Final Summary Report

**SUPPORTING THE MRPO'S PM
AND VISIBILITY MODELING:
CAMx EVALUATION AND IMPROVEMENTS**

Prepared for

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1. INTRODUCTION

Under a Section 103 grant from the U.S. Environmental Protection Agency, the Lake Michigan Air Directors Consortium (LADCO) over the past two years has sponsored ENVIRON to improve and evaluate the Comprehensive Air quality Model with extensions (CAMx). This project has led to many key enhancements geared toward advancing both the technical treatments of the model and its integrated analysis tools. The updates covered gas and PM chemistry, deposition processes, plume-in-grid capabilities, and new and improved source apportionment tools. Many enhancements have been incorporated into publicly released versions of CAMx and associated pre-processors, starting with v4.00 in May 2003 and culminating in v4.20 in Spring 2005. These improvements provide LADCO and the Midwest Regional Planning Organization (MRPO) with an important advance in modeling technology to meet regulatory goals that are coming up.

This summary report describes the major tasks undertaken for the LADCO CAMx evaluation and improvement project. The tasks are fully documented in separate reports, and are thus only summarized here. These include:

- Improvements to the wet deposition treatment (Kemball-Cook et al., 2004);
- Inclusion of deposition and PM chemistry into the full chemistry version of the CAMx Plume-in-Grid (PiG) module (Emery and Yarwood, 2005);
- Updates to the Carbon Bond IV (CB4) gas-phase chemistry mechanisms (Yarwood et al., 2005a); and
- Development of the Particulate Source Apportionment Technology (PSAT) Probing Tool (Yarwood et al., 2005b);

1.1 BACKGROUND

The LADCO model evaluation and improvement project began in 2003 subsequent to the public release of CAMx v3.10. At the time, LADCO and the MRPO were gearing up for regional PM modeling to meet the regulatory demands of the new fine particulate and regional visibility rules. CAMx v3.10 had a reduced-form PM chemistry capability based on the UAM-AERO/LT approach (Kumar and Lurmann, 1996) that included gas-phase formation of sulfate, nitrate and condensable organic gases (CGs), inorganic aerosol equilibrium, secondary organic aerosol (SOA) from CGs , and species-dependent aerosol size and density. However, another version of CAMx included a much more advanced "one-atmosphere" aerosol treatment, including explicit aqueous-phase chemistry, inorganic chemistry via ISORROPIA, SOA chemistry via SOAP, and a time-evolving multi-section size model. The version of CAMx with advanced PM chemistry was developed with support from the Coordinating Research Council (CRC) and referred to as PMCAMx (ENVIRON, 2003). PMCAMx is the predecessor to the version 4 series of CAMx.

Recognizing the technical requirements necessary for regional PM modeling, the LADCO project provided resources to assist in bringing PMCAMx to a state where it could be used for regulatory PM and visibility modeling by States. LADCO provided significant insight from a user-oriented perspective into areas of needing improvement in chemistry, deposition, and Probing Tool technology.

Table 1-1 shows the development timeline for CAMx during the course of the LADCO project, and lists the specific upgrades associated with each version release. Those components that were supported (e.g., through testing and analysis) or specifically developed as part of the LADCO project are noted.

Table 1-1. CAMx v4 development timeline from 2003 to 2005 with LADCO supported developments highlighted in gray.

CAMx Version	Key Model Updates
V4.00 Released 5/31/03	• Public release of the "CF" PM treatment (consistent with PMCAMx but with 2-mode static size distribution) • New detailed wet deposition algorithm for gasses and PM • Addition of deposition output files • Aligned drought stress adjustment to dry deposition rates with the GloBEIS3 biogenic emissions model • Addition of dry deposition adjustment to surface resistance for strong acids
	• Introduction of the RTRAC Probing Tool for air toxics and other tracers • Removal of the Smolarkiewicz advection and UAM-V type cloud files • Inclusion of Process Analysis for the SAPRC99 chemical mechanism • Layer-dependent time steps for horizontal advection
V4.10s Released 8/1/04	• Public release of the "CMU" PM treatment (equivalent to PMCAMx) • Updated empirical rainfall relationships for wet deposition (including revised MM5-CAMx interface for clouds/rain input fields)
V4.11s Release 12/6/04	• Revised memory initialization in ISORROPIA for compatibility with certain Fortran compilers • Engaged multi-processor capability using OMP for CF PM treatment
V4.20 Release Spring 2005	• Introduction of the PSAT Probing Tool for PM source apportionment • Introduction of IRON PiG (and a pre-release version of PM PiG to LADCO) • Introduction of LSODE gas phase chemistry solver option • Revised vertical diffusion solver to perform multiple steps on large grids • Added season-specific surface roughness based on AERMOD • Extended inorganic reaction set for the Carbon Bond mechanism (CB4xi) used for PM modeling
	• Introduction of Mercury chemistry in the CF PM treatment • Introduction of Mechanism 10 (user-defined simple chemistry) • Updates to RTRAC for air toxics (inclusion into IRON PiG puff model, optional sampling grid, tracers may be secondary species) • Additional surface information stored in the AHO file, including optional drought stress, snow cover, land-ocean and roughness maps • Conversion of the CAMx control file to Fortran "namelist" format • Reduced horizontal diffusivity as a function of grid size • Improved relationship between season and date/location for both northern and southern hemispheres • Updates to Process Analysis, including output of photolysis rates and radical concentrations

2. IMPROVEMENTS TO DEPOSITION MODELING

The project summarized in this section was sponsored by the Lake Michigan Air Directors Consortium (LADCO) to improve the rainfall information provided to the CAMx v4 wet deposition algorithm, and to evaluate model performance against acid deposition data from the National Trends Network (NTN) and Mercury Deposition Network (MDN) for a 2002 annual simulation on the National RPO modeling grid. The full report is given in Kemball-Cook et al. (2004) and the CAMx updates will be released in version 4.20.

2.1 WET DEPOSITION IMPROVEMENTS

Wet deposition is an important removal process for particulate matter (PM) and soluble PM precursors such as nitric acid and ammonia. The wet deposition scheme in CAMx v4 addresses in-cloud and below-cloud removal for both gases and PM by liquid precipitation. Wet removal is modeled throughout complete columns of grid cells so that rain collects (or releases) soluble material while its liquid water content evolves as it falls; the amount of dissolved gasses is limited by their solubility and diffusivity into falling rain drops. Consideration of wet removal from a complete column of cells is most important for sparingly soluble gasses that may super-saturate in rainwater as drops fall. This is an improvement over the wet deposition formulation in CAMx v3 in which: (1) wet removal was calculated independently in each grid cell according to the surface precipitation rate, (2) all removed material was transferred directly to the ground, and (3) all gasses were assumed to be completely dissolved to the limit of either their solubility or ambient concentration, with no diffusive or super-saturation limitations.

The CAMx v4 wet deposition scheme was quantitatively evaluated as part of the Wisconsin Department of Natural Resources (WDNR) mercury (Hg) modeling project for a 2002 annual simulation (Yarwood et al., 2003). The evaluation employed precipitation and mercury deposition data from the Mercury Deposition Network (MDN), and showed that CAMx produced too much mercury deposition as a result of an overestimation of rainfall in the meteorological fields provided to CAMx. When the bias in the input rainfall was reduced, the CAMx Hg deposition field better reproduced the observed deposition. The excess rainfall was found to be the result of MM5's tendency to overestimate the surface rain field (particularly its convective component), and partly due to the interface between MM5 and CAMx through the meteorological preprocessor "MM5CAMx".

Improved deposition performance is important to the Midwest Regional Planning Organization (MRPO) for ongoing regional particulate matter (PM) and visibility modeling. The main objective of this project was to improve the interface between MM5 and CAMx so that rainfall calculated by MM5 is more accurately represented in CAMx. We did not believe going into this work that major changes to the CAMx wet scavenging scheme were necessary since the problems seemed to be with the amount of rain and clouds provided to the model. Therefore, we focused on changes to the MM5CAMx preprocessor, rather than CAMx, and tested the suitability of an approach to scale MM5 precipitation fields based on observed rainfall patterns.

We developed a multi-step approach to test model sensitivity to the major issues we identified in the design document (ENVIRON, 2004a). This was done by sequentially changing MM5CAMx (and CAMx in some cases) in steps and testing each modification. Finally, we compensated for

the effect of biases in the MM5 precipitation field on the CAMx wet deposition fields by applying a scaling factor to the input precipitation. This adjusts the MM5CAMx precipitation so that the rainfall fields going into CAMx agree more closely with observations.

Summary of Results

A summary of the main results from the developmental portion of this study follows:

- The modifications made to the MM5CAMx preprocessor improved the estimation of resolved rainfall rates going into CAMx.

- These modifications caused overall reductions in Hg(II) wet deposition and increases in PSO4 wet deposition in areas of the domain where convective precipitation dominates.

- The use of observed precipitation data to scale MM5 rainfall results in further reductions in Hg(II) wet deposition, particularly in summer when convective rainfall is most important.

Tables 2-1 and 2-2 summarize the impacts of several modifications to the MM5CAMx preprocessor and to CAMx itself. CAMx was run for each of these modifications for two periods to illustrate the impacts in two different climatological regimes: January and July. Details on each modification are provided in Kemball-Cook et al. (2004).

Table 2-1. Summary of cumulative effects on wet deposition through Modification 5.

	January	July
Hg(II) Wet Deposition	DECREASE Largest change from Mod 2	DECREASE Largest change from Mod 3
Ozone Wet Deposition	**Decrease** Largest change from Mod 2	**Little change**
PSO$_4$ Wet Deposition	**Decrease** for resolved rainfall **Increase** for convective rainfall Largest change from Mod 2	**Increase** in East/Southeast U.S. where rainfall is mainly convective Largest change from Mod 3,5
PNO$_3$ Wet Deposition	**Increase**. Change not well correlated with change in rainfall	**Increase** in Midwest and along Eastern Seaboard.
PNH$_4$ Wet Deposition	**Little change**	**Increase** in East/Southeast U.S. where rainfall is mainly convective
Rainfall	**Decrease** in northern part of domain from Mod 2	**Little change**

Table 2-2. Summary of changes due to scaling MM5CAMx precipitation.

	January	July
Hg(II) Wet Deposition	**Little change**	DECREASE
Ozone Wet Deposition	**Little change**	DECREASE
PSO$_4$ Wet Deposition	LITTLE CHANGE	**Mixed** in east **Decrease** in the west
PNO$_3$ Wet Deposition	**Little change**	**Little change**
PNH$_4$ Wet Deposition	LITTLE CHANGE	**Little change**
Rainfall	**Little change**	**Decrease** over most of domain

The revisions to MM5CAMx combined with the scaling to observed precipitation data improved the representation of the rainfall fields supplied to CAMx. The changes in input precipitation fields had the effect of reducing Hg(II) deposition. The change in wet deposition of the two gaseous species was well correlated with the change in input rainfall amount. This was less true of the particulate species. The change in PSO$_4$ was sensitive to the partitioning of MM5 rainfall into convective and resolved components, with regions dominated by convection exhibiting an increase in PSO$_4$ deposition.

Comparisons of Predictions to Deposition Measurements

Hg Evaluation Against NADP/MDN Data

In the un-scaled precipitation case, the model over-predicts Hg wet deposition for all the seasons, with the largest over-predictions occurring during the summer season. The model explains less than 50% of the variance in the observations for all the seasons, as shown by the corresponding coefficients of determination. Nevertheless, it should be noted that the model performance in this simulation is considerably better than that obtained during the previous WDNR CAMx modeling study conducted for the same domain (Yarwood et al, 2003). The seasonal correlations between observed and modeled values are also generally higher in the current simulation than in the previous WDNR study, except for the spring season.

In the scaled precipitation case, the over-prediction bias in Hg wet deposition is reduced, with the largest effect for the summer season and the smallest effect for the winter season. The correlations between observed and predicted Hg wet deposition amounts for the scaled-precipitation simulation are comparable to or better than those for the base case simulation, although the model still explains less than 50% of the variance in observations for three of the four seasons. In general, these results indicate, as did the results from the previous WDNR study, that it is important to reduce the errors in input precipitation fields as much as possible to improve model performance for wet deposition.

Although scaling the precipitation fields to observed values improves the overall model performance for Hg wet deposition, the model still shows a tendency to over-predict the deposition amounts. Moreover, scaling the precipitation amounts to match the CPC and CMAP datasets does not always result in improving the agreement at the MDN sites. A major reason for this could be the simple seasonal-based approach used to scale hourly input precipitation rates. Clearly, there are other sources of error in the model simulation in addition to the input precipitation rates. These sources of error include the "usual suspects", such as meteorological

and emission inputs, as well as errors in model formulation introduced by gaps in our knowledge of the governing processes or by the approximations that are sometimes made to treat complex processes in a 3-D grid model that is used for practical applications.

<u>PM Evaluation Against NADP/NTN Data</u>

CAMx tends to consistently over-predict sulfate wet deposition and under-predict ammonium wet deposition for both seasonal and annual values. The model also over-predicts nitrate concentrations in summer and autumn, and under-predicts nitrate concentrations in the winter season. Annual nitrate wet deposition is over-estimated by the model. The discrepancies between observed and input precipitation amounts (and possibly the associated cloud coverage) are likely to be a major cause of the poor performance of the model for wet deposition of sulfate, nitrate, and ammonium. Scaling the input precipitation fields to observations from the CPC and CMAP datasets tends to improve model performance. However, even after scaling, there are still some large discrepancies in the ranges of the input and observed precipitation amounts and these discrepancies are reflected in the model wet deposition results.

The overall model performance for sulfate wet deposition is improved when the input precipitation amounts are scaled, particularly for the summer season. However, there is still a tendency to over-predict sulfate wet deposition. On the other hand, the under-estimation bias in ammonium wet deposition is increased when the precipitation fields are scaled, although there is a small improvement in the correlation between observed and modeled ammonium wet deposition fluxes. In the case of nitrate wet deposition, CAMx tends to over-predict in the summer season, and under-predict in the winter season. The best performance for nitrate wet deposition is noted for the spring season. Scaling the input precipitation rates results in a fairly significant improvement for the summer season, although the model still shows a tendency to over-predict nitrate wet deposition in summer. On the other hand, the precipitation-scaling causes a small degradation in model performance for the winter season. It is more difficult to diagnose the reasons for biases in model performance for nitrate wet deposition, primarily because there are many processes that govern the formation of nitric acid and particulate nitrate and their removal by precipitation.

Recommendations

Modeling wet deposition is subject to uncertainty due to difficulties in communicating information between meteorological models (e.g., MM5) and CAMx, and limitations in the ability of met models to predict precipitation. Continued development work will be needed to improve wet deposition performance both through better input data and improved algorithms.

2.2 DRY DEPOSITION

There were several improvements to the CAMx dry deposition scheme during the course of this project, including:

- Modified surface resistance adjustment for strong acids.
- Season dependant surface roughness from EPA's AERMOD model (EPA, 1998).

- Optional input of surface information that impacts dry deposition such as snow cover.
- Improved relationships between season (i.e. landcover) and day of year and latitude for both northern and southern hemispheres.

These updates are listed in Table 1-1 and are reflected in the CAMx version 4.2 User's Guide released in 2005. The first two updates listed were supported by this LADCO/MRPO project. The surface resistance update applies to strong acids such as HNO_3 and HCL that become permanently bound to ambient surfaces that they contact. This assumption over-rides the Wesely (1989) method of modeling surface resistance based on Henry's Law, but only in the case of strong acids.

3. PM PLUME IN GRID

The project summarized in this section was sponsored by the Lake Michigan Air Directors Consortium (LADCO) to incorporate PM chemistry, as well as dry and wet deposition processes for both gas and PM species, into the latest full chemistry version of the CAMx Plume-in-Grid (PiG) module. Source code, documentation, and an updated CAMx user's guide were provided to LADCO so that they and the MRPO could further test and evaluate the PM PiG treatment. The full report is given in Emery and Yarwood (2005).

3.1 INTRODUCTION

At a LADCO/MRPO modeling workshop in March 2003, several groups expressed interest in extending the CAMx PiG model to include PM. The PM PiG is needed to evaluate PM and visibility impacts of point sources within regional models. In response, ENVIRON proposed an approach to carry out that work, to include a design document (ENVIRON, 2004b), necessary coding modifications, testing and evaluation, and a final report (Emery and Yarwood, 2005).

In 2003, initial development of the new full-chemistry PiG algorithm was completed for gas-phase chemistry but had undergone only basic testing. The full gas-phase chemistry PiG is called IRON PiG standing for Incremental Reactions for Organics and NOx. We decided in 2003 that additional review and testing were necessary before releasing IRON PiG for general use, and so the new PiG was not included in the May 2003 release of CAMx v4.00. Since then, the IRON PiG has undergone significant improvement and testing, and additional capabilities have been incorporated including reactive tracers and a sampling grid. The IRON PiG will be released in CAMx version 4.20. The PM PiG is based on the IRON PiG.

The updates to PiG algorithms for PM chemistry were developed in design document. . The objectives of the design document were to:

1. Describe the current formulation/status of the IRON PiG option;
2. Propose an approach for incorporating PM chemistry and deposition into the IRON PiG code; and
3. Identify available LADCO/MRPO modeling databases that can be used to evaluate the PM PiG algorithm.

Background

In 2002/03, ENVIRON developed a new PiG model that includes full gas-phase chemistry (Carbon Bond or SAPRC) to simulate the chemical evolution of NOx and/or VOC point source plumes. The physical representation of plume segments (i.e., growth, dumping criteria, mass distribution, etc.) was updated to accommodate full chemistry. Chemical processes are simulated within each plume segment using an "incremental chemistry" approach where puffs carry the incremental contributions of the puff relative to the grid concentrations. Incremental puff concentrations can be positive or negative, depending upon the species and stage of plume evolution. A similar chemistry approach is used in the SCICHEM Lagrangian model (EPRI, 2000) and in the Advanced Plume Treatment (APT) that joins SCICHEM to CMAQ. The name

given to the new CAMx plume treatment is the IRON PiG (Incremental Reactions for Organics and NOx). The original CAMx GREASD PiG is retained as a separate option.

In 2003/04 the IRON PiG was significantly restructured to: tighten up the original code for incremental chemistry, puff dynamics and dumping, etc.; include improved puff expansion rates based on second-order closure methods; add the capability to track reactive tracers (RTRAC); and add high-resolution sampling grids to visualize plume concentrations of the reactive tracers at sub-grid scale. Also, the IRON PiG was tested for a number of configurations to ensure proper execution for both full photochemistry and reactive tracers.

The current IRON PiG is the foundation for the PM PiG model and we did not anticipate any major conceptual problems in extending IRON PiG to include PM chemistry. The physical representation of plume segments developed for treating ozone photochemistry within the IRON PiG were found to be equally appropriate for PM. Furthermore, the approach to implementing PM chemistry into the IRON PiG closely paralleled the approach for grid chemistry, by calling the same ISORROPIA, SOAP and RADM-AQ modules in the same order and manner. However, these PM chemistry modules are called for each puff using the incremental chemistry approach that IRON PiG uses for the gas-phase ozone chemistry; i.e., by separate integrations for background and puff+background in order to determine the evolution of puff incremental concentrations. Note that the PM PiG was designed specifically for the CF version of PM chemistry only, not for the CMU version of PM chemistry. Further testing is necessary to ensure correct implementation and to evaluate performance. The testing can be designed to consider performance for both ozone and PM and thus bring the PM PiG chemistry to the stage where it is ready for public release.

The original CAMx GREASD PiG model works with the OSAT ozone source apportionment technology. This was possible because of the simplified approach used in GREASD PiG and because compatibility with OSAT was an explicit design objective. GREASD PiG does not include any PM treatment, so it does not include PSAT. The incremental chemistry technique incorporated into IRON PiG, along with the puff-grid mass transfer constructs, are sufficiently complex that it would be very difficult to implement OSAT and PSAT within IRON PiG.

3.2 PM CHEMISTRY

The IRON PiG performs chemical calculations for a given puff over each time step of the host grid where the puff resides. This is done by calling a chemistry driver routine that closely matches the grid chemistry driver, except that layer-averaged ambient conditions over puff depth are used for the puff background. The driver routine contains the specific calls to all supported CAMx chemistry mechanism solvers, including the CF PM algorithm. The process of including the PM mechanisms was relatively straightforward. The calls to the gas and aerosol solvers were updated to pass the appropriate layer-averaged ambient conditions needed for PM chemistry consistent with the current version of the CF PM mechanism in CAMx v4.20.

One important change was made from the PM chemistry implementation of v4.20 that affects both grid and PiG puff chemistry. In v4.20 (and earlier), both the CF and CMU algorithms are called at the PM "coupling" time steps. The time interval between coupling steps is normally set to 15 minutes by the chemistry parameters file. The purpose of the coupling interval is to reduce the frequency of calls to the rather demanding ISORROPIA routine rather than calling it every

time step. In testing v4.11s and v4.20, we had noticed some sharp differences in PM concentrations along nested grid boundaries that crossed through cloudy regions – it appeared that different chemistry was occurring on either side of these boundaries. Investigation revealed that this is largely caused by inconsistencies in the time at which the aqueous PM chemistry algorithm is called for each grid. The PM coupling step can result in a different number of aqueous chemistry (and ISORROPIA/SOAP equilibrium) calls per hour, and/or different time step lengths for the chemistry integration, for each grid. For example, suppose the master time step on the 36-km grid is 10 minutes, and the time step on the 12-km grid is 5 minutes. With a 15 minute coupling interval, PM chemistry is called for the 36-km grid at 20, 30, 50, and 60 minutes past the hour (with aqueous integration time steps of 20, 10, 20, and 10 minutes), whereas PM chemistry is called for the 12-km grid at 15, 30, 45, and 60 minutes (all 15 minute aqueous time steps). This can exacerbate differences in output hourly average PM concentration fields between 2 or more nested grids.

To diminish the impact of grid-dependent chemical inconsistencies, we modified the PM PiG version of CAMx to call the aqueous PM chemistry algorithm at every time step for each grid. This is done for both grid and puff chemistry. The remainder of the PM chemistry (ISORROPIA and SOAP) continues to be called on the 15 minute coupling time step, as these routines are not based on integrating conversion rates, but rather are equilibrium calculations independent of time step. This also continues to maximize CAMx run time efficiency as ISORROPIA requires the most amount of CPU time and would slow the model considerably if it were to be called every time step.

3.3 DRY AND WET DEPOSITION

Deposition of gas and PM species was added to the PM PiG algorithm. Both dry and wet deposition calculations presented unique implementation issues for puffs. The most difficult issue for both forms of deposition was how to manage deposition exchange between puffs and the ground in the case of negative puff concentration increments. This and other issues were discussed in detail in the design document (ENVIRON, 2004b).

Dry Deposition

Dry deposition needed to consider the following: (1) the point at which puffs begin to deposit to the surface; (2) how to handle deposition through potentially deep puffs that may straddle several layers of varying stability since the puffs do not themselves resolve these stratifications or vertical concentration distributions; (3) managing deposition fluxes of negative concentration increments. Our solution to issue (1) was to ignore dry deposition within puffs until they diffusively grow to the ground, although deposition occurs on roughness elements that extend some distance above the nominal surface (trees, buildings, etc.). The heights of puff bottom and top are tracked in terms of distance above ground, so it is easy to identify when plumes reach the surface. We implemented a criterion that the bottom of the puff must extend to or below the midpoint of the surface layer, or below 10 m (whichever is larger), in order for dry deposition to be active.

Issue (2) can be handled in a variety of ways and levels of complexity. At this point we aimed to institute simpler solutions and will consider more complicated improvements for future

developments if evidence suggests that they would be necessary. Our initial implementation utilizes pre-computed species-dependent deposition velocities derived for the grid. Each puff in a particular grid cell uses the host cell's deposition velocities for each species, and these are used to determine the flux of mass through the fraction of puff depth occupying the model's surface layer.

Issue (3) is unique to the incremental chemistry concept introduced with IRON PiG. The flux of material depositing to the ground is given by $F = c \cdot v_d$, where by the normal definition a positive deposition velocity v_d leads to a positive deposition flux to the ground. If the puff increment c is negative, then a negative flux is calculated (flux from ground to puff). This is appropriate if we consider the following argument. Dry deposition applied to a grid cell removes some pollutant mass from the entire volume. If there is a puff existing in that cell with a negative concentration increment, then the amount of mass removed from the cell was over estimated if we consider the puff's contribution to total cell mass. The negative deposition flux calculated for this puff leads to the addition of mass to the puff increment. Adding mass to a negative increment reduces the magnitude of the increment, as expected for a deposition process. This mass is removed from the grid cell's accumulated deposited mass to maintain accurate mass accounting within the model.

Wet Deposition

Wet deposition needs to consider the following: (1) how to handle scavenging of pollutants through potentially deep puffs that may straddle several layers of varying cloud and rain water contents but that do not themselves resolve vertical concentration distributions; (2) managing deposition fluxes of negative concentration increments in combination with the potential for mass to move in and out of rainwater as it falls (e.g., for slightly soluble gasses); (3) accounting for the initial pollutant concentrations in rainwater as they enter the top of each puff.

It was important to maintain consistency between the treatment of wet deposition and the approach for puff chemistry. The chemistry relies on the assumption of vertically well-mixed puff reactors that can span multiple layers. To maintain this assumption for wet deposition, a single scavenging rate is applied through the entire puff depth. This was found to be the simplest implementation approach. This single scavenging rate is calculated according to layer-density weighted average ambient cloud and rainwater contents. Despite this simple implementation, a special wet deposition algorithm was needed for IRON PiG to handle the specific circumstances associated with the physical puff structure.

Wet scavenging is performed throughout the entire depth of the puff to determine the amount of flux in or out of rainwater. Total concentrations (puff + background) are used to determine species-dependent scavenging rates using the identical algorithm as for grid removal. The rates are used to derive removal fractions, and these fractions are then applied directly to the puff incremental mass for each species. Removal fractions are considered positive for the standard case of mass moving from puff to rain. Note that negative puff mass increments in combination with a positive removal fraction lead to a reversal of the flux direction (rain to puff), and this is logical by an argument similar to that presented for dry deposition, above. We account for impacts on the mass budget appropriately by adding or subtracting from the wet deposition mass array according to the net fluxes into and out of rainwater.

We further assume that the top boundary condition for rainwater entering the top of each puff is zero. This means that the removal fraction is always positive (from puff to rain) in the single-layer puff. In contrast, for gridded concentrations the layer-by-layer buildup of slightly soluble species can lead to a reversal of fluxes (from rain to grid) if super saturation is diagnosed in a particular layer. The effects of the zero initial condition assumption should be evaluated in future tests of the IRON PiG algorithm.

3.4 TESTING AND EVALUATION

Preliminary testing of CAMx v4.20_PMPiG was conducted using the standard test case available on the CAMx web site. This includes a 2-day (June 13, 14 2002), 2-grid (36-km and 12-km) simulation using inputs originally developed by the MRPO. The updated CF version of Mechanism 4 was employed, which includes new reactions for NOx recycling and five CG/SOA pairs. The original point source files from the MRPO for these dates were modified to select 488 point sources that emit greater than 10 TPD NOx. Note that even though our criteria for selecting PiG sources is based on NOx, all chemical species emitted by these sources are carried within the PiG for calculating ozone and PM chemistry and removal. The specifics of the simulation are provided in Table 3-1.

Table 3-1. Configuration of the preliminary PM PiG test case.

Simulation Dates	0000 EST 6/13/02 to 2400 EST 6/14/02
Map Projection	Lambert Conic Conformal
Projection Parameters	center lat/lon = -97/40, true lats = 33/45
Master Grid	97x90x14 36-km grid spacing origin = (900, -1620)
Nested Grid	119x134x14 12-km grid spacing master grid range = (31,29) to (69,72)
Chemistry Parameters	v4.2 Mechanism 4 CF
Environmental Inputs	Provided by MRPO
Emission Inputs	"BaseF"
PiG Sources	488 point sources emitting > 10 TPD NOx
IRON PiG Configuration	Number puff reactors: 1 Puff leakage: off Puff rendering: on Puff overlap: off Max puff age: 18 hours

The run required over five CPU hours/day on a single-processor AMD Athlon MP 2800+ Linux PC (1 Gb memory, ~2100 MHz clock speed). OMP is not currently supported in the PM PiG.

The purpose of the setup described above was to maximize combinations of point source types and potential ambient environments in a single run to test the stability of the model code in a variety of situations. We anticipate that a typical application of PM PiG will focus more on detailed research-level investigations on the evolution of pollutant plumes from a few key point sources of interest, rather than a broad-brush application as we have undertaken in the

preliminary evaluation. User's of PM PiG will find that the model does slow considerably for large number of PiG sources, since gas-phase chemistry is solved exclusively using the LSODE solver, and both gas and PM chemistry are effectively solved twice per puff (once for background, once for total puff) each time step. Run times will be longer with the use of multiple reactor cells per puff (the default is 1). Careful consideration should be given when defining each PM PiG application.

Emery and Yarwood (2005) provide plots to illustrate the impact of PM PiG on concentration fields of ozone, SO_2, individual secondary inorganic PM (sulfate, nitrate, ammonium), total secondary inorganic PM, and SOA. Impacts on SO_2 deposited mass from both dry and wet processes are also shown. Absolute concentration and deposition fields are shown from the run described above, with 488 PiG sources activated. Plots of differences in these fields are also provided, where the PM PiG run is differenced against a no-PiG run (same configuration otherwise).

Guidance on Testing PM PiG

Further testing of PM PiG is necessary to evaluate various PiG configurations over a broader range of potential mixtures of source types and ambient environments. We delivered the CAMx source code and a preliminary edition of the v4.20 User's Guide to LADCO so that the MRPO may design and undertake their own independent evaluations. Emery and Yarwood (2005) provide some additional information that is intended to assist future users of this particular version of CAMx to assess the results and performance of the PM PiG.

3.5 RECOMMENDATIONS

As suggested above, we recommend that LADCO and the MRPO undertake additional testing and evaluation of the operation and performance of the PM IRON PiG module. Our initial development and preliminary testing of the PM PiG enhancements suggest considering the following:

- Combine co-located source emissions to reduce puff overlap and the number of puffs (this to be handled in pre-processing when PiG sources are selected);
- Improve puff overlap – consider calculating puff overlap integrals, or merging puffs that substantially overlap;
- Consider allowing puffs to grow to twice the grid spacing, rather than the single grid spacing currently employed, to allow smoother transition in plume size representation between plume and grid.

4. UPDATES TO CARBON BOND CHEMISTRY

This project developed an updated version of the Carbon Bond 4 (CB4) chemical mechanism to be used by LADCO and the Midwest RPO for particulate matter (PM) and ozone modeling. The goal was to provide LADCO and the MRPO with a single, consistent chemical mechanism for use in upcoming ozone and PM state implementation plan (SIP) development activities. The new mechanism is called the CB4 with extended inorganic reactions (CB4xi) and will be released in CAMx version 4.20 as chemical mechanism number 4 (M4). The full report is given in Yarwood et al. (2005a).

4.1 INTRODUCTION

The CB4xi mechanism was developed after reviewing several other versions of the CB4 including the original published version (Gery et al., 1989), CAMx mechanisms 3 and 4 (ENVIRON, 2004c), versions of CB4 used in EPA's REMSAD model (EPA, 2004), CB2002 (Jeffries, Voicu, and Sexton, 2002) and CBM-Z (Zaveri and Peters, 1999). The CB4xi is the mechanism 4 version of CB4 from CAMx with 17 additional inorganic chemistry reactions. The added reactions are unimportant for smog chamber conditions (high NOx levels, 1-day experiments, room temperature and pressure) but potentially important for regional and annual modeling conditions (lower NOx levels, multi-day simulations, wide range of temperatures and pressures).

Two new chemical mechanisms were implemented in CAMx and tested for this study:

- The CB2002 mechanism (Jeffries, Voicu, and Sexton, 2002); and
- The CAMx mechanism 4 with 17 extra inorganic reactions (CB4xi), as described above.

The CB4xi mechanism improved model performance for ozone and did not significantly change model performance for PM species. The new inorganic reactions included in CB4xi improve the science in the mechanism without creating inconsistency with the evaluation of the CB4 against smog chamber data. The 17 extra inorganic reactions are appropriate for inclusion in any condensed chemical mechanism being used for annual PM and/or ozone modeling. The CB4xi is recommended for use in all future LADCO/MRPO modeling for both ozone and PM/visibility issues.

4.2 CHANGES TO CB4 FOR CB4xi

This project reviewed the inorganic reaction set in the CB4 and other mechanisms to identify reactions that should be added for regional/annual modeling conditions. Seventeen reactions were added to CAMx mechanism 4 (M4) as shown in Table 4-1. Since these reactions mostly involve the inorganic reaction set this modification is referred to as extended inorganic chemistry (CB4xi). CAMx M4 was selected as the basis for modification because it is most appropriate for regional PM, mercury and toxics modeling as well as ozone.

Table 4-1. Reactions added in the CB4xi mechanism and whether they are included in other condensed chemical mechanisms.

Number	Reaction	Included in CB2002	Included in CBM-Z	Included in mCB4	Included in SAPRC99
101	O1D + H2 = OH + HO2				
102	OH + H2 = HO2			Yes	Yes
103	OH + O = HO2				
104	OH + OH = O				
105	OH + OH = H2O2				
106	HO2 + O = OH				
107	H2O2 + O = OH + HO2				
108	NO3 + O = NO2				
109	NO3 + OH = HO2 + NO2	Yes		Yes	Yes
110	NO3 + HO2 = HNO3	Yes	Yes	Yes	Yes
111	NO3 + O3 = NO2				
112	NO3 + NO3 = 2 NO2	Yes	Yes		Yes
113	PAN = C2O3 + NO2				
114	HNO3 = OH + NO2		Yes		Yes
115	N2O5 = NO2 + NO3				
116	NTR = NO2 + XO2		Yes		Yes
117	PNA = 0.61 HO2 + 0.61 NO + 0.39 OH + 0.39 NO2		Yes		Yes

CB2002 from Jeffries, Voicu and Sexton (2002)
CMB-Z from Zaveri and Peters (1999)
mCB4 from EPA (2004)
SAPRC99 from Carter (2000)

The extended inorganic reactions are summarized as follows:
- Reactions of molecular hydrogen (101 and 102). Hydrogen is somewhat important to odd-hydrogen (OH and HO_2) for very dry conditions in the upper troposphere. Including hydrogen allows the air quality impacts of hydrogen as an alternative fuel to be evaluated. Currently, hydrogen is included in CAMx with a constant atmospheric concentration of 0.6 ppm (Novelli et al, 1999) but hydrogen could be made an active species.
- Odd-oxygen reactions (103 to 107) that may be important for pristine conditions such as the upper troposphere. Including these reactions provides a more complete description of hydroxyl radical (OH) chemistry in the upper troposphere to improve modeling for persistent air toxics and mercury.
- Additional NO_3 radical reactions (108 to 112) to improve nighttime chemistry. NO_3 radical is the main driver for atmospheric chemistry at night and including additional NO_3 removal reactions improves the calculation of nighttime destruction rates for several types of reactive hydrocarbons (e.g., aldehydes, olefins) and for NOx (via NO_3 and N_2O_5 reactions).
- NOx recycling reactions (113 to 117) to improve the representation of the fate of NOx over multi-day timescales. These are all photolysis reactions that occur quite slowly in the troposphere. Reactions 113, 115 and 117 are only important for very cold conditions such as the upper troposphere where corresponding thermal decomposition reactions are slow. Reactions 114 and 116, photolysis of nitric acid and organic nitrates, are important to regional ozone and oxidant chemistry in the lower troposphere (Zaveri and Peters,

1999). These "NOx recycling reactions" slowly recycle nitrogen from an inactive form (NOz) to an active form (NOx).

4.3 REVIEW OF CHANGES FROM CB4 TO CB2002

The CB2002 mechanism (Jeffries, Voicu, and Sexton, 2002) was compared to the OTAG version of the CB4 (i.e., CAMx M3) to document the changes. The main differences are:

- CB2002 updated the rate constants for many inorganic reactions. This was a major focus of the CB2002 work (Jeffries, Voicu, and Sexton, 2002).
    - The $OH + NO_2$ reaction rate is updated.
- New inorganic reactions were included for
    - NO_3 with OH, HO_2 and NO_3
    - O_3 with $O(^3P)$
- New HONO photolysis reaction to products $NO_2 + H$ in addition to $NO + OH$
- Different rate expressions for the N_2O_5 with water
    - $N_2O_5 + H_2O$ reaction rate deceased to be the same as CAMx mechanism 4 (Wahner et al., 1998)
    - $N_2O_5 + H_2O + H_2O$ reaction included (Wahner et al., 1998).
- Lower rate constants for radical-radical termination reactions (i.e., XO2 and HO_2)
- New reaction rates for olefins: ETH, OLE and ISOP.
- New reaction products for ETH and OLE.

The number of differences shows that CB2002 is a substantial update to the carbon bond mechanism. A sensitivity test showed that ozone differences between CB2002 and CB4 are attributable to more than just updating the $OH + NO_2$ reaction rate. Additional study would be required to explain how the changes in mechanism formulation from CB4 to CB2002 impact ozone and PM modeling results.

4.4 RATE CONSTANT FOR $OH + NO_2$

One of the motivations for developing CB2002 was that the $OH + NO_2$ reaction rate constant was revised in the late 1990s. The $OH + NO_2$ reaction is a major sink for both radicals and NOx under urban conditions and is so important that a chemical mechanism such as CB4 must be re-calibrated against smog chamber data if this rate constant is changed.

The $OH + NO_2$ reaction rates are compared in Table 4-2 for:
- CB2002 (Jeffries, Voicu and Sexton, 2002).
- CB4 mechanism 3 (Gery et al., 1989).
- CB4 mechanism 4 (JPL, 1994).
- SAPRC99 (Carter, 2000).

CB2002 has current values (Troe, 2001) that are consistent with the latest rate constant evaluations by both the NASA/JPL (2003) and IUPAC (2004) review panels. Comparing values at 298 K and 1013 mbar is most relevant to smog chamber data and urban ozone formation. For this condition, the $OH + NO_2$ reaction rate is about 15% low in SAPRC99 and 7% high in CB4

(both M3 and M4) compared to the current CB2002 value. For low-pressure conditions (491 mbar) CB4 (M3) is high because Gery et al. (1989) did not explicitly account for pressure dependence. The pressure dependence in CB4 (M4) is much improved by using the JPL (1994) expression. The SAPRC 99 OH + NO_2 reaction rate is 18% too low for the low-pressure condition. The OH + NO_2 reaction rate should be updated in both the Carbon Bond and SAPRC mechanisms, but this important rate constant should not be changed without re-evaluating the mechanisms against smog chamber data.

Table 4-2. Comparison of OH + NO_2 reaction rate constants in CB2002, CB4 and SAPRC99.

Temperature (K)	298	273	298	Difference from CB2002
Pressure (mbar)	1013	1013	491	
CB2002	1.57E+04	1.96E+04	5.19E+03	
CB4 (M3)	1.68E+04	2.29E+04	8.15E+03	+7% to +36%
CB4 (M4)	1.70E+04	2.22E+04	5.94E+03	+7% to +13%
SAPRC99	1.33E+04	1.80E+04	4.77E+03	-9% to -18%

Notes:
- CB2002 used as a reference because it has currently accepted values from Troe (2001) that are consistent with evaluations by JPL (2003) and IUPAC (2004).
- CB4 (M3) values from Gery et al., (1999).
- CB4 (M4) values from JPL (1994).
- SAPRC99 values from Carter (2000)

4.5 MODELING RESULTS FOR CB2002 AND CB4xi

The impacts of the CB2002 and CB4xi mechanism updates were evaluated using three LADCO/MRPO modeling databases. The new mechanisms were compared to CAMx mechanism 4 (M4). Kirk Baker of LADCO performed the model runs and provided results for analysis and inclusion in the project report (Yarwood et al., 2005a).

The main findings from comparing the mechanisms using LADCO regional modeling databases were:
- CB2002 predicted lower regional ozone than CB4 (M4) on all days.
- Areas of peak 8-hour ozone above 85 ppb were much reduced using CB2002 and the peak 8-hr ozone levels were reduced by 8 ppb to 9 ppb.
- The lower ozone with CB2002 degraded model performance.

As mentioned above, a sensitivity test showed that the different ozone predictions for CB2002 were not explained simply by changing the OH + NO_2 reaction rate.

- Compared to CB4 (M4), the CB4xi predicted higher ozone regionally on all days.
- Areas of peak 8-hour ozone above 85 ppb were much greater using CB4xi and the peak 8-hr ozone levels were increased by 3 ppb to 4 ppb.
- The higher ozone with CB4xi improved model performance.

The higher regional ozone with CB4xi than CB4 is due to the NOx recycling reactions (reactions 113 to 117) included in CB4xi. These reactions are the photolysis of organic nitrates and nitric acid that are included in other mechanisms such as SAPRC99 (Carter, 2000) and CBM-Z (Zaveri and Peters, 1999). The effect of these NOx recycling reactions partially explains why SAPRC99 tends to predict higher regional ozone than CB4. Zaveri and Peters (1999) previously concluded

that including photolysis of organic nitrates would increase regional ozone predictions. Conducting smog chamber experiments with organic nitrates included would be useful to confirm this result.

Including 17 extra inorganic reactions in CB4xi resulted in small difference in 24-hr average predictions for all PM species. The changes are summarized below for each PM species:

- The extra inorganic reactions resulted in slightly higher PM nitrate and sulfate in summer. This is consistent with slightly higher oxidant levels slightly accelerating the oxidation of NOx and SO_2 to nitrate and sulfate.
- Adding the NOx recycling reactions that convert a small amount of nitric acid back to NOx did not reduce PM nitrate. This is because only a small amount of nitric acid is recycled and the change in oxidant levels is the dominant effect.
- PM ammonium increased slightly along with, and because of, the PM sulfate and nitrate increases.
- Changes in PM sulfate/nitrate/ammonium were smaller in winter than summer because oxidant production is much less active in winter. In winter, oxidant levels are determined mainly by tropospheric ozone background (i.e., CAMx boundary conditions) rather than photochemistry within CAMx.
- There were no changes for soil and EC PM levels because they are inert primary PM species.
- There were small decreases in OC that are attributed to differences in secondary organic aerosol (SOA). The chemical reaction updates did not alter any reactions that produce SOA so differences must be due to differences in the oxidants that trigger SOA formation such as the changes for ozone, discussed above.

5. PM SOURCE APPORTIONMENT

The project summarized in this section was sponsored by the Lake Michigan Air Directors Consortium (LADCO) to incorporate PM source apportionment into the latest version of CAMx. Source code, documentation, and an updated CAMx user's guide were provided to LADCO so that they and the MRPO could further test and evaluate the PM source apportionment treatment. The full report is given in Yarwood et al. (2005) and PSAT will be released in CAMx version 4.20.

5.1 INTRODUCTION

A new method has been developed to source apportion particulate matter (PM) concentrations within a 3-D grid model. The method is called PSAT, which stands for PM Source Apportionment Technology. PSAT has been implemented in version 4.20 of the Comprehensive Air quality Model with extensions (CAMx). PSAT uses reactive tracers, also called tagged species, to follow source-receptor relationships for PM species within the grid model.

PSAT traces PM species to their respective sources.   Sources can be defined as individual sources, geographic areas (e.g., States) and/or emission categories (e.g., mobile sources). For chemically inert primary PM species, such as elemental carbon (EC), primary organics (POA), crustal material, particulate mercury [Hg(p)], etc., PSAT apportions PM concentrations to their respective sources within the grid model.   For secondary PM species, PSAT apportions PM concentrations to the sources of corresponding precursors:

- Sulfate (SO_4) is apportioned to sources of SO_2
- Ammonium (NH4) is apportioned to sources of NH_3
- Nitrate (NO3) is apportioned to sources of NOx
- Secondary organics (SOA) are apportioned to sources of VOC taking into account differences in SOA yields.

PSAT can account for all of the modeled PM2.5 and/or PM10 concentrations in a CAMx simulation performed using the CF (coarse/fine) particle size scheme. PSAT also can source apportion elemental mercury [Hg(0)] and reactive gaseous mercury [Hg(2)] to complement the apportionment for Hg(p).

5.2 WHAT CAN PSAT BE USED FOR?

The intended applications of PSAT are:

- Understanding model performance for PM species and thereby improving model inputs and or model formulation.
- Culpability assessments to identify what sources contribute significantly to PM and visibility problems
- Designing the most efficient and cost-effective PM and visibility control strategies.

PSAT source apportionment information should be used in combination with other sources of information, such as sensitivity analyses and application of observation based methods (e.g., PMF, UNMIX, and CMB), to guide control strategy development. For primary PM species, concentrations are directly proportional to emissions and knowing the source apportionment leads directly to PM control strategies. For secondary PM species that depend upon non-linear chemistry, sensitivity information should be used with source apportionment to guide control strategy design. Ammonium nitrate provides an example. PSAT can determine what sources contributed to both the ammonium and the nitrate, but control strategy design also should consider whether ammonium nitrate formation is limited by the availability of ammonia or nitric acid (ammonia lean or rich). A sensitivity analysis (e.g., reducing the ammonia emissions) will show whether control strategies should focus on the sources of ammonia or nitric acid (i.e., NOx). Source apportionment and source sensitivity analysis are complementary methods, as discussed in more detail below.

## 5.3 TESTING PSAT

PSAT was tested in CAMx by comparing PSAT contributions to independent calculations performed using two different methods. The PSAT implementation for primary PM was tested by comparison with brute force (zero-out) tests and the results were identical. PSAT also was compared to zero-out analysis for sulfate and example comparisons are shown in Figure 5-1. The spatial distributions of sulfate contributions are very similar in the PSAT and zero-out results as shown, for example, by the edge of contributions plume. There are some differences in the magnitudes of PSAT and zero-out contributions, and these are due to the effects of non-linear (oxidant-limited) sulfate chemistry on the zero-out result, as discussed below. Conclusions from these tests are:

- PSAT and zero-out give very similar sulfate contributions except for regions where oxidant-limited sulfate formation affects the zero-out result.
- The PSAT result provides a more reasonable source apportionment than zero-out for sulfate in oxidant-limited areas, as discussed below.
- The level of agreement between zero-out and PSAT contributions confirms that PSAT is implemented correctly in CAMx.

Zero-out analysis was not considered a useful approach to testing the PSAT implementations for secondary PM species that are more highly non-linear than sulfate, i.e., SOA and nitrate. The PSAT testing for SOA and nitrate focused on the chemistry implementation and used the Source-Oriented External Mixture (SOEM) method (Kleeman and Cass, 2001) to compare with PSAT. These tests showed that the PSAT chemical scheme for SOA is accurate. Nitrate is the most complex secondary PM species to apportion and it is unclear whether the SOEM method that we implemented was able to provide a perfect reference to compare with PSAT. The PSAT and SOEM apportionments for nitrate species were consistent and the PSAT scheme for nitrate apportionment is reasonable.
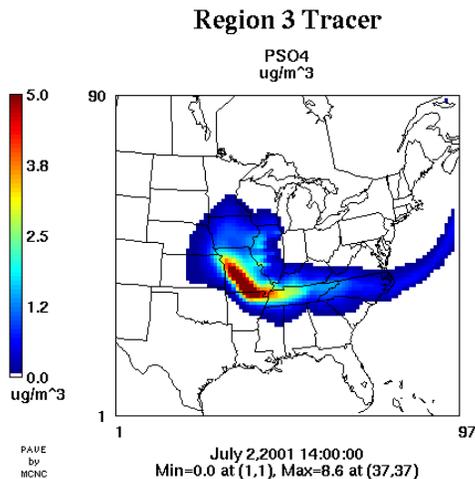
(a) PSAT   (b) Zero-out
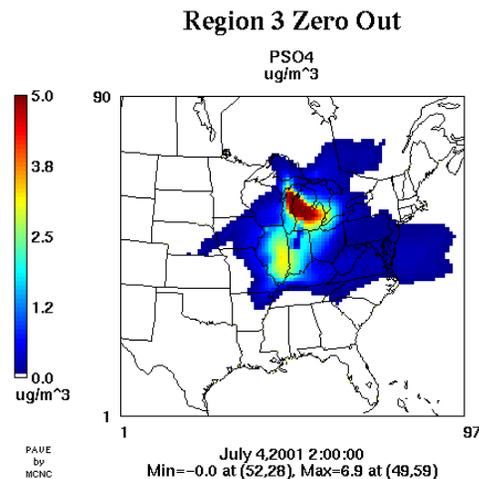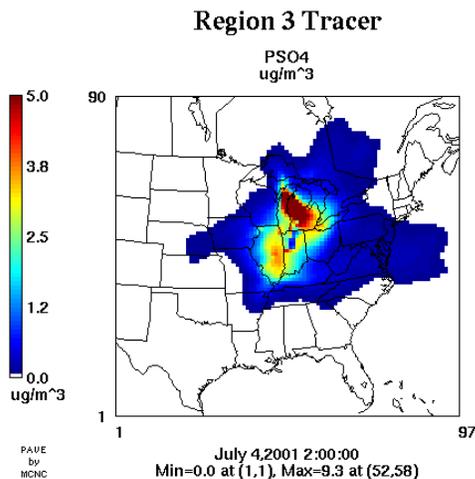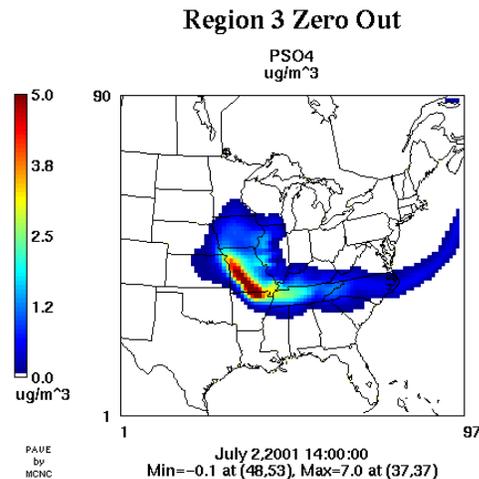
Figure 5-1. Comparison of hourly sulfate contributions (µg/m3) from the state of Illinois at two different times (a) PSAT result; (b) Zero-out result.

5.4 OXIDANT LIMITED SULFATE FORMATION

The sulfate comparisons between PSAT and zero-out analysis (e.g., Figure 5-1) consistently found that PSAT gave higher maximum sulfate contributions than zero-out analysis. This difference was attributed to the effects of oxidant-limited sulfate formation chemistry in the zero-out analysis. When sulfate formation is limited by the amount of oxidant rather than SO2, total sulfate may not respond to SO_2 reductions, such as zeroing-out a source, and zero-out analysis will under-state SO_2 source contributions to sulfate. PSAT does not suffer this problem because PSAT directly follows the relationships between SO_2 and sulfate. These issues are explained more fully in the PSAT report (Yarwood et al., 2005b).

Considering how oxidant-limited sulfate formation can impact the calculation of source contributions by PSAT and zero-out leads to several conclusions:

- Zero-out analysis will tend to under-state sulfate contributions in regions that are oxidant-limited.
- Because zero-out analysis underestimates sulfate contributions in oxidant-limited regions, zero-out will have a compensating tendency to over-state sulfate contributions downwind of oxidant-limited regions.
- PSAT sulfate contributions are not biased by oxidant limited chemistry.
- The differences between zero-out and PSAT sulfate contribution resulting from oxidant limited sulfate formation are a specific example of the general difference between source sensitivity and source apportionment for non-linear systems, summarized below.
- Zero-out is a source sensitivity method, not a source apportionment method.

Sulfate chemistry is closer to linear than the chemistry for other secondary pollutants such as nitrate and secondary organics (SOA). Zero-out analysis would be even more difficult to interpret as source apportionment for nitrate and SOA than for sulfate and, for this reason, zero-out analysis was not performed for nitrate and sulfate in this study.

5.5 SOURCE APPORTIONMENT AND SOURCE SENSITIVITY

PSAT is a source apportionment method, not a source sensitivity method. The difference between these methods may be summarized as:

- Source apportionment accounts for 100% of the PM mass and allocates contributions to sources of PM precursors.
- Source sensitivity describes how the PM mass will respond to changes in the sources of precursors and/or other related pollutants.

Sensitivity and apportionment are identical for primary PM species but differ for secondary PM species that depend upon non-linear chemical processes. An example of this difference was shown for the case of oxidant-limited sulfate formation, discussed above. Consequences are that if sensitivity methods (e.g., DDM, zero-out) are interpreted as source apportionment methods they may not account for 100% of the PM mass and may bias the relative contributions of sources, whereas if source apportionments (e.g., PSAT) are used to predict responses to emission reductions they may over- or under-predict the response to an actual strategy. It is important to understand and communicate these differences when source apportionment and/or sensitivity results are being used to evaluate "culpability" (i.e., responsibility for existing pollution) and/or to develop pollution control strategies.

5.6 APPLICATION TO INDIVIDUAL SOURCES – "HOW LOW CAN YOU GO?"

The "how low can you go" analysis investigated how small of a source can be evaluated with PSAT and zero-out methods. This is an important consideration if PSAT and photochemical grid models are to be used for evaluating the contribution of individual sources. The "how low can you go" analysis looked at sulfate contributions from several "hypothetical" point sources that were chosen to be generally representative of a large coal-fired utility source but not to represent actual sources. Two sets of emission rates were used for a "large source" and a "small

source." These emission rates differed by a factor of 1000 such that the large source emitted about 850 tons per day (TPD) of SOx and the small source emitted about 0.85 TPD of SOx.

There was good agreement between the PSAT and zero-out contributions for the large sources, except for the effects of oxidant-limited chemistry on zero-out results noted above, similar to the comparison shown in Figure 5-1. However, anomalous contributions were apparent in zero-out results for the small source scenarios. Figure 5-2 compares the PSAT and zero-out maximum sulfate contributions for a hypothetical small source located in Pennsylvania. The highest contributions occur near the source and to the east, with some contributions extending to the south and west. However, the zero-out result shows contributions to the northwest of the source (over lake Superior, Manitoba and Alberta) in locations that clearly lie outside the transport path from the source.
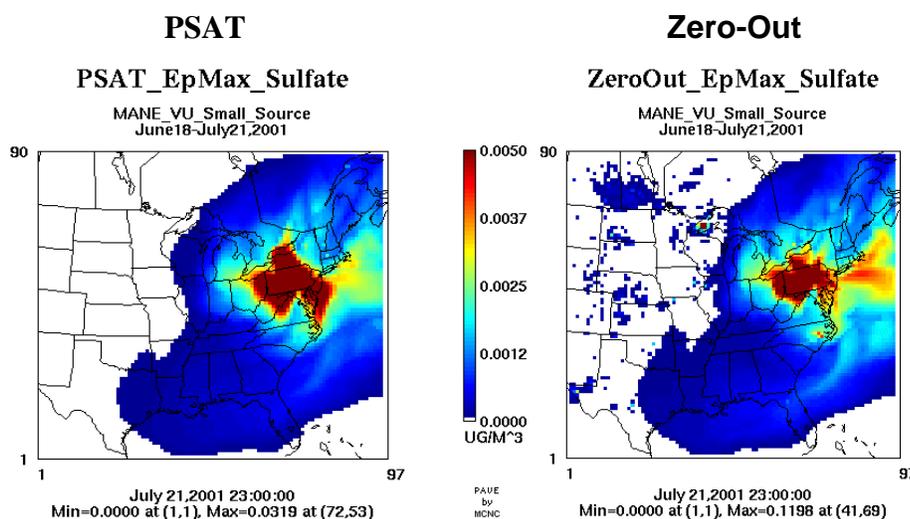
Figure 5-2. Comparison of episode average sulfate contributions (μg/m^3) with PSAT (left) and zero-out (right) analysis of small (0.85 TPD SOx) hypothetical point source located in Pennsylvania.

The anomalous zero-out sulfate contributions shown in Figure 5-2 (and also seen for other small source runs) are artifacts of numerical noise somewhere in the modeling system. In contrast, the PSAT results show no signs of anomalous results confirming that PSAT is inherently less noisy than zero-out. This is because the tracer method directly tracks the contribution of the small source rather than calculating the contribution from the difference between two model runs, i.e., calculating a small number from the difference between two larger numbers. We believe that the noise in the zero-out runs is attributable to the ISORROPIA module for several reasons discussed in the PSAT report (Yarwood et al., 2005b).

The conclusions from the "how low can you go" analysis are:

- Brute-force analysis methods such as zero-out can suffer significant "noise" problems if they are applied to small sources. For sulfate, such problems were apparent for a source emitting about 1 ton per day of SOx.
- PSAT is inherently less subject to model noise than zero-out and showed no symptoms of model noise for SOx sources emitting 1 ton per day.

## 5.7 EXAMPLE USE OF PSAT TO ADDRESS VISIBILITY BART REQUIREMENTS

As discussed above, the PSAT technique has several potential uses. Below we discuss one such potential use to address the BART requirements of the Regional Haze Rule (RHR). Section 169A of the RHR requires that reasonable progress be made at Class I areas toward natural visibility conditions. Once such provision is that each major stationary source (in existence in 1977, but not in operation in 1962) which may reasonably be anticipated to cause or contribute to any impairment of visibility in any Class I area shall procure, install and operate Best Available Retrofit Technology (BART). A majority of the visibility impacts from such a sources would be due to secondarily formed sulfate and nitrate particulate matter (PM).

In May 2004 EPA issued a proposed BART rule (Federal Register, 2004) in which the CALPUFF model (Scire et al., 2000) was identified for use to assess whether a potential BART source may cause or contribute to visibility impairment at a Class I area. However, the CALPUFF model has been criticized because the chemistry is out-of-date (over 20 years old) and inaccurate (Morris et al., 2003). Photochemical grid models incorporate current science chemistry and would provide a more accurate assessment of secondary PM estimates, and consequently, visibility impacts due to potential BART-eligible sources. However, photochemical grid models are more computationally demanding and would require extensive computational resources to assess the contributions of many potential BART-eligible sources if zero-out modeling was used. PSAT, allows a grid model to provide more cost effective modeling assessments of the visibility contributions of many potential BART-eligible sources.

The MRPO has run CALPUFF and CAMx/PSAT for many potential BART-eligible sources and found CAMx/PSAT to be computationally efficient and more scientifically accurate than CALPUFF (Baker, 2004). Figure 5-3 displays a comparison of the 24-hour average sulfate concentrations on July 20, 2002 from a potential BART-eligible source in northern Indiana. CALPUFF estimates much higher sulfate contributions than CAMx/PSAT, both in terms of a higher local sulfate peak (0.8 $\mu g/m^3$ CALPUFF vs. 0.3 $\mu g/m^3$ CAMx/PSAT) as well as much higher impacts further downwind. CALPUFF also estimates secondary sulfate peaks away from the source over Virginia and the Gulf of Maine. These secondary peaks appear to be unphysical as it is difficult to formulate a physically plausible hypothesis of how these high secondary sulfate peaks could occur far downwind from the source.

5.8 PSAT COMPUTATIONAL EFFICIENCY

The PSAT tests were used to estimate the computational efficiency of PSAT compared to a brute-force method such as zero-out analysis. A model run without PSAT required about 1.15 hours of CPU time per day. PSAT analyses were performed for 80 source groups (13 source regions and six emission categories, plus initial and boundary conditions). For sulfate, the PSAT run took 3 hours per day. The corresponding brute-force analysis would take about 93 hours per day (1.15 hours/day x 80 source groups). Therefore, PSAT was about 31 times more efficient than zero-out for this analysis. This efficiency analysis for sulfate is shown in Table 5-1 along with the corresponding efficiencies for SOA and ammonium nitrate.
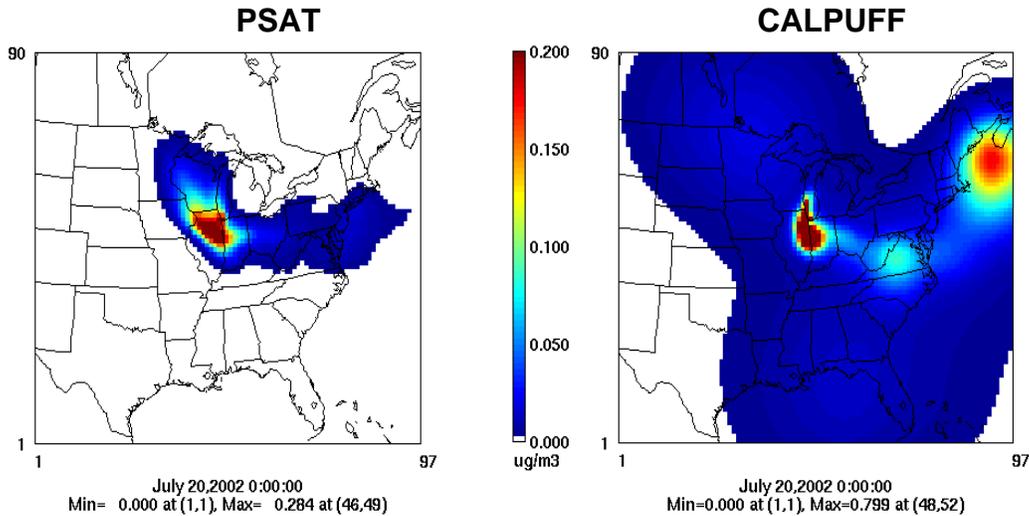
Figure 5-3. 24-hour average sulfate estimates on July 20, 2002 for a potential BART-eligible source located on northern Indiana using CAMx/PSAT (left) and CALPUFF (right).

Table 5-1. Computational efficiency of PSAT compared to zero-out analysis for 80 source groups.

Type of Analysis	PSAT Run-Time (hours/day)	Zero-out Run-Time (hours/day)	PSAT Efficiency Gain
Base run	1.15	N/A	N/A
Sulfate contributions	3	93	31
SOA contributions	10	93	9
Nitrate and Ammonium contributions	5.5	93	17

The conclusions on PSAT computational efficiency are:

- PSAT is computationally much more efficient than a brute-force method such as zero-out analysis.
- The PSAT efficiency gain ranged from factors of about 9 for SOA to 30 for sulfate. PSAT is less efficient for SOA than sulfate because more tracers are required to calculate apportionments for SOA than for sulfate.
- These PSAT efficiencies were determined in realistic full-scale tests. Efficiency may vary depending upon the analysis being performed and the computer system being employed ("your mileage may vary").

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