO3.
- Fixed an inaccuracy problem in the polynomial fit used for the water activity database that has sometimes caused too high water content for relative humidity near saturation.
- Temperature correction to the water activity database was turned off.

Some of the changes required to update the current DDM implementation in ISORROPIA. The updated DDM code was tested in the stand-alone mode with the same input configurations as used in the previous CRC study (Koo et al., 2006a). The DDM and BFM sensitivities were calculated for the following three aerosol types with RH range of 25% to 95% (with increments of 5%). Temperature was set to 298 K.

Sulfate poor (sulfate ratio greater than 2)

Total Na	$= 1.0 \times 10^{-9} \text{ mol/m}^3$
Total SO <sub>4</sub>	$= 1.0 \times 10^{-7} \text{ mol/m}^3$
Total NH <sub>4</sub>	$= 2.5 \times 10^{-7} \text{ mol/m}^3$
Total NO <sub>3</sub>	$= 2.0 \times 10^{-7} \text{ mol/m}^3$
Total Cl	$= 1.0 \times 10^{-9} \text{ mol/m}^3$

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

Total Na	$= 1.0 \times 10^{-9} \text{ mol/m}^3$
Total SO <sub>4</sub>	$= 1.0 \times 10^{-7} \text{ mol/m}^3$
Total NH <sub>4</sub>	$= 1.7 \times 10^{-7} \text{ mol/m}^3$
Total NO <sub>3</sub>	$= 2.0 \times 10^{-7} \text{ mol/m}^3$
Total Cl	$= 1.0 \times 10^{-9} \text{ mol/m}^3$

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

Total Na	$= 1.0 \times 10^{-9} \text{ mol/m}^3$
Total SO <sub>4</sub>	$= 2.0 \times 10^{-7} \text{ mol/m}^3$
Total NH <sub>4</sub>	$= 1.7 \times 10^{-7} \text{ mol/m}^3$
Total NO <sub>3</sub>	$= 2.0 \times 10^{-7} \text{ mol/m}^3$
Total Cl	$= 1.0 \times 10^{-9} \text{ mol/m}^3$

Figures B-5 to B-7 show the sensitivities predicted by the DDM and BFM. As in the test results of the previous CRC project, the DDM and BFM sensitivities agree well except for a few cases where ISORROPIA shows abrupt change in the slope of the concentrations as a function of input changes.

For the sulfate poor system, there are three RH's where the DDM and BFM don't agree well. Table B-1 shows that for the cases with input changes in total SO4 and total NH4, ISORROPIA predicted different sub-cases for +10% and -10% changes resulting in abrupt changes in the concentration slope (note that although the cases with  $\pm 10\%$  changes in total NH4 at RH=60% fall into the same sub-case, ISORROPIA actually predicted different aerosol types). The case with input changes in total NO3 at RH=65% is an exception in that even though ISORROPIA predicted the same sub-case and aerosol type, the DDM and BFM sensitivities are slightly different. We investigated this case in detail and discovered that ISORROPIA's solution algorithm didn't converge in this case yielding a slightly incorrect solution (see Section 5). We have contacted the developers of ISORROPIA and they are currently investigating this problem. Fortunately, the discrepancy between the DDM and BFM sensitivities in this case is not large.

For the sulfate rich, no free acid system, the DDM and BFM sensitivities of HNO3 differ at RH =95% (indicated by red arrows in Figure B-6). This is due to ISORROPIA's assumption that the dissolution of HNO3 in this regime is minor. The same discrepancy was experienced in the previous CRC study and explained in the Final Report (Koo et al., 2006a).

Input Change	RH (%)	Sub-cases		
		-10% input change	+10% input change	
Total SO4	65	G2S1 (solid & liquid possible)	G2S2 (solid only)	
Total NH4	60	G1S2 (solid only)	G1S2 (solid & liquid possible)	
	65	G2S2 (solid only)	G2S1 (solid & liquid possible)	
	70	G2S2 (solid only)	G2S1 (solid & liquid possible)	
Total NO3	65	G2S1 (solid & liquid possible)	G2S1 (solid & liquid possible)	

**Table B-1.** Sub-cases at +10% and -10% input changes for the sulfate poor system at RH = 60, 65, and 70\%.



**Figure B-5.** The DDM and BFM sensitivities of a sulfate poor system to the change of total SO4 (a), total NH3 (b), and total NO3 (c); the units are  $\mu$ mol/m<sup>3</sup> except for water which is in mg/m<sup>3</sup>; the black, red, and blue arrows indicate RH = 60%, 65%, and 70%, respectively.



**Figure B-6.** The DDM and BFM sensitivities of a sulfate rich, no free acid system to the change of total SO4 (a), total NH3 (b), and total NO3 (c); the units are  $\mu$ mol/m<sup>3</sup> except for water which is in mg/m<sup>3</sup>; the red arrows indicate RH = 95%.



**Figure B-7.** The DDM and BFM sensitivities of a sulfate rich, free acid system to the change of total SO4 (a), total NH3 (b), and total NO3 (c); the units are  $\mu$ mol/m<sup>3</sup> except for water which is in mg/m<sup>3</sup>.

#### 2.2. Updated SOA Chemistry

With CAMx v4.5, gas-phase chemistry of SOA precursors (e.g., aromatics, monoterpenes, etc.) is separated from the main gas-phase chemistry to facilitate modeling SOAs with different oxidant mechanisms (e.g., CB05, SAPRC99, etc.). Therefore, new DDM codes need to be developed for the SOA precursor chemistry routine. Also, new SOA forming pathways have been added based on recent advances in the SOA chemistry, which include SOA formation from isoprene, sesquiterpenes, and polymerization of SOA into non-volatile PM species (Koo et al., 2006b). The DDM code for the CAMx SOA module needs to be updated accordingly.

The following gas-phase reactions for SOA precursors are handled separately from the main gasphase chemistry:

Toluene + OH	→ 0.044 CG1 + 0.085 CG2	; k <sub>12</sub>
Xylene + OH	→ 0.027 CG1 + 0.118 CG2	; k <sub>22</sub>
Isoprene + O	$\rightarrow$	; k <sub>31</sub>
Isoprene + OH	→ 0.015 CG3 + 0.12 CG4	; k <sub>32</sub>
Isoprene + O3	$\rightarrow$	; k <sub>33</sub>
Isoprene + NO3	$\rightarrow$	; k <sub>34</sub>
Monoterpene + O	→ 0.065 CG5 + 0.29 CG6	; k <sub>41</sub>
Monoterpene + OH	→ 0.065 CG5 + 0.29 CG6	; k <sub>42</sub>
Monoterpene + O3	→ 0.065 CG5 + 0.29 CG6	; k <sub>43</sub>
Monoterpene + NO3	→ 0.065 CG5 + 0.29 CG6	; k <sub>44</sub>
Sesquiterpene + OH	→ 0.85 CG7	; k <sub>52</sub>
Sesquiterpene + O3	→ 0.85 CG7	; k <sub>53</sub>
Sesquiterpene+NO3	→ 0.85 CG7	; k <sub>54</sub>

The concentrations of oxidants (O, OH, O3, and NO3) are assumed constant for the current time step and taken from the main gas-phase chemistry module at the mid-point of the time step. This results in simple first-order reactions. The analytic solutions for the concentrations and sensitivities are:

$$C_{1}(P_{i}) = C_{0}(P_{i})\exp\left[-\Delta t\sum_{j}k_{ij}C_{1/2}(O_{j})\right]$$

$$C_{1}(CG_{k}) = C_{0}(CG_{k}) + \sum_{i}\left[(C_{0}(P_{i}) - C_{1}(P_{i}))\sum_{j}\frac{Y_{ijk}k_{ij}C_{1/2}(O_{j})}{\sum_{j}k_{ij}C_{1/2}(O_{j})}\right]$$

$$S_{1}(P_{i}) = S_{0}(P_{i})\exp\left[-\Delta t\sum_{j}k_{ij}C_{1/2}(O_{j})\right] - \Delta tC_{1}(P_{i})\sum_{j}k_{ij}S_{1/2}(O_{j})$$

$$S_{1}(CG_{k}) = S_{0}(CG_{k}) + \sum_{i} \begin{bmatrix} (S_{0}(P_{i}) - S_{1}(P_{i}))\sum_{j} \frac{Y_{ijk}k_{ij}C_{1/2}(O_{j})}{\sum_{j}k_{ij}C_{1/2}(O_{j})} + \\ (C_{0}(P_{i}) - C_{1}(P_{i}))\sum_{j} \begin{bmatrix} \frac{Y_{ijk}k_{ij}S_{1/2}(O_{j})}{\sum_{j}k_{ij}C_{1/2}(O_{j})} - \frac{Y_{ijk}k_{ij}C_{1/2}(O_{j})\sum_{j}k_{ij}S_{1/2}(O_{j})}{\left(\sum_{j}k_{ij}C_{1/2}(O_{j})\right)^{2}} \end{bmatrix}$$

where  $C_0$ ,  $C_1$ , and  $C_{1/2}$  are concentrations at  $t_0$ ,  $t_0+\Delta t$ , and  $t_0+\Delta t/2$ , respectively;  $S_0$ ,  $S_1$ , and  $S_{1/2}$  are sensitivities at  $t_0$ ,  $t_0+\Delta t$ , and  $t_0+\Delta t/2$ , respectively;  $P_i$ ,  $O_j$ , and  $CG_k$  are the i-th precursor, the j-th oxidant, and the k-th condensable gas (CG) species, respectively;  $k_{ij}$  is the rate constant for reaction of the i-th precursor with the j-th oxidant; and  $Y_{ijk}$  is the stoichiometric coefficient of the k-th CG species for reaction of the i-th precursor with the j-th oxidant.

In addition to 7 SOA species corresponding to 7 CG species, there are two more SOA species from polymerization of anthropogenic and biogenic SOAs: SOPA and SOPB. Due to limited available data, current implementation simply assumes a fixed polymerization rate:

$$C_{1}(SOPA) = C_{0}(SOPA) + r_{P}\Delta t [C_{1}(SOA1) + C_{1}(SOA2)]$$
  

$$C_{1}(SOPB) = C_{0}(SOPB) + r_{P}\Delta t [C_{1}(SOA3) + C_{1}(SOA4) + C_{1}(SOA5) + C_{1}(SOA6)]$$

where  $r_P$  is the fixed polymerization rate. Note that SOA from sesquiterpene does not participate in polymerization since it is already assumed non-volatile. Sensitivities of these species are:

$$S_{1}(SOPA) = S_{0}(SOPA) + r_{P}\Delta t [S_{1}(SOA1) + S_{1}(SOA2)]$$
  

$$S_{1}(SOPB) = S_{0}(SOPB) + r_{P}\Delta t [S_{1}(SOA3) + S_{1}(SOA4) + S_{1}(SOA5) + S_{1}(SOA6)]$$

The updated DDM implementation in the SOA module is tested with full model runs in the following section because organic species mostly do not interact with inorganic species in the CAMx PM modules.

#### 3. Full Model Test

The updated CAMx DDM code was applied for the June 2002 episode for the Midwest Regional Planning Organization (MRPO) which is the same test case used for the previous CRC project. Notable changes in the model configuration between the previous and current tests are as follows:

- ISORROPIA was upgraded from v1.6 to v1.7.
- The EBI chemistry solver was used instead of the CMC solver.

• IC, BC, and emissions for SOA precursors are changed according to the updated SOA module.

The DDM and BFM sensitivities of PM<sub>2.5</sub> sulfate (PSO4), nitrate (PNO3), ammonium (PNH4), and SOA (SOA1+SOA2+SOA3+SOA4+SOA5+SOA6+SOA7+SOPA+SOPB) to domain-wide emissions of NOx, VOC, SO2, NH3, and POA were calculated. Linear regression analysis was performed to examine the level of agreement between the DDM and BFM sensitivities and the result was compared with that of the previous CRC study (Figure B-8).

In most cases, the results from the current study (CRC A64) show similar or better agreement between the DDM and BFM sensitivities to those from the previous study (CRC A51). Notable exception is the sensitivity of PNO3 to SO2 emissions. However, the mean BFM sensitivity (BFM sensitivity averaged over the domain) in this case is very small (less than  $0.1 \,\mu\text{g/m}^3$  change in PNO3 for 100% change in SO2 emissions) and that of the current test is even smaller (~-0.01  $\mu\text{g/m}^3$ ). With such a small sensitivity, the BFM sensitivity is known to suffer from numerical noise (numerical uncertainty in two very similar outputs will contaminate the BFM calculation).

Based on these test results, it appears that the DDM implementation has been successfully ported to the new version of CAMx.



**Figure B-8.** Mean BFM sensitivities and linear regression analysis statistics for the agreement between the 24-hr average DDM and BFM sensitivities from the previous and current CRC studies.

#### 4. Impact of Aerosol Water on Deposition

The previous CRC study raised a potential problem related to the CAMx deposition processes. The issue arose from the fact that unlike for gas-phase species, the deposition rates (dry deposition velocity and wet scavenging rate) for PM species depend on the physical properties (size and density) of the particle itself as well as environmental factors. If a particle absorbs significant water, it will change particle density and diameter, which in turn affects dry deposition velocity and wet scavenging rate. Under the previous CRC study, the DDM and BFM test runs were conducted with and without the deposition processes. Although the discrepancies between the DDM and BFM sensitivities slightly increased when deposition was included, it was unclear that the increased discrepancies were caused by lack of particle size effects in the DDM solution algorithm or added nonlinearity due to the deposition processes. To identify the real cause, we have conducted an experiment where the DDM and BFM simulations were run with modified deposition modules in which particle size and density remain constant. Only one of either dry or wet deposition processes is included in each test to examine their effects separately. The sensitivity of PSO4 to PSO4 emissions was selected because it shows mostly linear response in the PM modules such as ISORROPIA and RADM-AQ yet can have a significant impact on the particle water absorption. Since the original emissions inputs have very little PSO4 emissions, we artificially boosted them by transferring 20% of SO2 emissions to PSO4. Figure B-9 shows scatter plots of normalized errors between the DDM and BFM:

$$E = \frac{|S(DDM) - S(BFM)|}{|S(BFM)|}$$

It turned out that the effect of particle size and density on the deposition rate has little impact on the overall agreement between the DDM and BFM sensitivities. In addition, the full test conducted in the above section was repeated with the modified deposition modules and the linear regression analysis results were compared with those with standard deposition modules. Figure B-10 shows that the runs with the standard and modified deposition modules yield almost identical results. Therefore, we believe that lack of particle size effects in the current DDM implementation does not significantly affect the agreement between the DDM and BFM sensitivities.



**Figure B-9.** Scatter plots of normalized errors between the DDM and BFM sensitivities for the simulations with standard or modified deposition vs. no deposition.



**Figure B-10.** Mean BFM sensitivities and linear regression analysis statistics for the agreement between the 24-hr average DDM and BFM sensitivities from the CAMx runs with standard and modified deposition modules.

#### 5. Convergence Problem in ISORROPIA

The ISORROPIA sub-case "G2S1" represents the sulfate poor, sodium poor, sodiumammonium-nitrate-sulfate-chloride aerosol system, when the RH is between the DRH of NH4NO3 and NH4Cl. An aqueous phase is assumed to exist and possible solid salts are (NH4)2SO4, NH4Cl, and Na2SO4. The relevant equilibrium reactions are as follows:

$$\begin{split} &Na_{2}SO_{4}(s) \leftrightarrow 2Na^{+} + SO_{4}^{2-} & K_{5} = [Na^{+}]^{2}[SO_{4}^{2-}]\gamma_{Na^{+}}^{2}\gamma_{SO_{4}^{2-}} \\ &(NH_{4})_{2}SO_{4}(s) \leftrightarrow 2NH_{4}^{+} + SO_{4}^{2-} & K_{7} = [NH_{4}^{+}]^{2}[SO_{4}^{2-}]\gamma_{NH_{4}^{+}}^{2}\gamma_{SO_{4}^{2-}} \\ &NH_{3}(g) + H_{2}O(aq) \leftrightarrow NH_{4}^{+} + OH^{-} & K_{2} = \frac{[NH_{4}^{+}]\gamma_{NH_{4}^{+}}}{P_{NH_{3}}[H^{+}]\gamma_{H^{+}}}K_{w} \\ &HCl(g) \leftrightarrow H^{+} + Cl^{-} & K_{3} = \frac{[H^{+}][Cl^{-}]\gamma_{H^{+}}\gamma_{Cl^{-}}}{P_{HCl}} \\ &HNO_{3}(g) \leftrightarrow H^{+} + NO_{3}^{-} & K_{4} = \frac{[H^{+}][NO_{3}^{-}]\gamma_{H^{+}}\gamma_{NO_{3}^{-}}}{P_{HNO_{3}}} \end{split}$$

And the mass and charge balance equations are:

$$\begin{split} Y_{0}(tNa) &= Y_{1}(Na^{+}) + 2Y_{1}(Na_{2}SO_{4}) \\ Y_{0}(tNH_{4}) &= Y_{1}(NH_{3}) + Y_{1}(NH_{4}^{+}) + 2Y_{1}((NH_{4})_{2}SO_{4}) + Y_{1}(NH_{4}Cl) \\ Y_{0}(tSO_{4}) &= Y_{1}(SO_{4}^{2^{-}}) + Y_{1}((NH_{4})_{2}SO_{4}) + Y_{1}(Na_{2}SO_{4}) \\ Y_{0}(tNO_{3}) &= Y_{1}(HNO_{3}) + Y_{1}(NO_{3}^{-}) \\ Y_{0}(tCl) &= Y_{1}(HCl) + Y_{1}(Cl^{-}) + Y_{1}(NH_{4}Cl) \\ Y_{1}(H^{+}) + Y_{1}(Na^{+}) + Y_{1}(NH_{4}^{+}) &= 2Y_{1}(SO_{4}^{2^{-}}) + Y_{1}(NO_{3}^{-}) + Y_{1}(Cl^{-}) + \frac{K_{w}a_{w}Y_{1}(W)^{2}}{Y_{1}(H^{+})} \end{split}$$

Note that equilibrium between  $SO_4^{2^-}$  and  $HSO_4^-$  is assumed not to disturb the established equilibrium and thus solved separately. Assuming all the sodium to exist in the form of Na2SO4 (whose dissociation is later determined), the system is solved iteratively using bi-section method with chloride ion concentration as the independent variable. The objective function used is the departure of  $Y_1(C\Gamma)$ ,  $Y_1(NH_4^+)$ ,  $Y_1(HCl)$ , and  $Y_1(NH_3)$  from the equilibrium state, according to the reaction:  $NH_3(g) + HCl(g) \leftrightarrow NH_4^+ + Cl^-$ .

$$Objective \ Function = \frac{\frac{Y_{1}(NH_{4}^{+})Y_{1}(Cl^{-})}{Y_{1}(NH_{3})Y_{1}(HCl)}}{\frac{K_{2}K_{3}[RTY_{1}(W)]^{2}}{K_{w}\gamma_{NH_{4}^{+}}\gamma_{Cl^{-}}}} - 1 \qquad \Rightarrow \qquad 0$$

The ISORROPIA code was modified to output the objective function value for each iteration and applied for the test case described in Section 2.1. Figure B-11 shows progression of the bisection root finding. Apparently, it fails to converge. Tightening the error tolerances of the solver routine didn't help in this case (Figure B-12).



**Figure B-11.** Progression of the bi-section root finding for the ISORROPIA sub-case G2S1 (with default error tolerances).



**Figure B-12.** Progression of the bi-section root finding for the ISORROPIA sub-case G2S1 (with tightened error tolerances).

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