



CALPUFF CHEMISTRY UPGRADE

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EXECUTIVE SUMMARY

This report describes improvements made to CALPUFF, the preferred U.S. EPA model for assessing long-range transport of air pollutants and their impacts on Federal Class I areas under the Prevention of Significant Deterioration (PSD) program. These improvements were made to the chemistry modules of CALPUFF to address some of the shortcomings of the model.

The improvements to CALPUFF were tested using an existing plume chemistry database for a large coal-fired power plant in central Tennessee. CALPUFF simulations were conducted for three days in July 1999. Sensitivity studies with CALPUFF were conducted to examine the effects of variations in relative humidity, temperature, and background ammonia concentrations on model results. Box-model sensitivity studies were also conducted to test the changes to the inorganic aerosol thermodynamic equilibrium module.

The improvements made to CALPUFF include:

- Correction of an error in the RIVAD gas-phase chemistry scheme treatment of background ozone (O_3), which can lead to an overestimation of the formation of secondary particulate matter (PM) from the oxidation of primary species such as sulfur dioxide (SO_2) and nitrogen oxides (NO_x). The error was due to a lack of update of the O_3 concentrations; it was corrected by saving a history of puff O_3 concentrations so that the O_3 concentration at a given time step is calculated as a weighted average of the puff concentration from the previous time step and the background O_3 concentration. The correction of this error did not have a significant effect on model results for the case studies simulated in this work.
- Implementation of an alternative state-of-the-science module for the treatment of inorganic aerosol thermodynamic equilibrium. The new module, ISORROPIA, is currently used in several contemporary operational 3-D air quality models such as CMAQ, CMAQ-MADRID, CAMx and REMSAD. The testing of this alternative module with both CALPUFF and a box-model showed that it generally produced much lower (by factors of 3 to 10) particulate nitrate concentrations than the original CALPUFF module, except at subzero temperatures ($-10^\circ C$). The low temperature sensitivity studies also highlighted another shortcoming of CALPUFF, namely, its treatment of ammonia (NH_3) for multiple or overlapping puffs, where the same background NH_3 concentration is used for distinct puffs, thereby violating mass conservation. This shortcoming results in particulate nitrate concentrations that are higher than the theoretical maximums corresponding to the background ammonia concentrations.
- Implementation of an alternative module for secondary organic aerosol (SOA) formation based on the treatment used in the 3-D air quality model, CMAQ-MADRID. In general, the new module predicts higher (by about a factor of 2) SOA concentrations than the original CALPUFF module. This difference is partly

attributed to the incorrect treatment of temperature dependence of the partition coefficients in the original CALPUFF module.

- Implementation of a new module for aqueous-phase chemistry. This module is based on the aqueous-phase chemistry modules used in operational models such as CMAQ, CMAQ-MADRID and CAMx. The original CALPUFF does not have any explicit aqueous-phase chemistry treatment. Testing of this new module showed the expected result that aqueous-phase chemistry can play an important role in converting SO₂ to sulfate. For the case study simulated in this work, about 20% more SO₂ is converted to sulfate when aqueous-phase chemistry is activated.

Based on the results from the study, the following recommendations are made:

- The changes to CALPUFF made in this study should be evaluated using an existing CALPUFF modeling and evaluation database. One possible option is to use the Southwest Wyoming Technical Air Forum (SWWYTAF) data base, which includes a complete CALPUFF modeling data base for 1995, as well as monitoring data from IMPROVE, CASTNET and NADP for model performance evaluation.
- The current treatment of background ammonia in CALPUFF leads to substantial overestimation of particulate nitrate formation because CALPUFF does not account for ammonia limitation for multiple overlapping puffs. Instead, each puff is allowed to “see” the same background ammonia concentration. It is recommended that this shortcoming should be corrected, e.g., by a post-processing step to recalculate inorganic aerosol equilibrium at receptor locations.
- The current treatment of gas-phase chemistry in CALPUFF is overly simplified and its chemistry calculations are strongly dependent on the specified background oxidant concentrations. While it is not desirable to implement a comprehensive gas-phase chemistry mechanism, such as CB-IV, in CALPUFF, it is certainly feasible to improve the specification of background concentrations of O₃, H₂O₂ (for aqueous-phase chemistry) and NH₃ (for particulate nitrate formation). One option is to use the outputs (if available for the CALPUFF modeling domain and period) of a 3-D grid model, such as CMAQ, to specify temporally and spatially varying background concentrations.

1. INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has adopted CALPUFF (Scire et al., 2000) as the preferred model for assessing long range transport of pollutants and their impacts on Federal Class I areas under the Prevention of Significant Deterioration (PSD) program and on a case-by-case basis for certain near-field applications involving complex meteorological conditions. CALPUFF is also the preferred option in Best Available Retrofit Technology (BART) determinations for assessing the visibility impacts of one or a small group of sources.

In most of the United States, visibility impairment is primarily caused by light extinction from fine particles ($PM_{2.5}$) in the atmosphere. The key components of $PM_{2.5}$ contributing to visibility impairment include sulfate, nitrate, ammonium, organic carbon, elemental carbon, and crustal material. Many of these components are secondary, i.e., they are formed as a result of the chemical transformations of the primary emitted pollutants. These transformations can occur in the gas phase and in cloud droplets as well as heterogeneously on particles and droplet surfaces. Thus, a model, such as CALPUFF, which is applied for assessing the impacts of sources on visibility and air quality, should incorporate an adequate treatment of the relevant chemical processes including gas-phase chemistry, aqueous-phase chemistry and aerosol formation. However the current treatment of atmospheric chemistry in CALPUFF is highly simplified and inadequate for simulating particulate matter (PM) formation, as shown in several recent studies (Karamchandani et al., 2006; Santos and Paine, 2006; Morris et al., 2005; 2006).

In this work, we have incorporated several improvements to the treatment of chemistry in CALPUFF. These improvements were incorporated in both the unofficial Version 6 release (April 2006 release, available from the model developers), as well as the official EPA Version 5.8 release (June 2007). The improvements include both corrections to errors in the existing gas-phase chemistry module, as well as incorporation of new science modules for inorganic and organic aerosols and aqueous-phase chemistry. Section 2 describes the changes to CALPUFF. Section 3 presents the results of simulations with the original and improved versions of CALPUFF using an existing plume chemistry CALPUFF modeling database. Section 4 presents results from sensitivity studies conducted with CALPUFF Version 5.8, as well as results from sensitivity studies conducted with box-model implementations of the original and revised CALPUFF HNO_3 /nitrate partitioning schemes. Section 5 provides conclusions as well as recommendations for further evaluation to validate some of the new chemistry modules that could not be validated in this study because the modeling database did not include the required measurements.

2. IMPROVEMENTS TO CALPUFF

The improvements to CALPUFF described in the following sections were made to two versions of CALPUFF that were available at different times during the course of this project. We first made improvements to the unofficial Version 6 release (dated April 2006), which was available from the model developers). At that time, the official U.S. EPA release of CALPUFF was Version 5.7, dated July 2004. We used the developer's Version 6 release for the improvements, since this release had many improvements as compared to the older official release. Subsequently, towards the end of the current study, the U.S. EPA officially released Version 5.8 of CALPUFF in June 2007. On API's request, the improvements made to Version 6 of CALPUFF were reincorporated into the official Version 5.8 release.

2.1 Improvements to Gas-phase Chemistry

CALPUFF provides several options to calculate the conversion rates of SO₂ to sulfate and NO_x to nitrate. The simplest option is for the user to specify diurnally-varying transformation rates. The second option is based on the MESOPUFF II scheme, in which the pseudo-first-order constants for the daytime gas-phase conversions of SO₂ to sulfate and NO_x to nitric acid and other (organic) nitrates are parameterized as functions of the background ozone concentration (provided as input to CALPUFF), the total solar radiation intensity, the stability index, and the plume NO_x concentrations. Constant nighttime gas-phase SO₂ and NO_x conversion rates are specified as default values in the model. Aqueous-phase conversion of SO₂ to sulfate is parameterized as a function of the relative humidity. The third option is the RIVAD/ARM3 chemical scheme, which treats the NO and NO₂ conversion process in addition to the conversion of NO₂ to inorganic nitrate and SO₂ to sulfate. The improvements made to CALPUFF in this study were to the RIVAD/ARM3 scheme, as discussed below.

The RIVAD/ARM3 scheme is derived from the PLUVUE scheme of Bergstrom et al. (1981). This scheme assumes low background VOC concentrations and is not suitable for urban regions or areas with significant biogenic emissions. The NO-NO₂-O₃ chemical system is first solved to get pseudo-steady-state concentrations of NO, NO₂, and O₃. During the day, this system consists of the NO₂ photolysis reaction to yield NO and O₃ and the NO-O₃ titration reaction to yield NO₂. During the night, only the NO-O₃ titration reaction is considered. The RIVAD/ARM3 scheme is incorrectly implemented in CALPUFF because the background O₃ concentration is used as the initial O₃ concentration at each puff chemistry time step (i.e., the plume O₃ concentration does not evolve as a function of the downwind distance but instead it is replenished at each time step). In reality, the high NO concentrations in the plume deplete the O₃ concentrations in the near field and, as a result, OH concentrations are very low and the gas-phase rates of NO₂ and SO₂ oxidation to HNO₃ and H₂SO₄, respectively, are negligible (Richards et al., 1981; Gillani et al., 1998; Karamchandani et al., 1998, Karamchandani and Seigneur, 1999). In CALPUFF, the hydroxyl radical, OH, is produced from the photolysis of O₃ and the OH concentration is calculated from the final O₃ concentration after the solution

of the NO-NO₂-O₃ system. Since CALPUFF does not account for the depletion of O₃ in the plume, OH concentrations are overestimated in the near field. This, in turn, leads to the overestimation of the rates of HNO₃ and H₂SO₄ formation of in the near field.

To correct this error in CALPUFF's RIVAD/ARM3 scheme, we made the following modifications to the code. First, we keep track of the puff O₃ concentrations between time steps. Then, at each chemistry time step, the puff O₃ concentration is calculated as a weighted average of the previous time step's concentration and the background concentration. The weighting factors are determined from the change in volume of the puff between the previous and current time step. Note that we employ the same approach to calculate the puff H₂O₂ concentrations, required for the aqueous-phase chemistry module described in Section 2.4.

In addition to these corrections, we also updated the oxidation rates of SO₂ and NO₂ by OH to the rates employed in contemporary photochemical and regional PM models, such as the U.S. EPA's Community Multiscale Air Quality (CMAQ) model.

Note that this updated RIVAD/ARM3 scheme is implemented as a new option (MCHEM=5) in CALPUFF. We have retained the option of using the original RIVAD/ARM3 scheme (MCHEM=3), since that scheme is part of the official EPA release.

It should also be pointed out that the changes to the RIVAD/ARM3 scheme described here correct errors in the scheme, but do not address one of the shortcomings of the treatment of gas-phase chemistry in CALPUFF, namely that it is overly simplified and does not provide an adequate treatment of atmospheric chemistry. This shortcoming can be overcome by either 1) implementing comprehensive gas-phase chemistry mechanisms, such as CB-IV, into CALPUFF or 2) adapting CALPUFF to use the output of comprehensive three-dimensional grid models, such as CMAQ or CAMx, to provide the background concentrations of relevant species, such as ozone, hydrogen peroxide and ammonia. The first option was not considered for the study described here, since it would require significantly more resources to implement and would slow the model considerably, making it impractical for its intended use. In addition, other reactive puff models, such as SCICHEM (Karamchandani et al., 2000), are available for applications requiring a more comprehensive treatment of gas-phase chemistry. The second option is more practical to implement but was not part of the scope of work for this study. It may be considered as a candidate for future enhancement of CALPUFF (see Section 5).

Thus, the primary objective of this study was to correct the RIVAD/ARM3 scheme, as described above, and to implement new modules for inorganic and organic PM and aqueous-phase chemistry that were based on existing modules used in SCICHEM as well as three-dimensional models such as CMAQ, CMAQ-MADRID and CAMx. The following sections provide further details on the implementation of these new modules.

2.2 Improvements to Treatment of Inorganic PM

CALPUFF uses a simple approach to simulate the partitioning of nitrate and sulfate between the gas and particulate phases. This approach is used for both the MESOPUFF chemistry and the RIVAD/ARM3 chemistry options. In this approach, sulfate is assumed to be present totally in the particulate phase (which is an appropriate treatment), and nitrate is assumed to be formed by the reaction between nitric acid and ammonia. A simple stoichiometric thermodynamic model is used to estimate the partitioning of total inorganic nitrate between gas-phase nitric acid and particle-phase ammonium nitrate. Total ammonia concentrations are provided as background values to the model, and the available ammonia for creating ammonium nitrate is computed as total ammonia minus sulfate (with a factor of two to account for the stoichiometry of ammonium sulfate) to account for the preferential scavenging of ammonia by sulfate. Then, the gas-particle partitioning of total nitrate is estimated using the available ammonia concentration, the total nitrate concentration, and the equilibrium constant for the $\text{HNO}_3\text{-NH}_3\text{-NH}_4\text{NO}_3$ system (calculated as a function of the temperature and relative humidity).

For this study, we implemented an additional treatment for inorganic gas-particle equilibrium. This treatment is based on the ISORROPIA model of Nenes et al. (1999), version 1.7 (i.e., the version currently used in CMAQ 4.6). ISORROPIA provides an appropriate compromise between accuracy and computational efficiency for the calculation of the partitioning of inorganic PM. This improvement is similar to what was recommended (Seigneur et al., 1999) and implemented for the improvement of PM formation in REMSAD. ISORROPIA is currently used in several 3-D air quality models such as CMAQ, CMAQ-MADRID, CAMx and REMSAD. Thus, with this new module, CALPUFF now includes a treatment of inorganic PM formation that is consistent with the state of the science in air quality modeling. Note that the incorporation of the ISORROPIA treatment in CALPUFF has very little impact on its computational efficiency.

As in the case of the gas-phase chemistry mechanism, we have also retained the original CALPUFF treatment for inorganic PM for consistency with EPA's distribution of CALPUFF. The original treatment in CALPUFF is used with the MESOPUFF chemistry option (MCHEM=1) and the original RIVAD/ARM3 scheme (MCHEM=3), while the ISORROPIA treatment implemented in this study is employed with the corrected RIVAD/ARM3 scheme (MCHEM=5 or MCHEM=6).

2.3 Improvements to Treatment of Organic PM

CALPUFF was updated for the Wyoming Department of Air Quality to include a treatment for the formation of secondary organic aerosols (SOA) from VOC emissions (Scire et al., 2001). Note that the CALPUFF User's Guide (Scire et al., 2000) does not describe this option (MCHEM=4), nor is this update documented at the official CALPUFF web site (<http://www.src.com/calpuff/calpuff1.htm>).

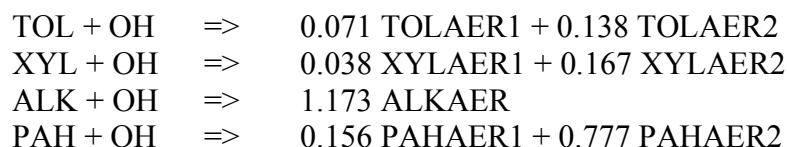
The current CALPUFF treatment includes SOA formation from aromatics (represented by toluene and xylenes) and monoterpenes (represented by α -pinene and β -pinene). Note that this treatment is not coupled with the RIVAD/ARM3 NO_x/SO_x scheme, i.e., this option only allows the simulation of terpene and aromatic emissions and the formation of SOA. Thus, a separate simulation must be performed if one also needs to calculate secondary PM formation from SO₂ and NO_x emissions.

In this study, we have added a treatment for SOA that is coupled with the corrected RIVAD/ARM3 scheme described in Section 2.3. The treatment is based on the algorithm that is used in CMAQ-MADRID for anthropogenic SOA formation. CMAQ-MADRID (Zhang et al., 2004) is a 3-D model that is publicly available via www.cmascenter.org. The MADRID algorithm (Pun et al., 2005) currently treats SOA formation from both anthropogenic and biogenic VOC emissions. For this work, we have not included biogenic SOA formation because it results from the emissions of VOC from vegetation; CALPUFF, being a puff model, is unlikely to be applied in this context and a 3-D model would be needed to correctly treat biogenic SOA formation. Thus, we have only included the anthropogenic SOA component of MADRID in CALPUFF. However, the original CALPUFF biogenic SOA option is still available for users interested in applying CALPUFF for biogenic sources.

Anthropogenic SOA formation results from the oxidation of aromatic compounds, long-chain alkanes and alkenes and some PAH. The new CALPUFF SOA module treats SOA formation from mono-substituted aromatics (represented by toluene), poly-substituted aromatics (represented by xylenes), long-chain alkanes (represented by a 16-carbon alkane) and gas-phase PAH (represented by methyl-naphthalene). Alkenes are not treated at this point due to a lack of experimental data for long-chain aliphatic alkenes (some modelers have used cyclohexene as a surrogate compound for long-chain alkenes). Benzene has also been suggested as a SOA precursor; however, insufficient quantitative information is available at the moment to treat it in a model (Pun and Seigneur, 2007).

The SOA formation algorithms are based on the results of smog chamber experiments for the aromatics (Odum et al., 1997) and from chemical kinetic simulations conducted with a comprehensive mechanism (Griffin et al., 2005) for alkanes and PAH (smog chamber experimental data are not available for alkanes and PAH at the moment). The partitioning of condensable products from the oxidation of the VOCs into the gas and particulate phases is based on the absorption algorithm of Pankow (1994).

The following reactions for the oxidation of anthropogenic VOC precursors of SOA were added to the RIVAD/ARM3 scheme with the SOA option (MCHEM=6):



In the above set of equations, TOLAER1, TOLAER2, etc. are the condensable products from the oxidation of the various VOCs. The stoichiometric coefficients were derived from smog chamber experiments or kinetic simulations with a comprehensive mechanism. The OH radical concentration is determined from the RIVAD/ARM3 scheme, as discussed in Section 2.1.

The partitioning of the condensable products into the particle and gas phases is determined from the following equation:

$$K_i = \left(\frac{A_i / M_{sum}}{G_i} \right) \quad (1)$$

In Equation 1, K_i is the partition coefficient ($\text{m}^3 \mu\text{g}^{-1}$), A_i and G_i are the mass concentrations ($\mu\text{g m}^{-3}$ air) of species i in the particulate- and gas-phase, respectively, and M_{sum} ($\mu\text{g m}^{-3}$ air) is the sum of primary organic carbon (nonvolatile) and secondary organic carbon (semi-volatile) in the particulate phase that serve as the organic absorbing medium. Note that the smog chamber experiments from which the partition coefficients are derived were conducted at temperatures higher than typical ambient temperatures. Thus, a temperature correction based on the Clausius-Clapeyron equation is applied to determine K_i :

$$K_i(T) = K_i^* \frac{T}{T^*} \exp \left[\frac{\Delta H_{vap,i}}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \right] \quad (2)$$

where $K_i(T)$ and K_i^* are the partition coefficients at temperature T and a reference temperature T^* , respectively. R is the ideal gas constant and $\Delta H_{vap,i}$ is the enthalpy of vaporization of the pure species i . The values of the partition coefficients at 298 K and the enthalpies of vaporization are presented in Table 2-1. Note that the original CALPUFF SOA module only applies the first part of the temperature correction in Equation 2, i.e.

$$K_i(T) = K_i^* \frac{T}{T^*} \quad (3)$$

From Equation 3, we see that the partition coefficient in the original CALPUFF formulation always decreases as temperature decreases, which is incorrect. For example, the enthalpy of vaporization for SOA products from toluene is estimated to be 73 kJ mole^{-1} . For an ambient temperature of 298 K with a reference temperature of 310 K, Equation 2 yields a partition coefficient at the ambient temperature that is about 3 times larger than that at the reference temperature. In contrast, Equation 3 gives a value for the partition coefficient at the ambient temperature that is about 96% of the value at the reference temperature. Thus, the original CALPUFF formulation significantly underestimates the partition coefficient (by more than a factor of 3 for this example).

Table 2-1. Partition coefficients (at 298K) and heats of vaporization of condensable species.

Condensable Species	K (m ³ μg ⁻¹)	ΔH _{vap} (kJ mole ⁻¹)
TOLAER1	0.1586	72.67
TOLAER2	0.0057	72.67
XYLAER1	0.1257	72.67
XYLAER2	0.0042	72.67
ALKAER	0.0229	72.67
PAHAER1	0.0150	72.67
PAHAER2	0.0020	72.67

From Equation 1, we see that the partitioning of the condensable product between the gas and particle phases also depends on the absorbing medium, i.e., the total organic mass, consisting of both primary (emitted) organic carbon as well as secondary organic carbon. Thus, it is necessary to provide an estimate for the concentrations of primary organic carbon. CALPUFF already allows the user to specify a background total fine PM concentration and a value for the fraction of this concentration that consists of organic carbon. In addition, we have included an option for emitted primary organic carbon to be carried as a species in CALPUFF when the new SOA chemistry option is selected. Thus, the total primary organic carbon is the sum of the background organic carbon and the emitted carbon from the source that is being simulated by CALPUFF.

The calculation of SOA formation that we have implemented in CALPUFF should be seen as a screening calculation. In the RIVAD/ARM3 scheme, the OH concentration is calculated in CALPUFF from NO_x/O₃ chemistry and the VOC/NO_x chemistry is not treated. Therefore, the OH concentration estimates will be uncertain if VOC concentrations are significant. If SOA formation appears to be a potential issue, a more refined calculation can be performed using a model with a comprehensive treatment of VOC/NO_x chemistry, which will be computationally more demanding.

2.4 Implementation of Aqueous-phase Chemistry and Wet Removal

The aqueous-phase formation of sulfate in CALPUFF's RIVAD/ARM3 scheme is currently approximated with a simplistic treatment that uses an arbitrary pseudo-first-order rate in the presence of clouds (0.2% per hour), which is added to the gas-phase rate (Scire et al., 2000). There is no explicit treatment of aqueous-phase SO₂ oxidation chemistry.

In this study, we have incorporated into CALPUFF a mechanistic treatment of sulfate formation in clouds that is based on the treatment (Walcek and Taylor, 1986) used

in EPA's CMAQ. The CMAQ aqueous-phase mechanism represents sulfate formation with five reactions and includes the calculation of pH since some reactions depend on pH. These five reactions include oxidation by O₃, oxidation by H₂O₂, trace metal catalyzed oxidation, oxidation by organic peroxides, and oxidation by peroxyacetic acid.

For this study, we have included the first three reactions in the new aqueous-phase chemistry module. For the first reaction, the O₃ concentration is calculated by the RIVAD/ARM3 scheme. As described in Section 2.1, we have corrected CALPUFF so that the O₃ concentration that is input to the RIVAD/ARM3 scheme is a weighted average of the O₃ concentration in the puff at the previous time step and the background O₃ concentration. A similar approach is used to adjust the H₂O₂ concentration that is input to the aqueous-phase chemistry module for the second reaction. This is important because the SO₂ + H₂O₂ in the aqueous-phase is very fast and H₂O₂ is usually the limiting reactant. Thus, it is consumed rapidly and the puff H₂O₂ concentration at the end of the aqueous-phase chemistry time step is zero or very small. If the H₂O₂ concentration at the next time step does not reflect this puff history, then aqueous-phase SO₂ oxidation rates in CALPUFF will be overestimated. Finally, for the third reaction, typical background concentrations of the trace metals (iron and manganese) are used in the code.

An iterative approach is used to calculate the pH of cloud water from the concentrations of the various species in solution (HSO₃⁻, SO₃⁼, NO₃⁻, HSO₄⁻, SO₄⁼, HCO₃⁻, CO₃⁼, OH⁻ and NH₄⁺). The bicarbonate (HCO₃⁻) and carbonate (CO₃⁼) ion concentrations are based on a background value of 340 ppm for CO₂.

The aqueous-phase chemistry module implemented in this work also includes the information required to calculate the scavenging and wet deposition of soluble gases and particles by precipitating clouds. This information is used to calculate scavenging coefficients that are used in place of the default CALPUFF scavenging coefficients.

The new CALPUFF aqueous-phase chemistry module requires cloud liquid water contents for its calculations. Since this variable is not yet part of the CALPUFF meteorological inputs, we use liquid water contents of 0.1 g m⁻³ and 0.5 g m⁻³ for non-precipitating and precipitating clouds, respectively. Note that modifying CALMET, the CALPUFF meteorological pre-processor, to prepare meteorological input files that include liquid water content was out of the scope of this study.

The new aqueous-phase chemistry option (MAQCHEM=1) is included with both the new chemistry options discussed previously (MCHEM=5 and MCHEM=6). Note that the aqueous-phase chemistry flag, MAQCHEM, was in the original CALPUFF, but could not be selected since there was no aqueous-phase chemistry treatment in the original CALPUFF. Thus, when the user selects MAQCHEM=1 in the original CALPUFF, an error message is printed stating that the aqueous-phase chemistry option is not available. MAQCHEM=0 is the only option allowed in the original CALPUFF. For consistency with the official EPA release of CALPUFF, MAQCHEM=1 is only available in the new CALPUFF when the selected chemistry option is MCHEM=5 or MCHEM=6.

2.5 User Guidance for New CALPUFF Chemistry Options

In this section, we provide guidance to CALPUFF users that would be using the new chemistry options implemented in this project. This section is in lieu of an updated CALPUFF User's Guide, since the official guide is maintained and distributed by the CALPUFF developers and the U.S. EPA. As pointed out previously, this guide was prepared in 2000 and has not been updated to reflect many of the changes and improvements made to CALPUFF during the intervening time period, including the implementation of the SOA module for the Wyoming Department of Environmental Quality.

For the updated RIVAD/ARM3 chemistry scheme and the ISORROPIA inorganic aerosol module, the only change required is to select MCHEM=5 as the chemistry option in the CALPUFF control file. There are no changes to the input files.

If the CALPUFF user is also interested in calculating SOA formation from the source emissions, then the desired chemistry option in the control file is MCHEM=6. Note that this option also includes the updated RIVAD/ARM3 chemistry scheme and the ISORROPIA inorganic aerosol module, so it is a superset of the previous option (MCHEM=5). Thus, the user can also simulate SO_x and NO_x transport and chemistry and inorganic PM formation with this option. The control file also needs to be updated to include the additional species associated with the SOA treatment. These species include the precursor VOCs toluene ("TOL"), xylene ("XYL"), long-chain alkanes ("ALKH") and polycyclic aromatic hydrocarbons ("PAH"), the condensable products from these species and their particle-phase counterparts, and primary organic carbon ("POC"). The condensable products from the four VOC species are "TOLAER1", "TOLAER2", "XYLAER1", "XYLAER2", "ALKHAER", "PAHAER1", and "PAHAER2". The particle-phase counterparts of these species are "ATOLA1", "ATOLA2", "AXYLA1", "AXYLA2", "AALKHA", "APAHA1" and "APAHA2". A sample control file for this option is provided with the code distribution. For the SOA option, the emissions input file also needs to be updated to include emissions of the VOC species of interest and primary organic carbon emissions if available. Note that it is not necessary to provide emissions of all species. For example, if a given source only emits the aromatic VOCs ("TOL" and "XYL") then all the other species can be designated as non-emitted species in the control file, and only "TOL" and "XYL" emissions are required in the emissions file.

The aqueous-phase chemistry option (MAQCHEM=1) is available with both the new chemistry options (MCHEM=5 and MCHEM=6) but not with the original CALPUFF chemistry options. However, it is not necessary to activate the aqueous-phase chemistry option for MCHEM=6 when there are no SO₂ and NO_x emissions from the source being simulated. This option requires the user to specify H₂O₂ concentrations in either a separate observations data file (hourly) or as monthly values in the control file. Note that the CALPUFF developers have already included the code necessary to read H₂O₂ concentrations in CALPUFF, since they were probably intending to implement an aqueous-phase chemistry module at some point.

3. MODEL SIMULATION RESULTS

The changes to CALPUFF were tested using a plume chemistry database consisting of helicopter measurements of the plume from a large coal-fired power plant in central Tennessee. The power plant (Cumberland) is operated by the Tennessee Valley Authority (TVA), and is located approximately 80 km to the west-northwest of downtown Nashville. It is the largest single source of NO_x emissions (~20 tons of NO_x/hour) in the region. Plume measurements were taken in July 1999 by the TVA Bell 205 helicopter (Imhoff et al., 2000). The gas analyzers included an O₃ monitor, an SO₂ monitor, as well as NO, NO₂, NO_x, and NO_y monitors.

As discussed in Section 2, we incorporated the chemistry improvements into two separate versions of CALPUFF. Most of the simulations described in this section were conducted with the unofficial release (Version 6) of CALPUFF. When the latest official release of CALPUFF (Version 5.8) became available later during the project, we conducted additional simulations, some of which are described in this section, while the remaining are described in Section 4.

3.1 Description of Simulations

CALPUFF simulations were conducted for 3 days in July 1999: July 6, July 13, and July 15. July 6 was a clear day with light winds from the west. On July 13, the conditions were partly cloudy and hazy and the winds were moderate from the north. July 15 was hot and hazy with low to moderate winds from the south-west. A total of 37 sampling traverses of the Cumberland plume were conducted during these three days. However, many of these traverses were a few minutes apart at the same downwind distance from the power plant, and had similar plume characteristics. Thus, we present CALPUFF results for selected traverses at different representative downwind distances. Table 3-1 lists the plume traverses that were simulated.

Table 3-1. Plume sampling summary for selected flights.

Date	Plume Traverse	Start Time (GMT)	Average Sampling Altitude (m)	Average Distance (km) from the Source
July 6, 1999	187003	17:19	496	10.6
	187006	17:53	496	31.3
	187010	21:05	496	64.7
July 13, 1999	194004	17:35	423	15.8
July 15, 1999	196001	16:20	419	16.6

Three-dimensional meteorological fields for the CALPUFF simulations were generated with CALMET for a previous study (Karamchandani et al., 2006), using hourly surface

and upper air data from four sites (Dickson, Gallatin, Eagleville and Cumberland) in the region. The first three of these sites are about 29 km southeast, 113 km east and 120 km southeast, respectively, of Cumberland, the source location. The CALMET/CALPUFF domain was centered on the source location, and extended 400 km in the east-west direction and 296 km in the north-south direction, with a horizontal grid spacing of 4 km. The vertical domain extended to 2 km, and the vertical grid spacing varied from 20 m at the surface to 400 m at the top. The landuse data for the simulations were developed from U.S. Geographical Survey (USGS) data. Default values were used for albedo, Bowen ratio, soil heat flux, anthropogenic heat flux, and leaf area index. The diagnostic wind module of CALMET was used along with computation of kinematic effects, slope flow effect, and Froude number adjustment. The maximum radius of influence for a station was chosen as 100 km. For the calculation of mixing heights, default options were mostly chosen. The maximum mixing height was limited to 2 km.

Hourly-varying SO_x and NO_x emissions from the two Cumberland units that were operational in 1999 were used in the simulations. For the tests of the secondary organic aerosol (SOA) module, hypothetical emissions of the two aromatics, toluene and xylene, were assigned to the power plant. We did not include emissions of PAH and higher alkanes, because the original CALPUFF SOA module does not treat these species. For the tests of the new aqueous-phase chemistry module, we assumed 5% cloud cover everywhere (the original meteorological files from CALMET did not have any cloud cover during the time period of the simulation). Fixed background concentrations of 60 ppb for O₃, 10 ppb for ammonia and 1 ppb for H₂O₂ (for the aqueous-phase chemistry module) were used in the simulations.

The results from our simulations are described in the following sections where we present the differences between the new and original (where applicable) versions of the CALPUFF chemistry modules. However, for the aqueous-phase chemistry tests, we only present the results for the new version of CALPUFF. We do this because the original CALPUFF did not have an explicit treatment of aqueous-phase chemistry, and the 0.2 percent per hour rate that was used to parameterize aqueous-phase chemistry had a negligible effect on model results.

3.2 Effect of Modifications in RIVAD/ARM3 Scheme

In this section, we determine the effect of the modifications to the RIVAD/ARM3 scheme described in Section 2.1. These changes include 1) the corrections to CALPUFF to carry the puff O₃ concentrations, and 2) updates to the rate constants for SO₂ and NO₂ oxidation to sulfate and total nitrate, respectively. As discussed in Section 2.1, the first modification will lead to lower O₃ concentrations (and consequently to lower OH concentrations) in the early stages of the plume, resulting in lower NO to NO₂ conversion, and less OH available for the SO₂ to sulfate and NO₂ to nitrate conversion. The second modification results in lower SO₂ oxidation rates (about 34% lower at 298 K and 1 atm) and higher NO₂ oxidation rate constants (about 21% higher at 298 K and 1 atm) than the original RIVAD/ARM3 rate constants.

Figure 3-1 shows plume NO and NO₂ concentrations for plume traverse 3 on July 6, 1999 (referred to as traverse 187003), at a downwind distance of about 11 km from the point source. The dotted line (MCHEM=3) shows the results for the original CALPUFF RIVAD/ARM3 scheme and the solid line (MCHEM=5) shows the results for the revised scheme. The figure shows that NO concentrations in the plume are higher (by about 5%) with the revised scheme than with the original scheme. Correspondingly, the NO₂ concentrations are lower (by about 2.2%) with the revised scheme as compared to the concentrations with the original scheme. These results are consistent with the changes described above.

Figure 3-2 shows plume sulfate and total nitrate (NO_x) concentrations for traverse 187003. As expected, with the revised RIVAD/ARM3 scheme, CALPUFF predicts lower sulfate concentrations (by about 9%) than with the original scheme. This is due to both the lower OH concentrations and SO₂ oxidation rate constants in the updated scheme as compared to the original scheme. In contrast, we see that NO_x concentrations are slightly larger (by about 1.4%) with the revised scheme than with the original scheme because the higher NO₂ oxidation rate constant more than compensates for the lower OH concentration in the revised scheme.

Figure 3-3 shows the NO and NO₂ results for plume traverse 6 on July 6, 1999 (traverse 187006) at about 31 km downwind of the power plant. At this distance, we see that both NO and NO₂ concentrations with the revised RIVAD/ARM3 scheme are slightly lower than those with the original scheme. The NO results are in contrast to those for the traverse at a downwind distance of 11 km, shown earlier in Figure 3-1. It appears that at larger downwind distances, the higher NO₂ to nitrate oxidation rate constant in the revised scheme changes the equilibrium of the NO-NO₂-O₃ system, resulting in more conversion of NO to NO₂. From Figure 3-4, which shows the sulfate and total nitrate concentration profiles, we see that there is indeed more total nitrate (about 5.5%) produced with the revised scheme (due to the higher NO₂ oxidation rate constant). The sulfate produced with the revised scheme is about 23% lower than that with the original scheme.

The results for plume traverse 10 on July 6, 1999 (traverse 187010) at a downwind distance of 65 km are shown in Figures 3-5 and 3-6. The results are qualitatively similar to those for traverse 187006.

Figures 3-7 and 3-8 show the results for traverse 4 on July 13, 1999 (traverse 194004) at a downwind distance of about 16 km from the power plant. The results are consistent with those for the 11 km plume traverse (187001) on July 6, 1999. The results for traverse 1 on July 15, 1999 (traverse 196001) at a downwind distance of 17 km, shown in Figures 3-9 and 3-10, are also qualitatively similar.

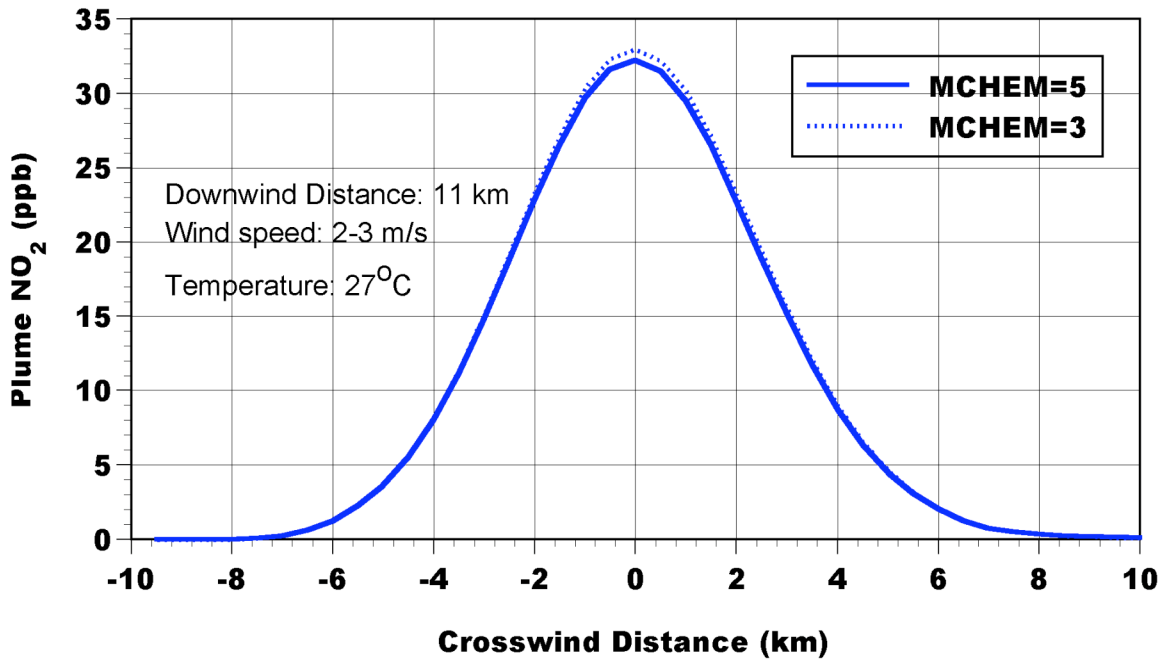
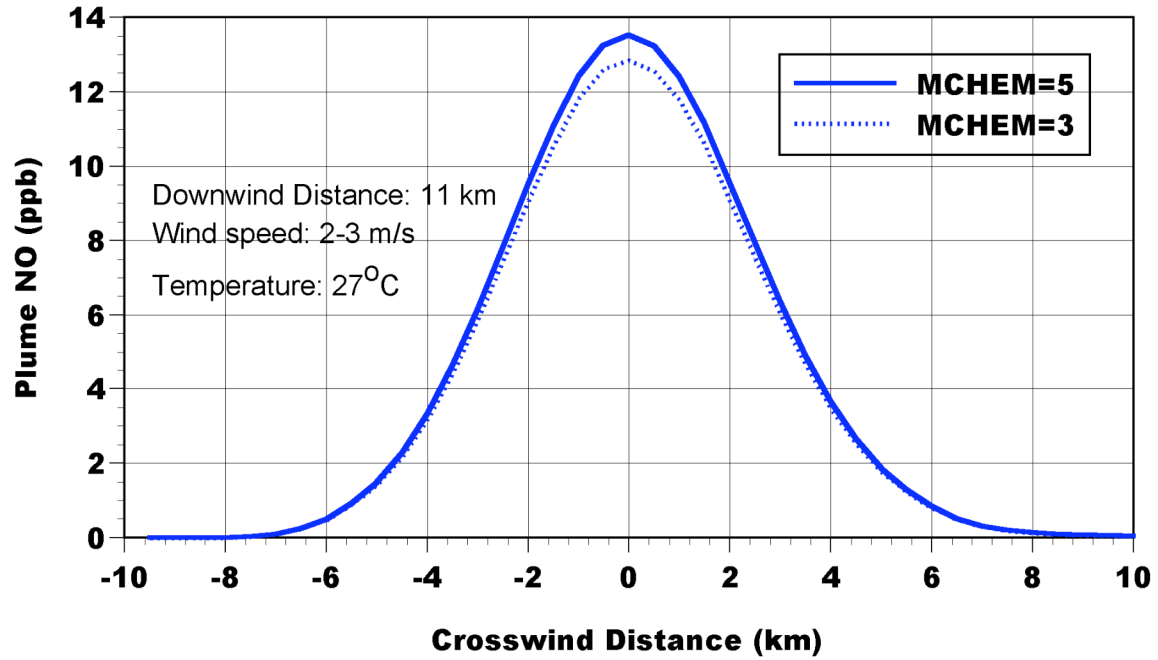


Figure 3-1. NO and NO₂ concentration profiles for plume traverse 187003. MCHM=3 refers to the original CALPUFF RIVAD/ARM3 formulation, while MCHM=5 refers to the corrected formulation.

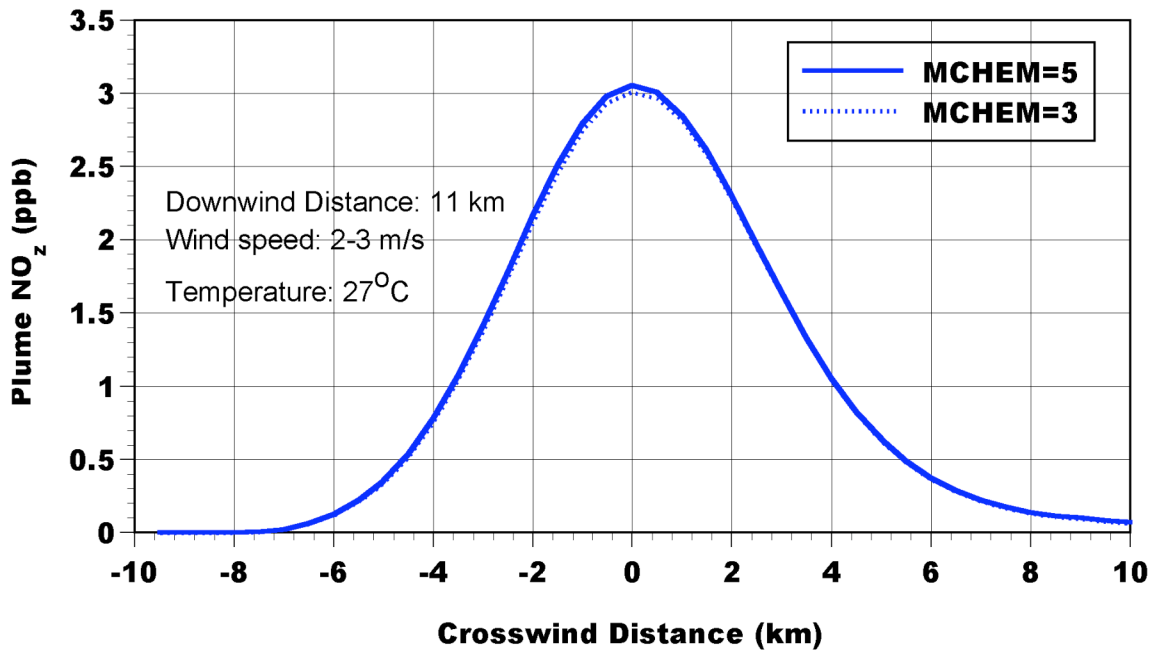
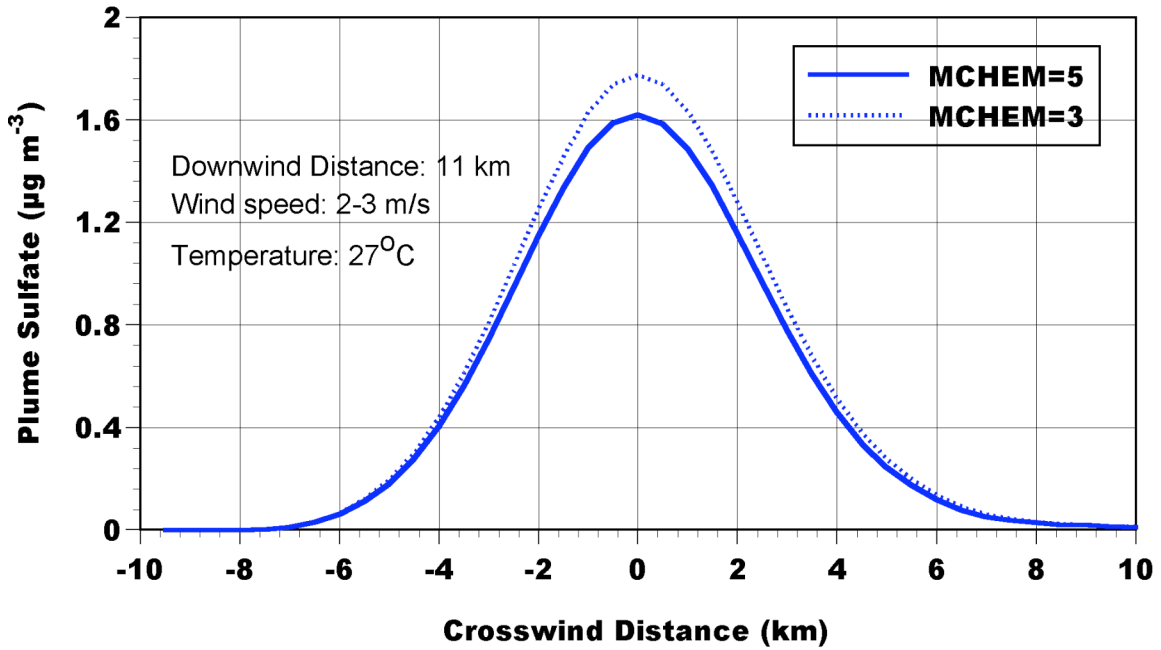


Figure 3-2. Sulfate and NO_z concentration profiles for plume traverse 187003. MCHM=3 refers to the original CALPUFF RIVAD/ARM3 formulation, while MCHM=5 refers to the corrected formulation.

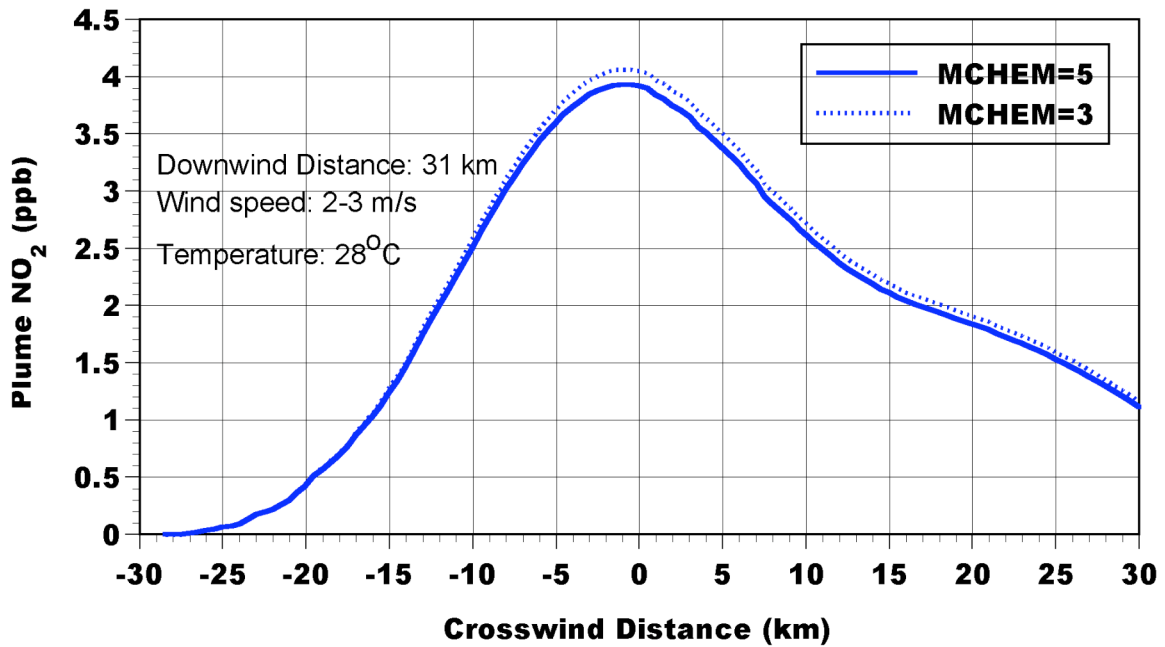
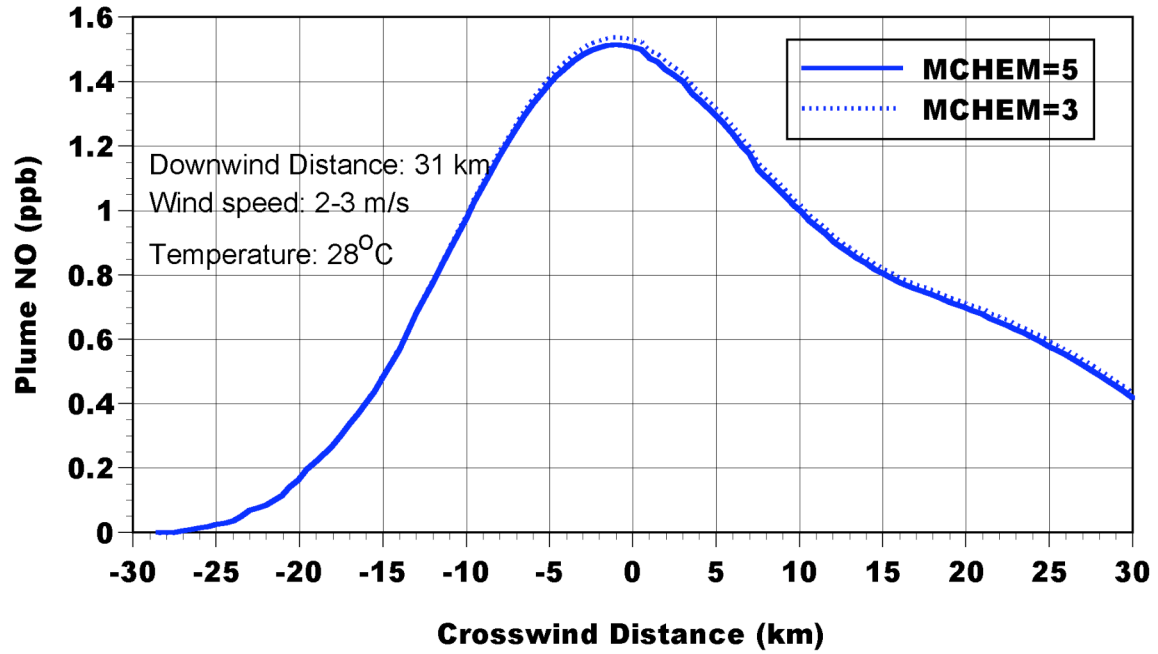


Figure 3-3. NO and NO₂ concentration profiles for plume traverse 187006. MCHM=3 refers to the original CALPUFF RIVAD/ARM3 formulation, while MCHM=5 refers to the corrected formulation.

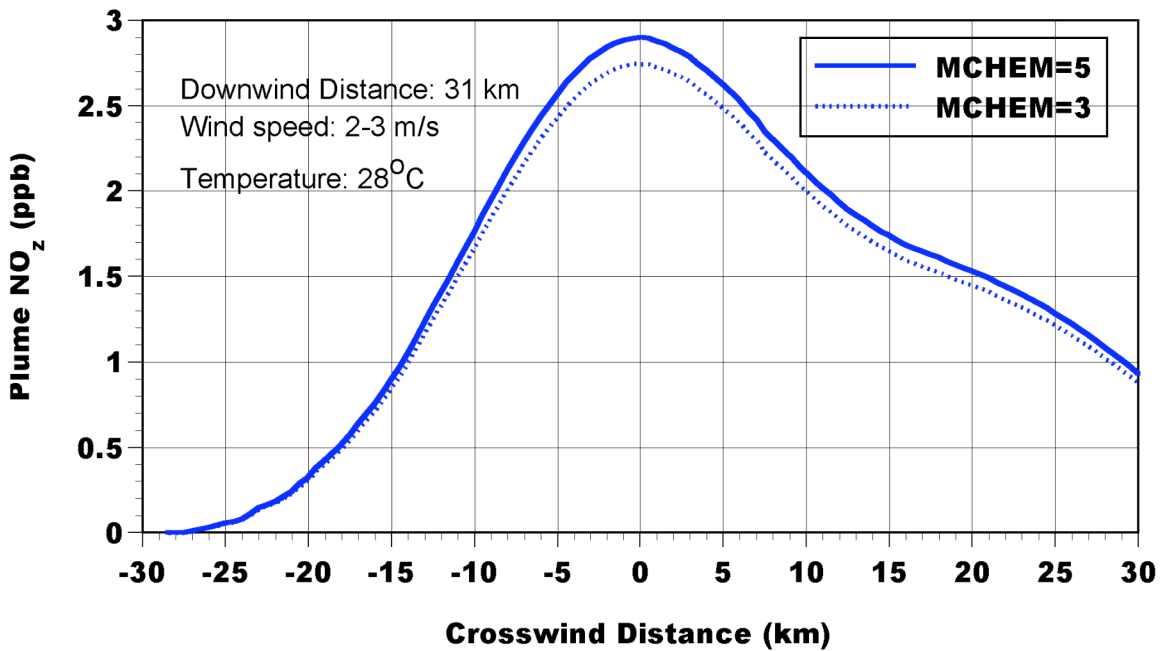
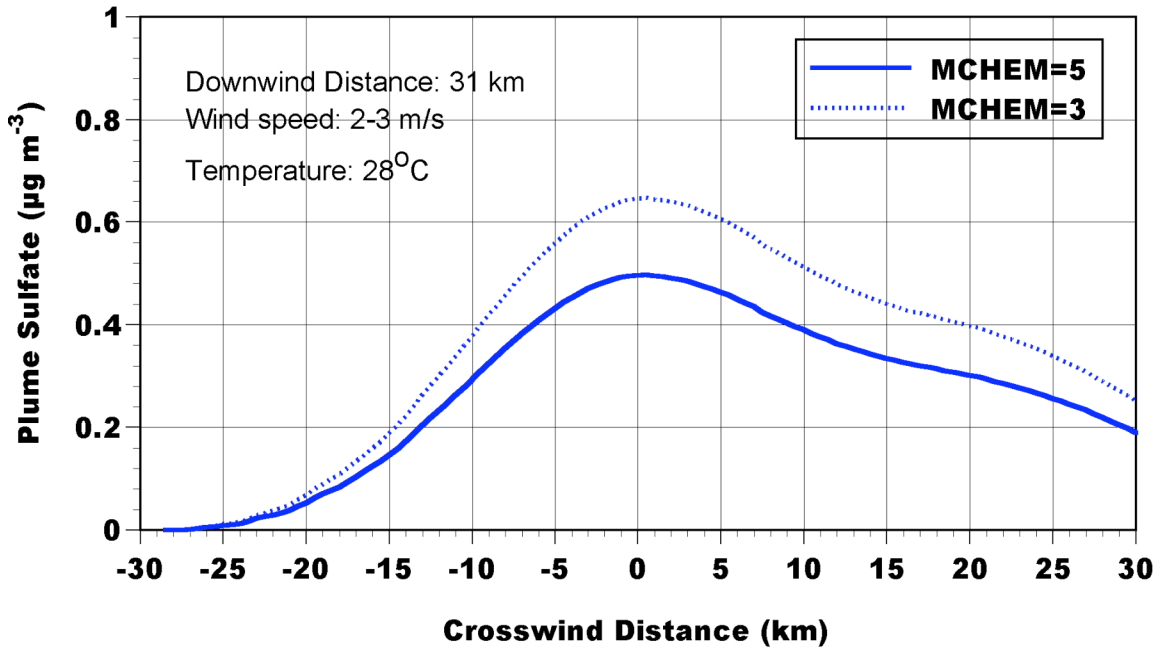


Figure 3-4. Sulfate and NO_z concentration profiles for plume traverse 187006. MCHM=3 refers to the original CALPUFF RIVAD/ARM3 formulation, while MCHM=5 refers to the corrected formulation.

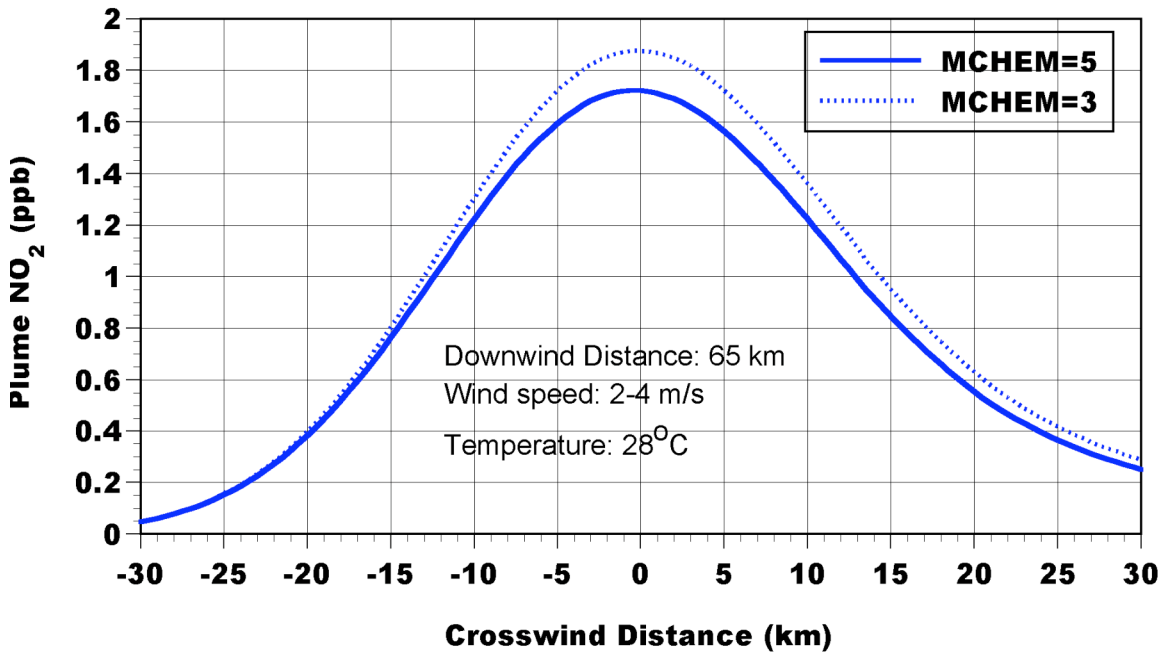
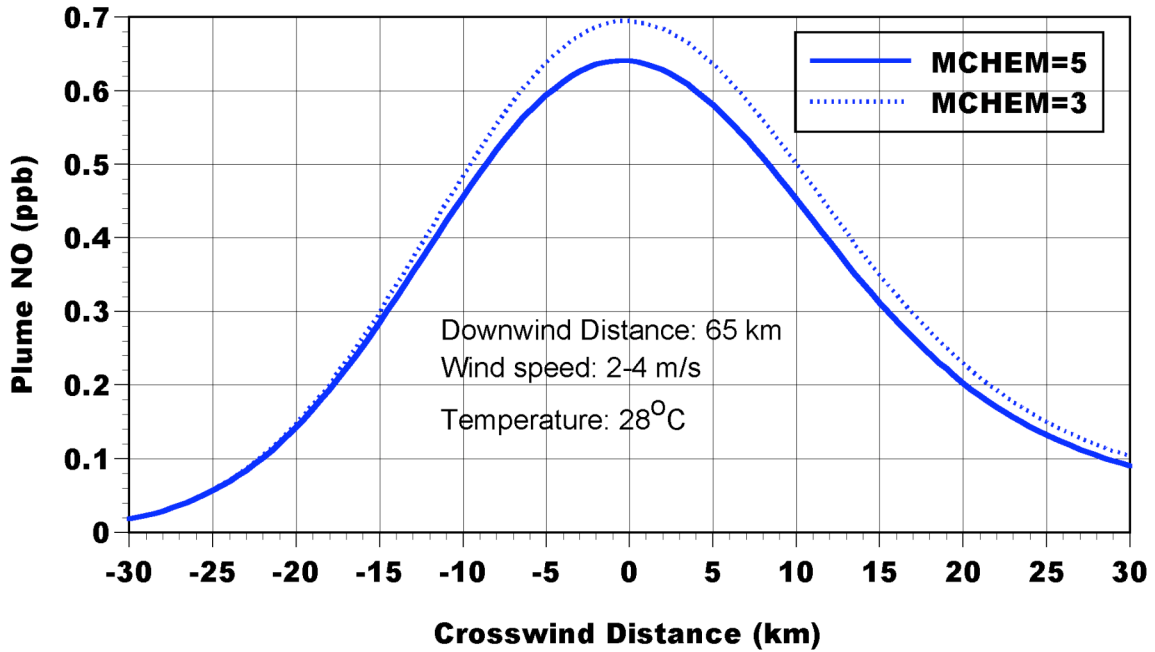


Figure 3-5. NO and NO₂ concentration profiles for plume traverse 187010. MCHM=3 refers to the original CALPUFF RIVAD/ARM3 formulation, while MCHM=5 refers to the corrected formulation.

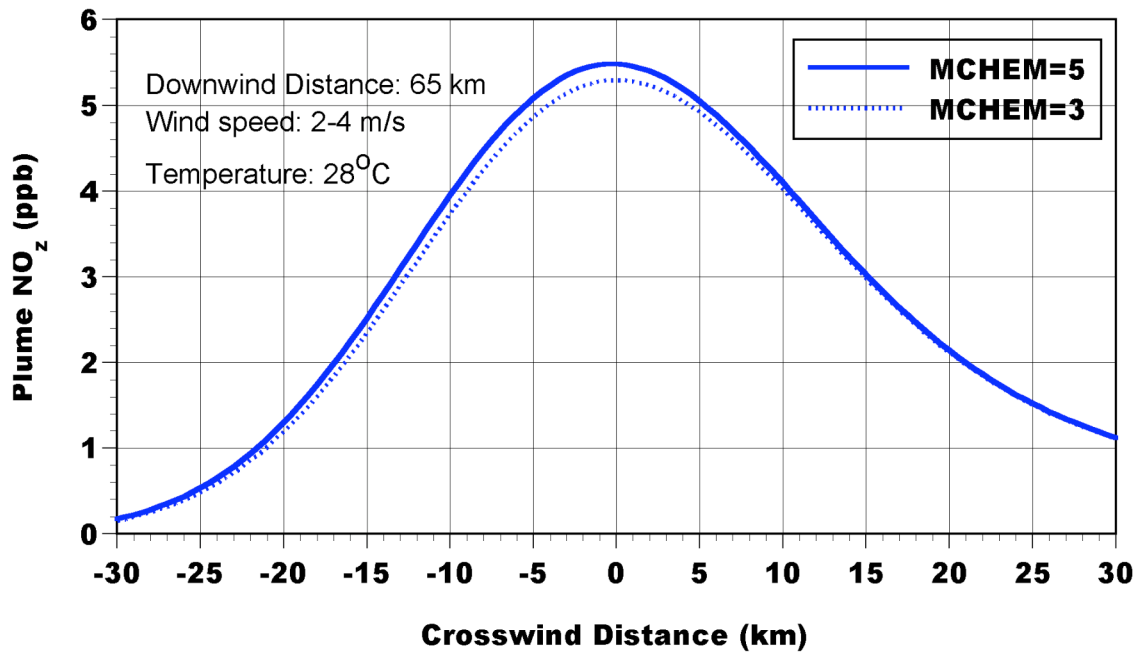
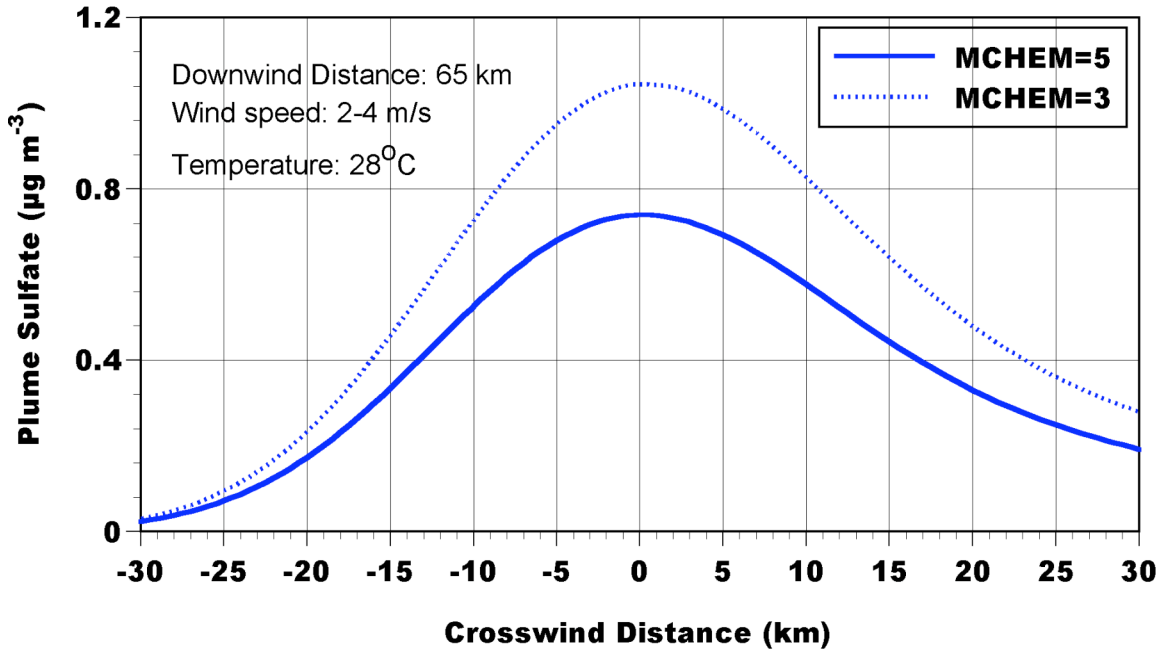


Figure 3-6. Sulfate and NO_z concentration profiles for plume traverse 187010. MCHM=3 refers to the original CALPUFF RIVAD/ARM3 formulation, while MCHM=5 refers to the corrected formulation.

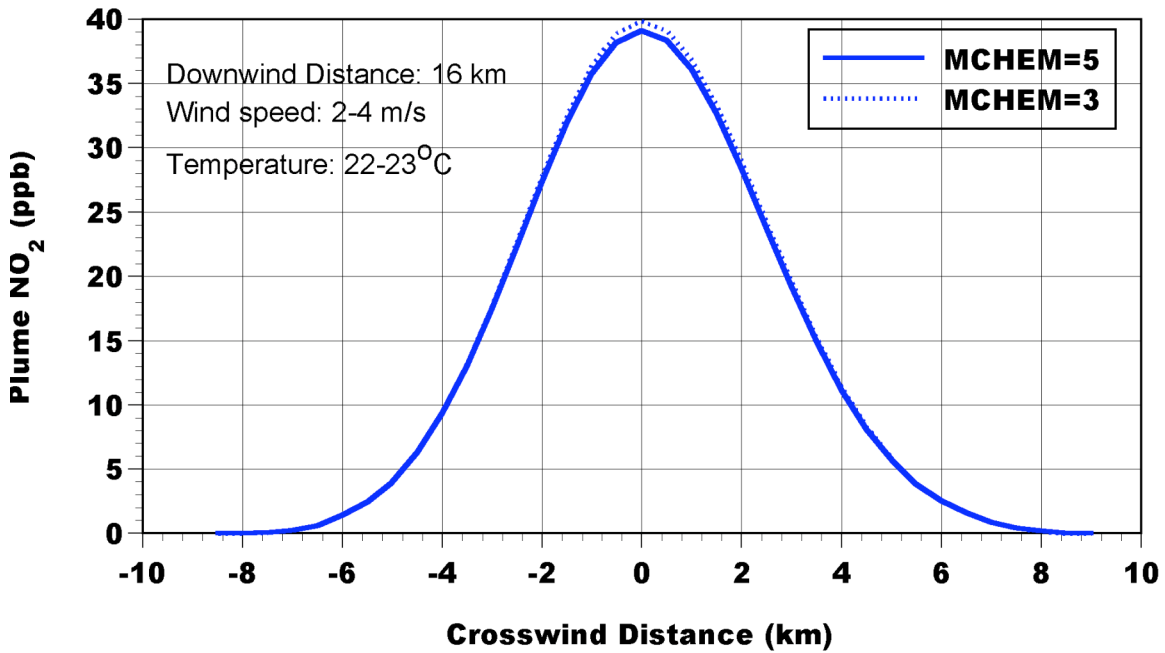
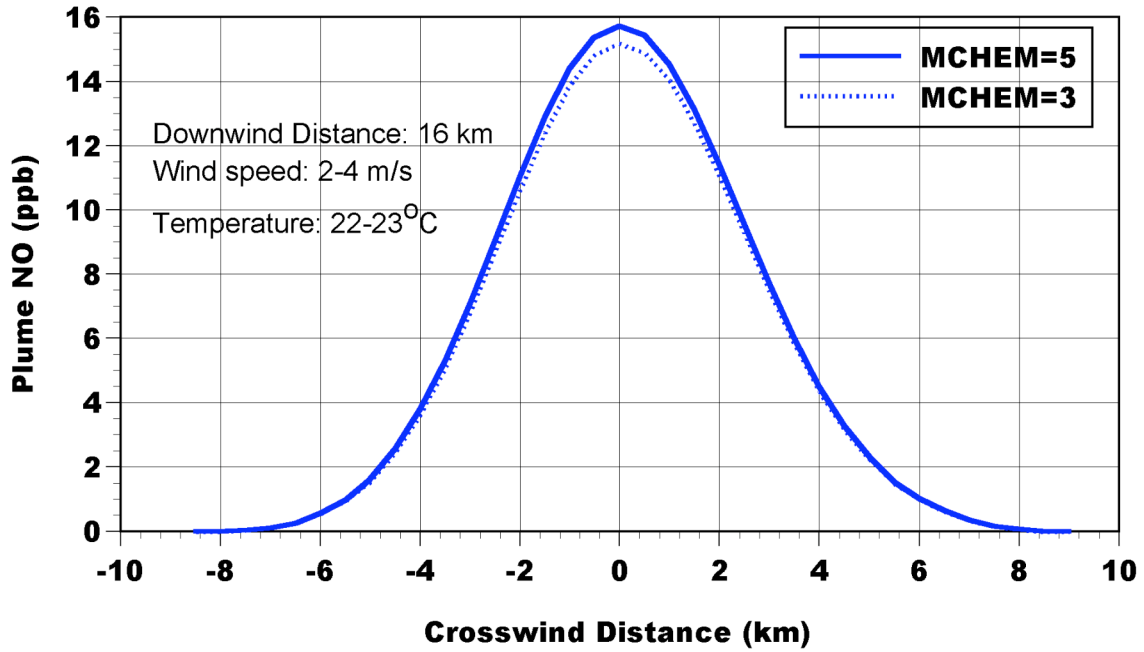


Figure 3-7. NO and NO₂ concentration profiles for plume traverse 194004. MCHEM=3 refers to the original CALPUFF RIVAD/ARM3 formulation, while MCHEM=5 refers to the corrected formulation.

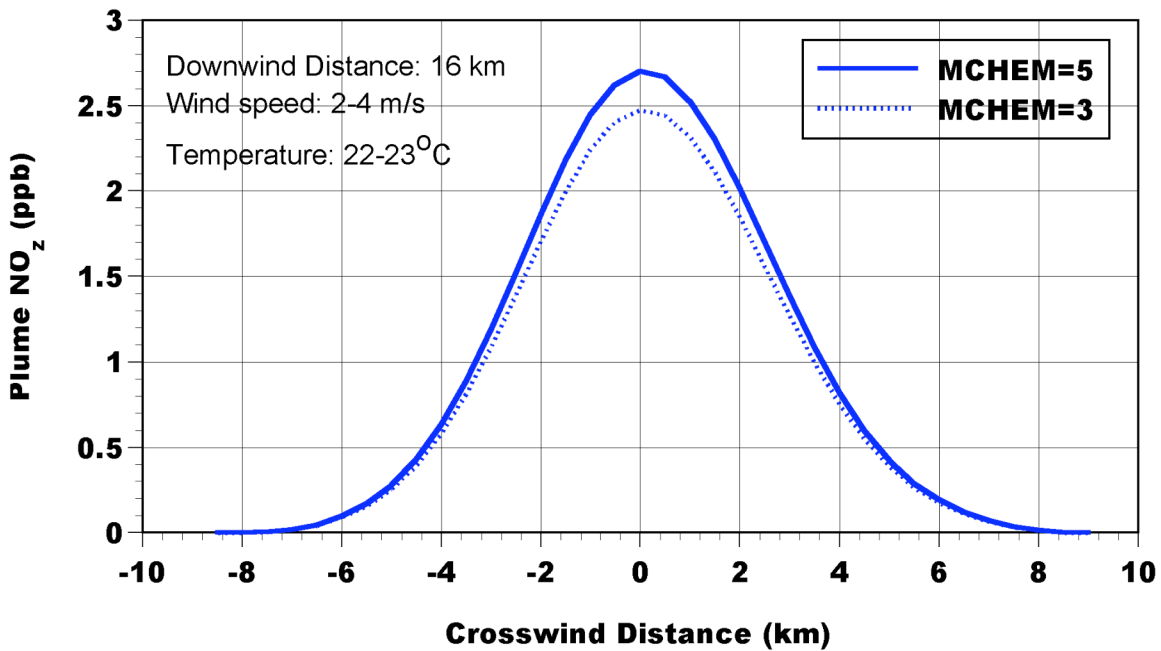
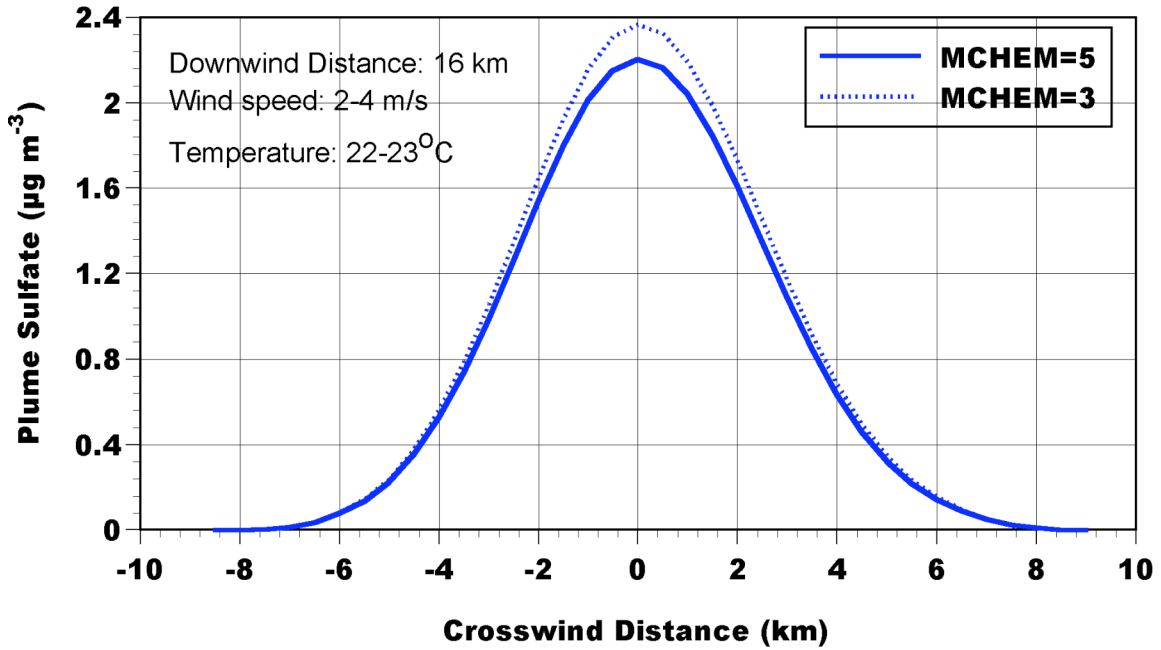


Figure 3-8. Sulfate and NO_z concentration profiles for plume traverse 194004. MCHM=3 refers to the original CALPUFF RIVAD/ARM3 formulation, while MCHM=5 refers to the corrected formulation.

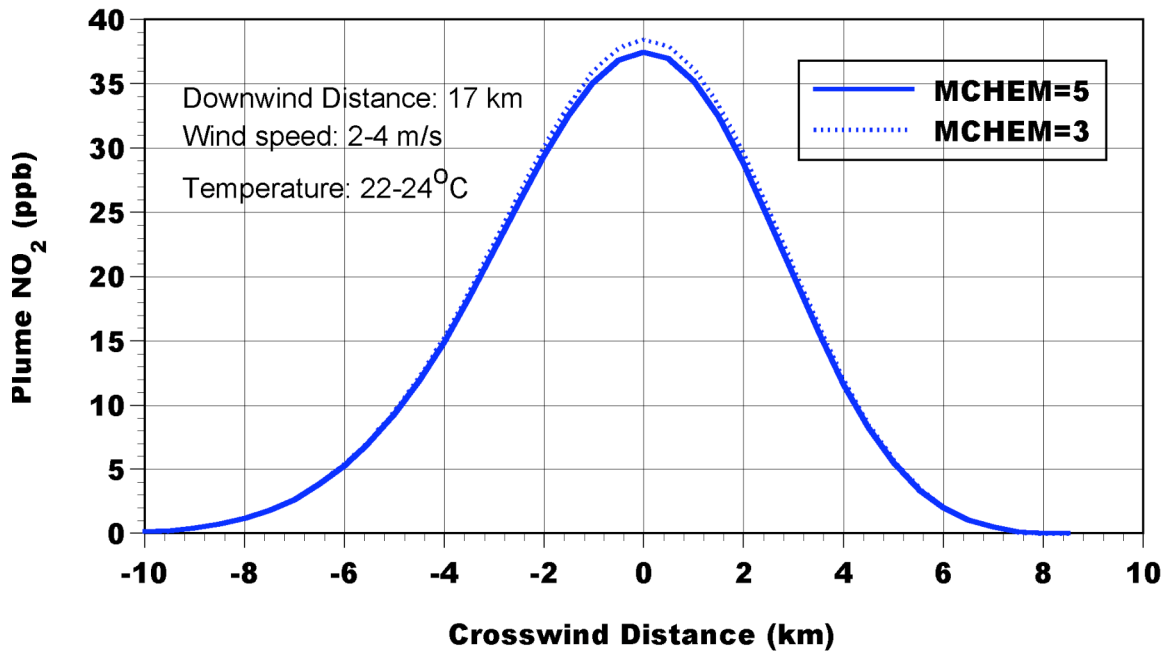
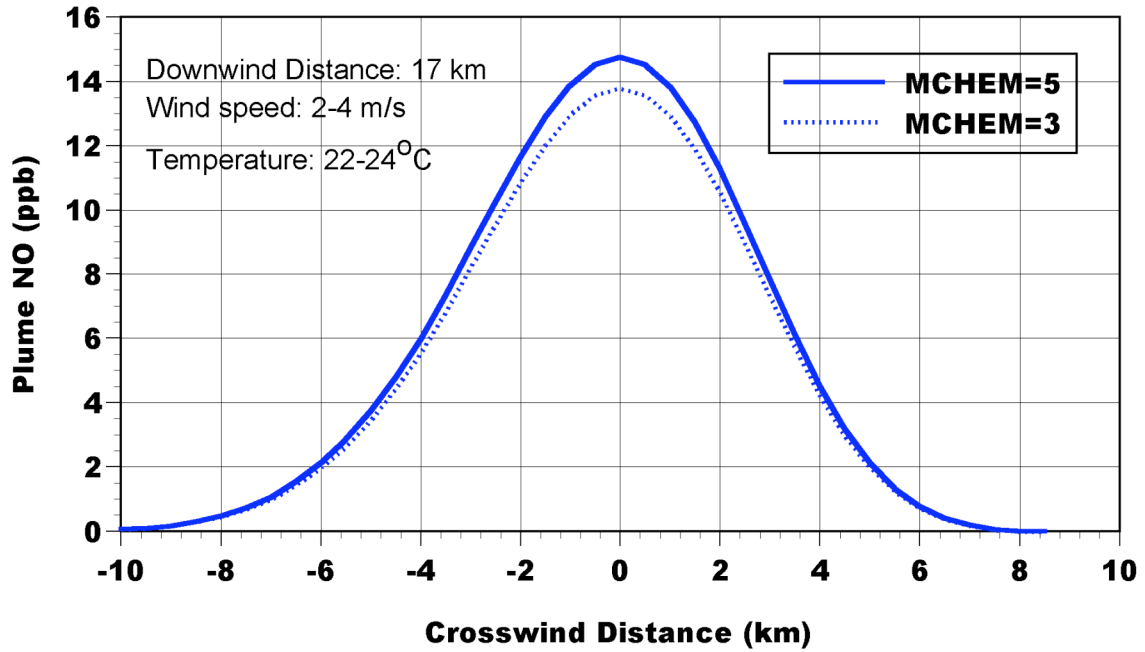


Figure 3-9. NO and NO₂ concentration profiles for plume traverse 196001. MCHM=3 refers to the original CALPUFF RIVAD/ARM3 formulation, while MCHM=5 refers to the corrected formulation.

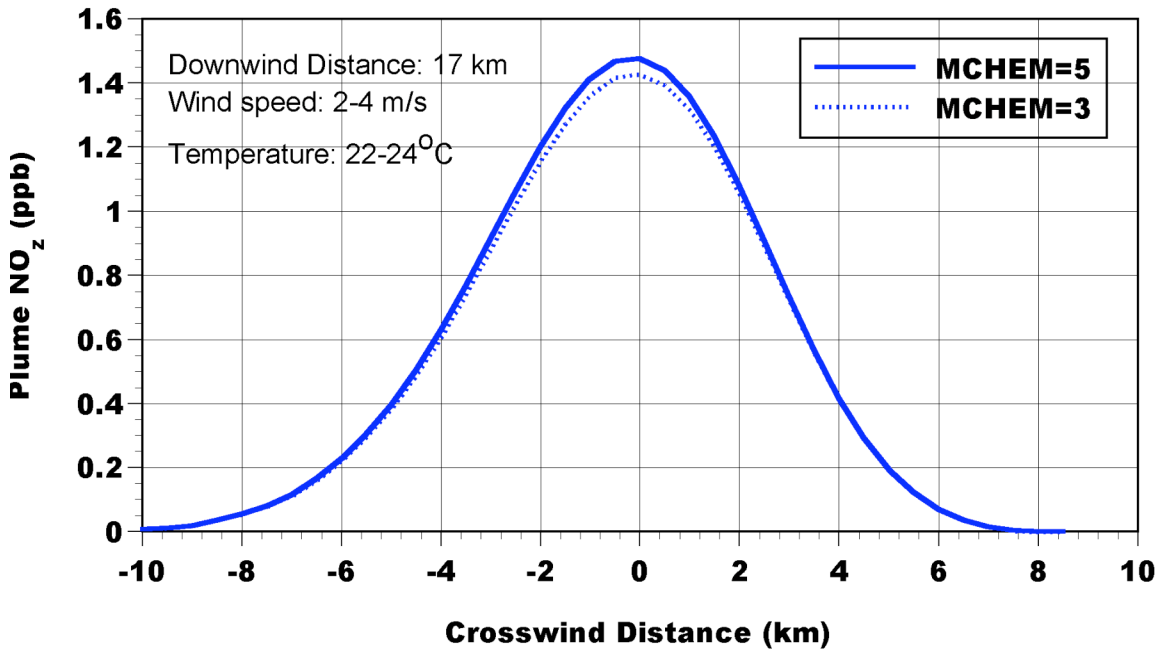
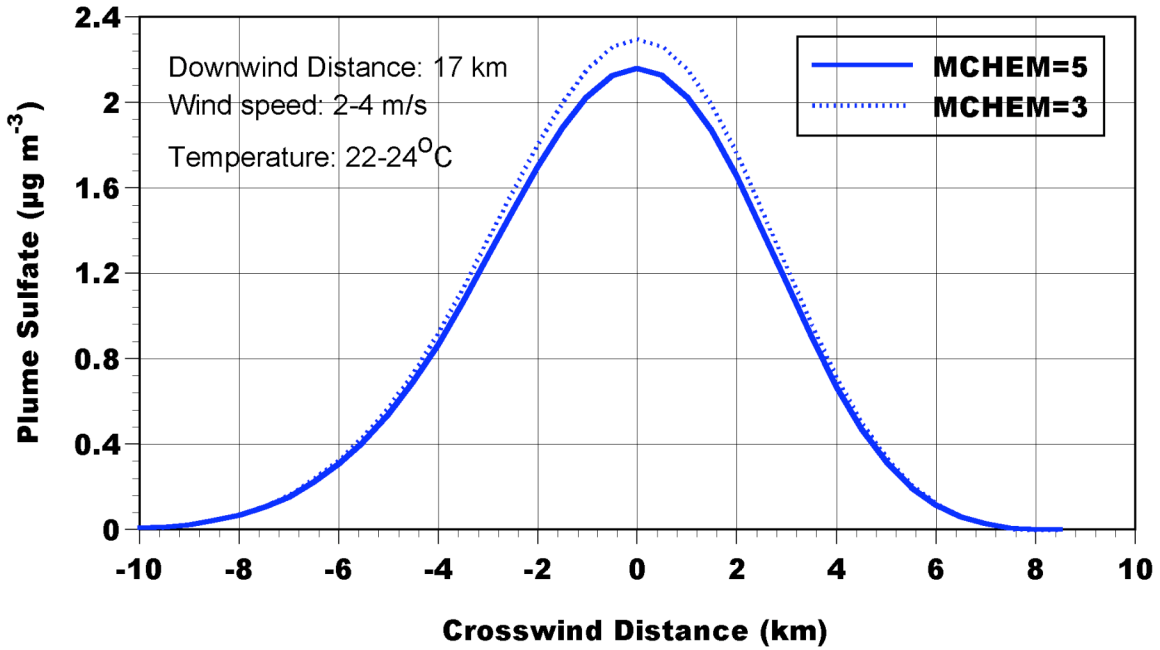


Figure 3-10. Sulfate and NO_z concentration profiles for plume traverse 196001. MCHM=3 refers to the original CALPUFF RIVAD/ARM3 formulation, while MCHM=5 refers to the corrected formulation.

3.3 Effect of Improvements to Inorganic Aerosol Equilibrium Treatment

In this section, we examine the differences between the new and original versions of CALPUFF in terms of the partitioning of total nitrate (shown in the previous section) between the gas and particulate phases. The new treatment of inorganic aerosol equilibrium, described in Section 2.2, is based on the ISORROPIA module, which is used in a number of three-dimensional grid models such as CMAQ, CMAQ-MADRID and CAMx.

We first present the comparison of the revised and original RIVAD schemes for crosswind traverses of the power plant plume. Figure 3-11 shows the concentrations of gas-phase nitric acid and particulate nitrate for traverse 187003 for the two versions of the model. Both versions predict that most of the total nitrate partitions into the gas-phase. However, the ISORROPIA treatment results in significantly lower PM nitrate concentrations than the original CALPUFF treatment.

The low amount of PM nitrate formed with both the original and new treatments is due to the low relative humidity on July 6. As described in Section 3.1, July 6 was a clear and dry day. To examine the effect of relative humidity on the results, we conducted sensitivity studies in which the relative humidity was fixed at 95%. The results for traverse 187003 are shown in Figure 3-12. We see that significantly more PM nitrate is formed for both the original and new inorganic aerosol treatments when relative humidity is increased. As in the base simulations, the PM nitrate from the ISORROPIA treatment is still much smaller (by more than a factor of 3) than the PM nitrate from the original CALPUFF treatment.

The results for other traverses on July 6, 1999 are qualitatively similar to those for traverse 187003 and are not shown here. The results for July 15, 1999, which was a hot and hazy day, are also generally similar. However July 13 was partly cloudy with high relative humidity. Figure 3-13 shows the nitrate partitioning results for traverse 194004 on July 13. In comparison with the base simulation for July 6, we see that higher PM nitrate concentrations are predicted with both treatments. The simulation with the ISORROPIA algorithm still predicts about a factor of 4 lower PM nitrate than the simulation with the original CALPUFF treatment.

To get a better understanding of nitric acid and nitrate formation in CALPUFF as a function of downwind distance, we conducted additional simulations for July 6 for various downwind distances along the plume centerline. In addition to the two (original and improved) RIVAD options for chemistry, we also included the recommended IWAQM (Interagency Workgroup on Air Quality Modeling) and FLAG (Federal Land Managers' AQRV Workgroup) MESOPUFF II option (MCHEM=1) in this analysis. These simulations were conducted with the official 2007 release of CALPUFF (Version 5.8).

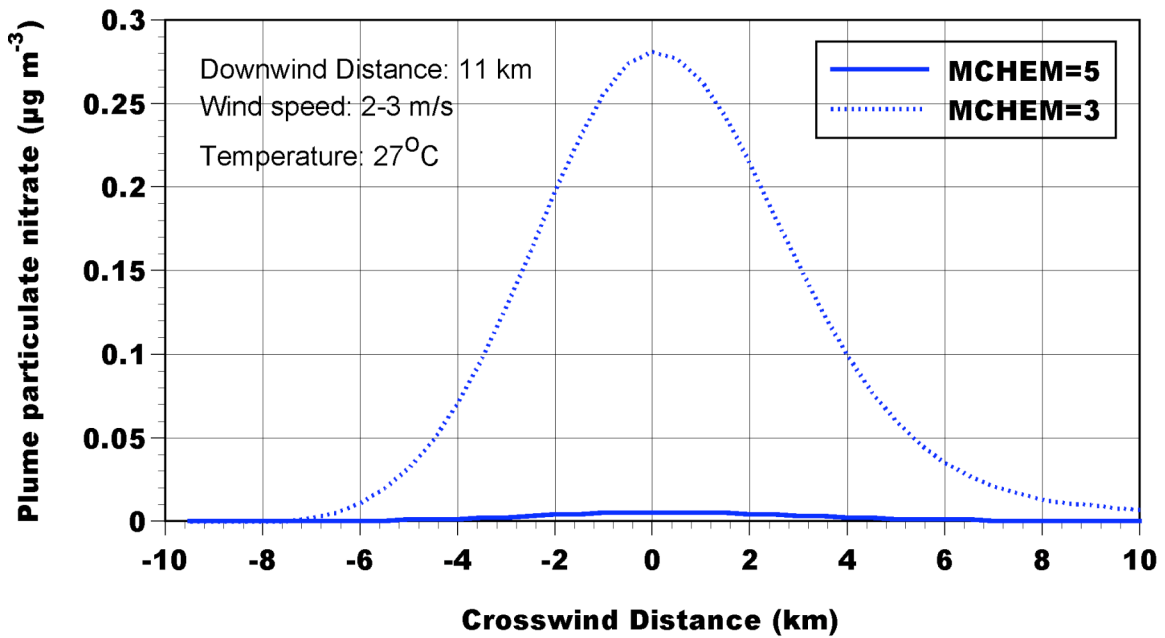
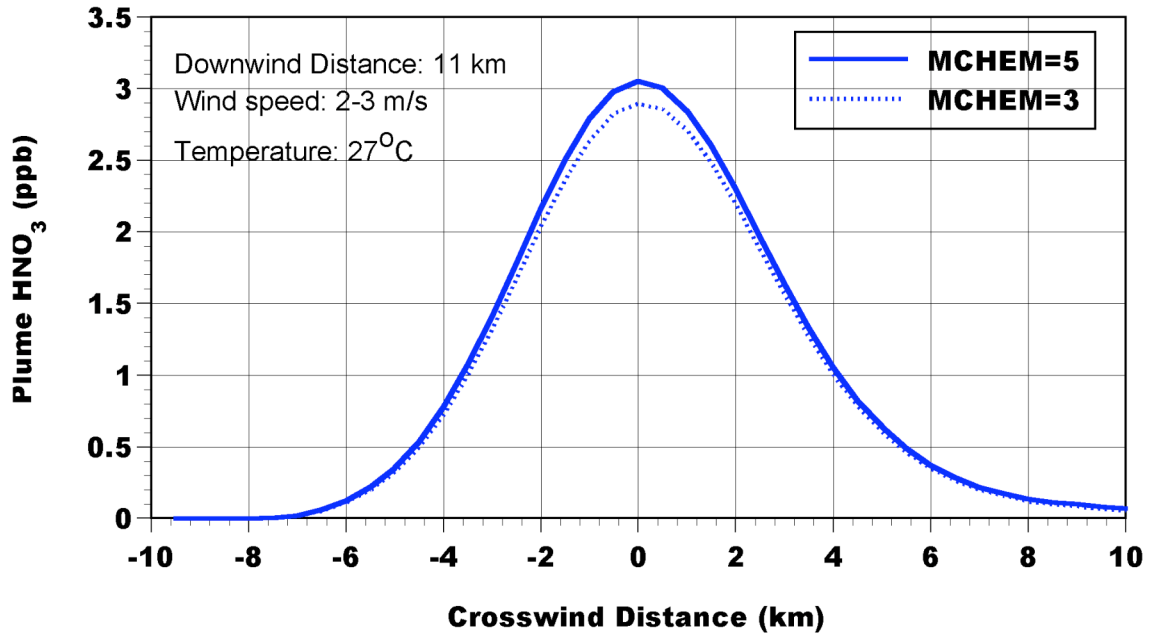


Figure 3-11. HNO₃ and particulate nitrate concentration profiles for plume traverse 187003. MCHM=3 refers to the original inorganic PM treatment, while MCHM=5 refers to the new treatment (ISORROPIA).

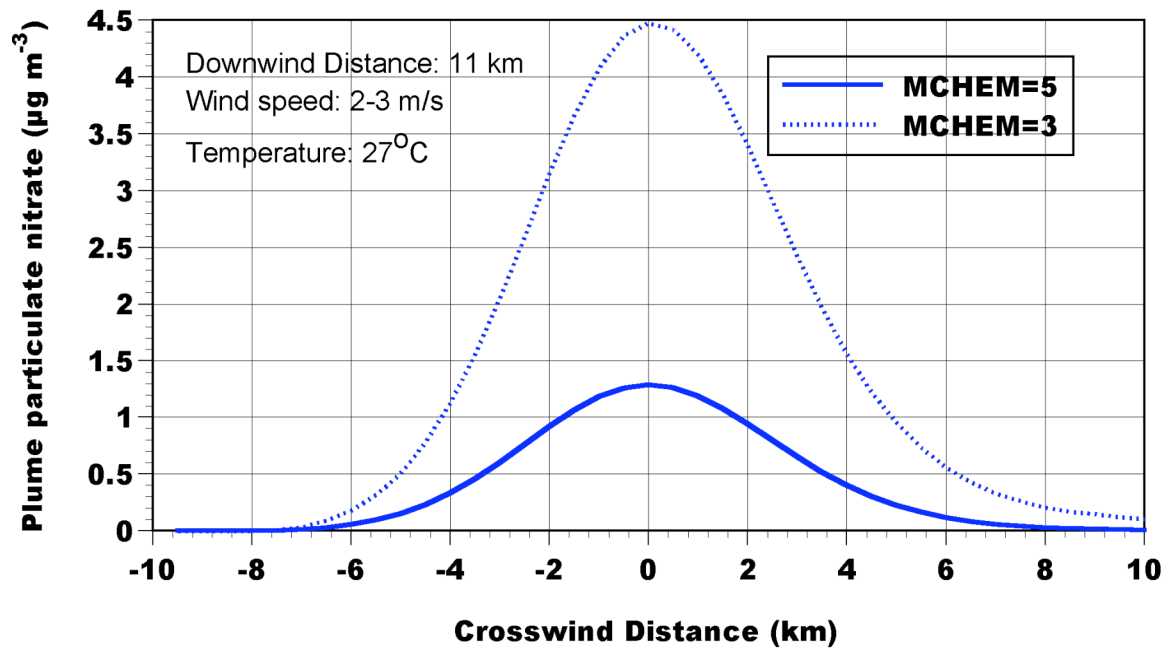
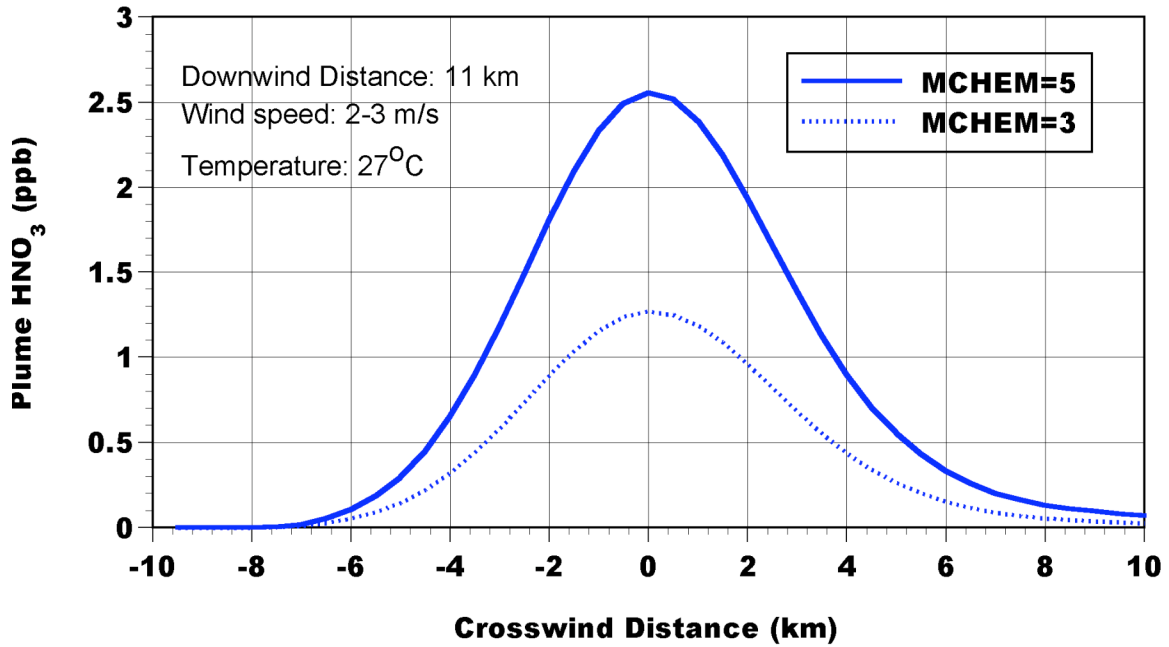


Figure 3-12. HNO₃ and particulate nitrate concentration profiles for plume traverse 187003 (relative humidity set to 95%). MCHM=3 refers to the original inorganic PM treatment, while MCHM=5 refers to the new treatment (ISORROPIA).

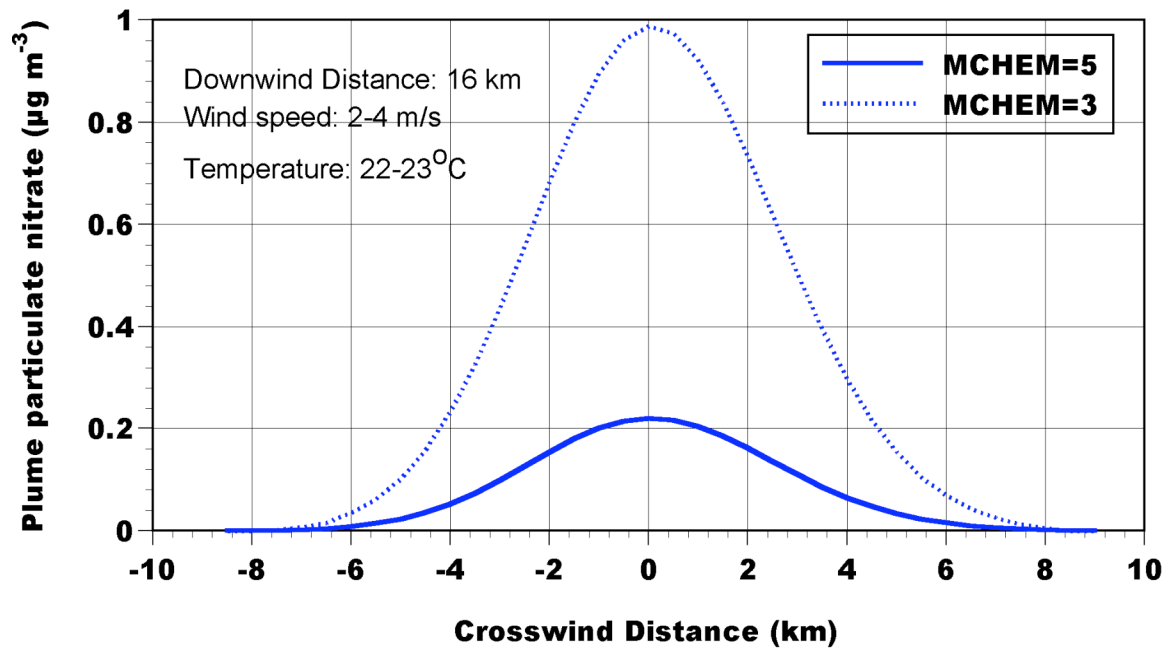
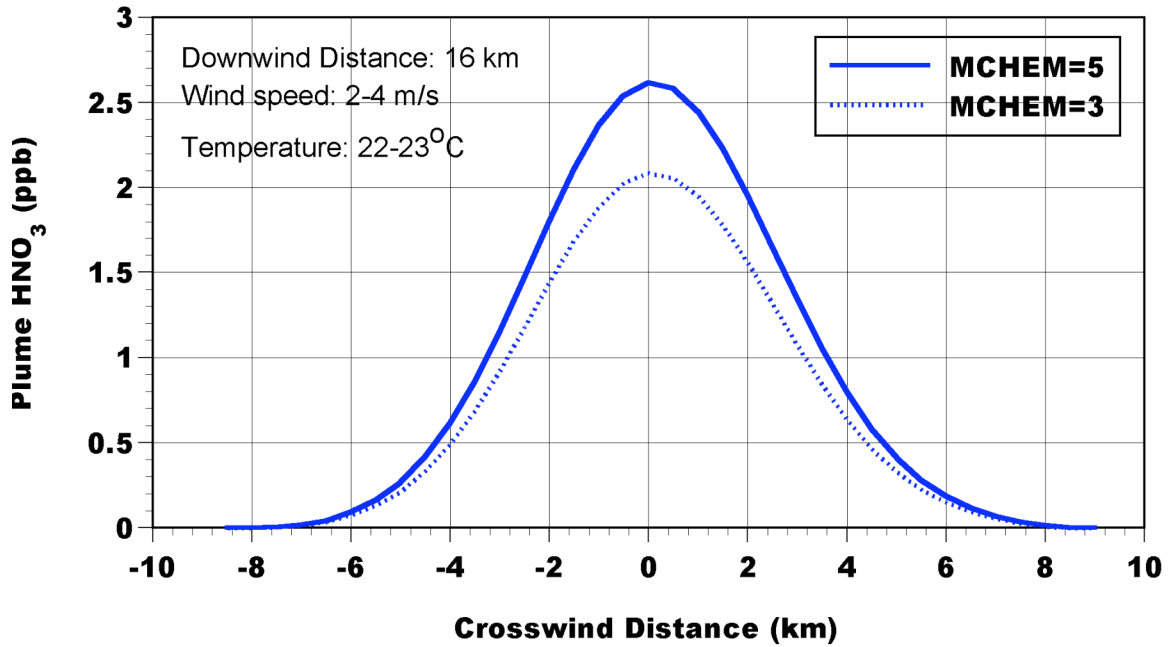


Figure 3-13. HNO₃ and particulate nitrate concentration profiles for plume traverse 194004. MCHM=3 refers to the original inorganic PM treatment, while MCHM=5 refers to the new treatment (ISORROPIA).

Figure 3-14 shows the HNO_3 and particulate nitrate concentrations as a function of downwind distance for July 6, 1999. We see that the MESOPUFF II option predicts higher initial total nitrate concentrations than both the RIVAD options near the source to about 20 km downwind of the source. At larger downwind distances, the two RIVAD options predict significantly larger total nitrate concentrations than the MESOPUFF II option. The total nitrate concentrations from the two RIVAD options are generally similar, but the original RIVAD treatment predicts more particulate nitrate and less nitric acid concentrations than the improved RIVAD treatment, consistent with the earlier results shown in Figure 3-11. The maximum downwind particulate nitrate concentration is about $0.24 \mu\text{g}/\text{m}^3$ for the MESOPUFF II option (at about 30 km downwind), while the maximum concentration for the original RIVAD option is about $0.5 \mu\text{g}/\text{m}^3$ at about 50 km downwind of the source. Particulate nitrate concentrations for the improved RIVAD treatment are negligible for this case.

As discussed previously, the generally low particulate nitrate concentrations for July 6 can be attributed to the dry conditions on that day. We conducted additional sensitivity studies for July 6 in which we set the relative humidity for the inorganic aerosol modules to 95%. Figure 3-15 shows the results for these sensitivity studies. We see that both the MESOPUFF II and original RIVAD options predict significantly higher partitioning of the total nitrate into the particulate phase than the improved RIVAD treatment with ISORROPIA. The maximum downwind particulate nitrate concentration from the improved RIVAD option is less than $1 \mu\text{g}/\text{m}^3$ while the corresponding maximum for MESOPUFF II is about $4.5 \mu\text{g}/\text{m}^3$ and the value for the original RIVAD treatment is almost $10 \mu\text{g}/\text{m}^3$.

3.4 Effect of New Aqueous-Phase Chemistry Treatment

To test the effect of the new aqueous-phase chemistry treatment implemented in CALPUFF for this study, we assigned a hypothetical cloud cover of 5% to all grid cells, since the CALMET files did not have cloud cover information. In this section, we examine the impact of aqueous-phase chemistry on plume SO_2 and sulfate concentrations. Because the original CALPUFF does not have explicit treatment of aqueous-phase chemistry, we compare the results with those from simulations without aqueous-phase chemistry. For both sets of simulations compared here, the gas-phase chemistry is based on the updated RIVAD/ARM3 scheme with the ISORROPIA module (MCHEM=5). The differences between the two simulations are in the selection of the aqueous-phase chemistry flag (MAQCHEM).

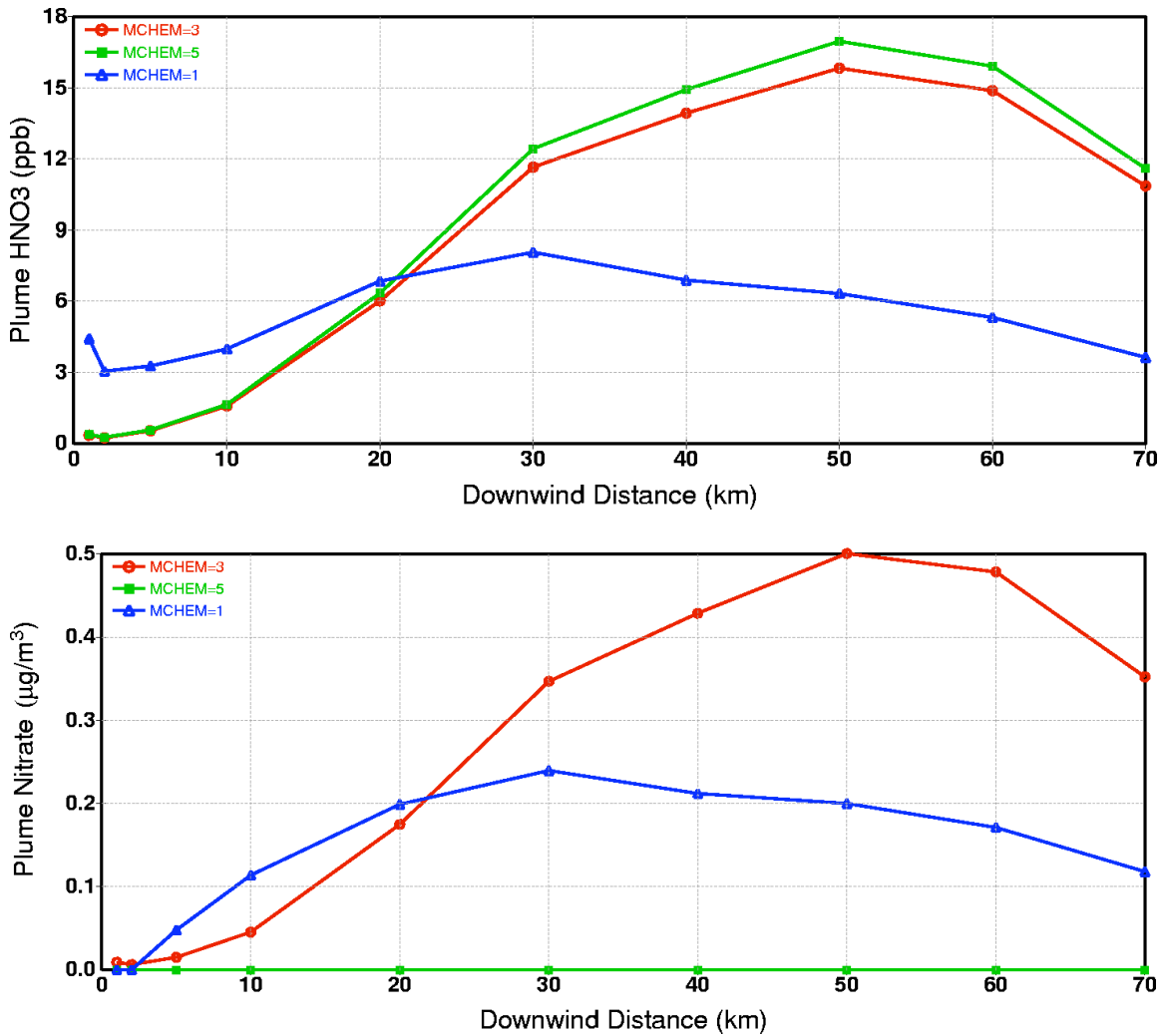


Figure 3-14. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance. MCHEM=1 refers to the MESOPUFF II option, while MCHEM=3 refers to the original RIVAD treatment, and MCHEM=5 refers to the new RIVAD treatment (ISORROPIA).

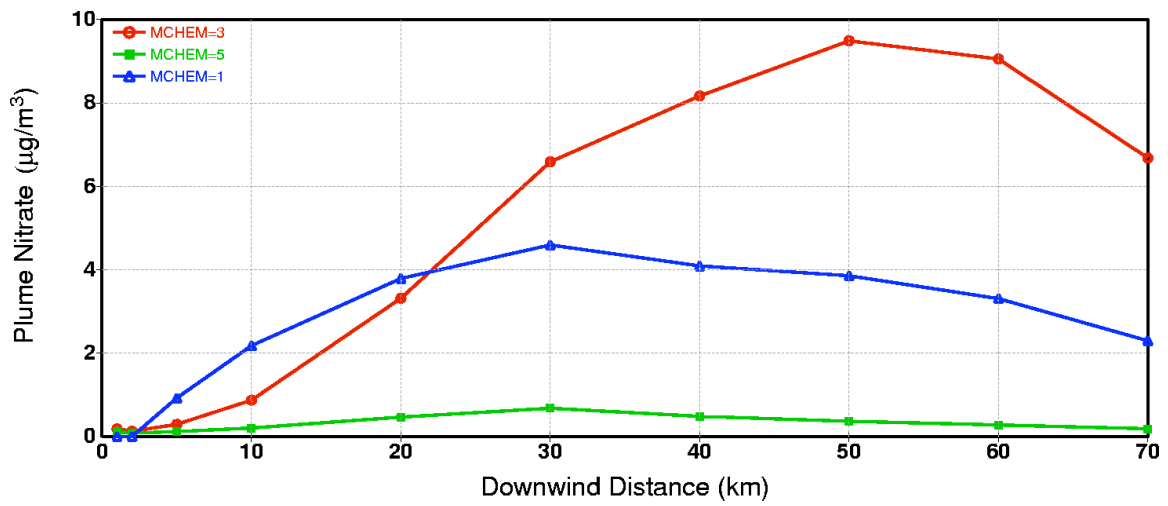
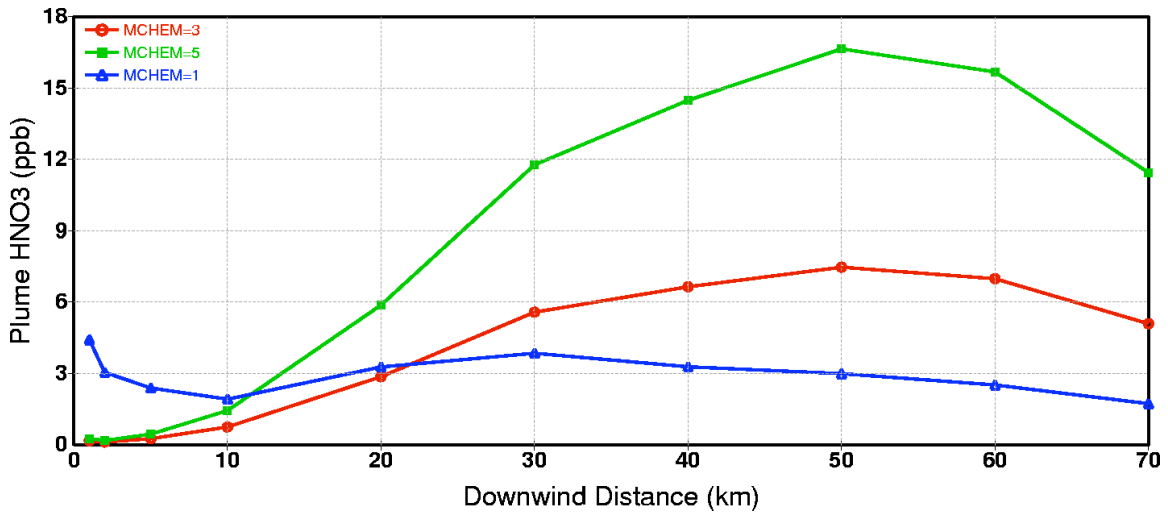


Figure 3-15. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance (relative humidity set to 95%). MCHM=1 refers to the MESOPUFF II option, while MCHM=3 refers to the original RIVAD treatment, and MCHM=5 refers to the new RIVAD treatment (ISORROPIA).

Figure 3-16 shows the predicted SO₂ and sulfate concentrations for traverse 187003 (downwind distance of 11 km). The solid line (MAQCHEM=1) refers to the simulation with aqueous-phase chemistry turned on, while the dotted line (MAQCHEM=0) refers to the simulation without aqueous-phase chemistry. We see from Figure 3-16 that about 20% more SO₂ is converted to sulfate when aqueous-phase chemistry is activated. Figure 3-17 shows the results for traverse 187006, at a downwind distance of 31 km. At this distance, aqueous-phase chemistry results in about 40% more conversion of SO₂ to sulfate. Finally, from Figure 3-18 for traverse 187010, we see that at a downwind distance of 65 km, about 68% more SO₂ is converted to sulfate when aqueous-phase chemistry is activated.

The results for the other days are similar to those for July 6, and are not shown here.

3.5 Effect of Improvements to Secondary Organic Aerosol (SOA) Treatment

For these tests, we had to assign hypothetical emission rates for the VOCs that are the precursors of SOA, since the Cumberland power plant has negligible emissions of these species. Also, for the purposes of comparison between the original CALPUFF SOA formulation and the new formulation implemented here, we only assigned emissions for the aromatics (toluene and xylene) since these are the two common SOA precursors between the two treatments. As described in Section 2.3, the original CALPUFF formulation has 2 additional biogenic precursors, while the new CALPUFF formulation has 2 additional anthropogenic precursors.

Figure 3-19 shows the total SOA produced from both formulations for plume traverses 187003 and 187006. In the original CALPUFF formulation, there is only one SOA species, while in the new formulation there are 4 SOA species from the aromatics and 3 SOA species from PAH and long-chain alkanes. In the comparison shown here, the total SOA for the new CALPUFF formulation is the sum of the 4 SOA species from the aromatics. From Figure 3-19, we see that the SOA formed with the original CALPUFF formulation (MCHEM=4) is more than a factor of 2 lower than that with the new formulation (MCHEM=6). This is consistent with our finding in Section 2.3 that the original CALPUFF formulation does not treat the temperature dependence of the partition coefficients correctly, and underestimates them by a factor of 3 or more at ambient temperatures.

The results for plume traverses 194004 and 196001 are shown in Figure 3-20. These results are qualitatively similar to those for July 6 shown in Figure 3-19.

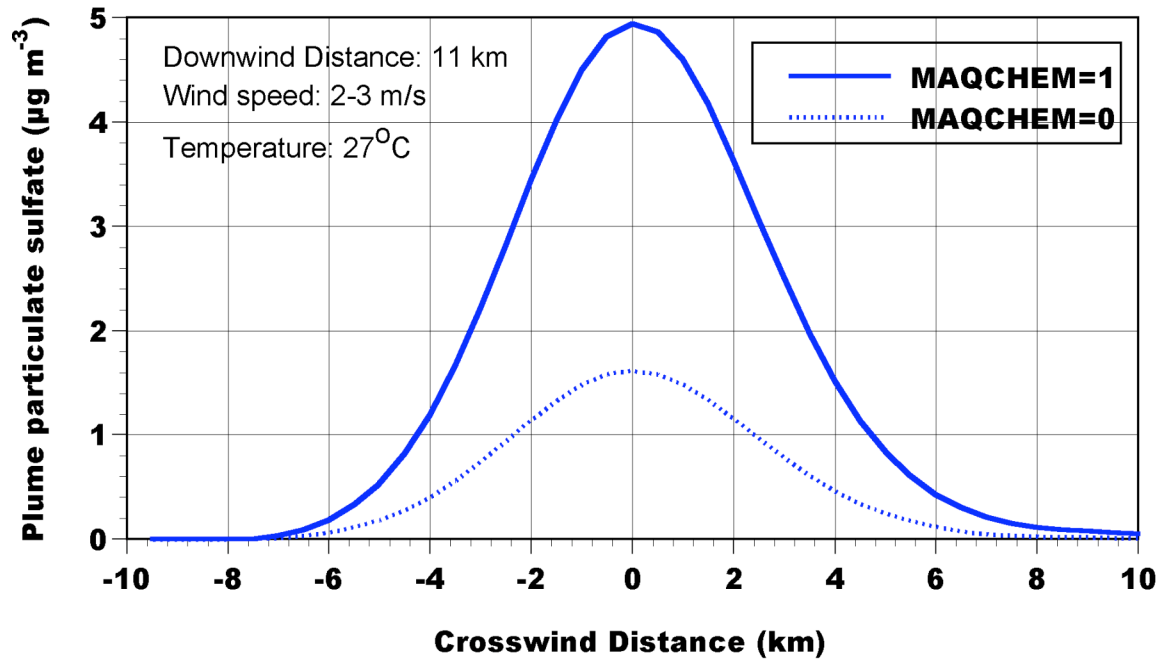
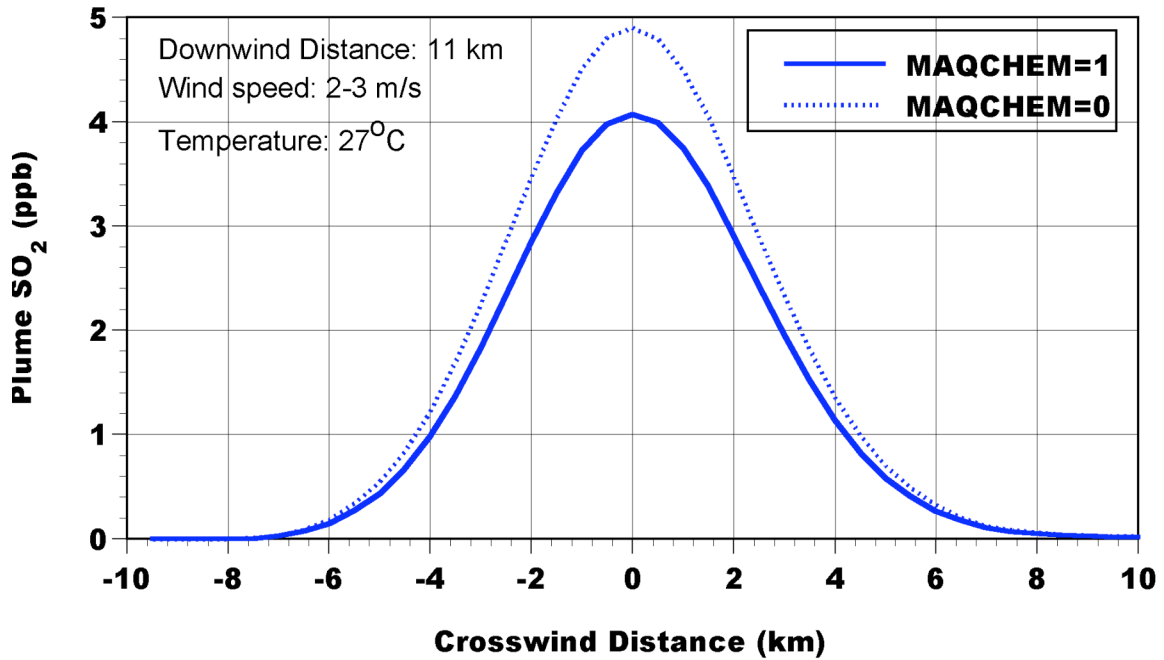


Figure 3-16. Effect of aqueous-phase chemistry on SO₂ and sulfate concentrations for plume traverse 187003. MAQCHEM=0 refers to the case with no aqueous-phase chemistry, while MAQCHEM=1 refers to the case with aqueous-phase chemistry.

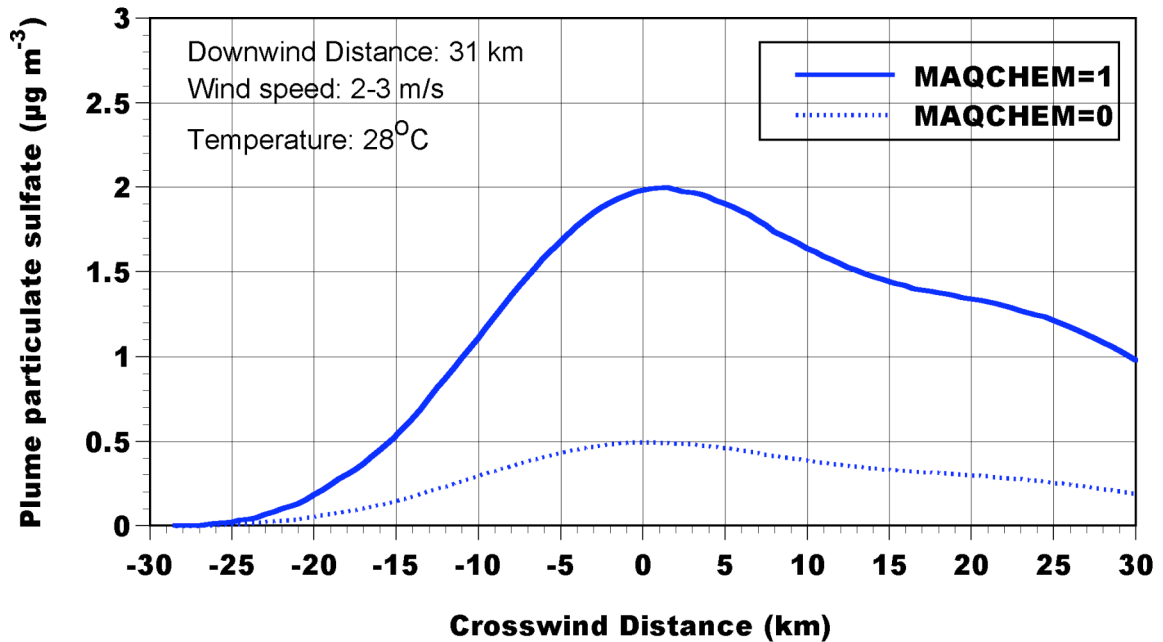
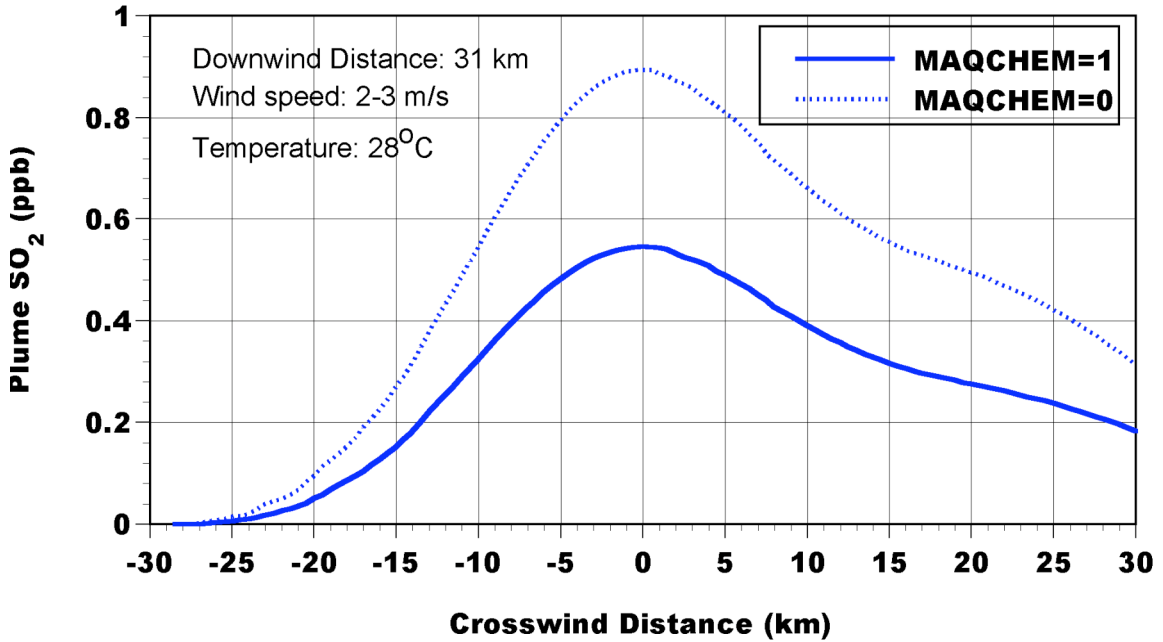


Figure 3-17. Effect of aqueous-phase chemistry on SO₂ and sulfate concentrations for plume traverse 187006. MAQCHEM=0 refers to the case with no aqueous-phase chemistry, while MAQCHEM=1 refers to the case with aqueous-phase chemistry.

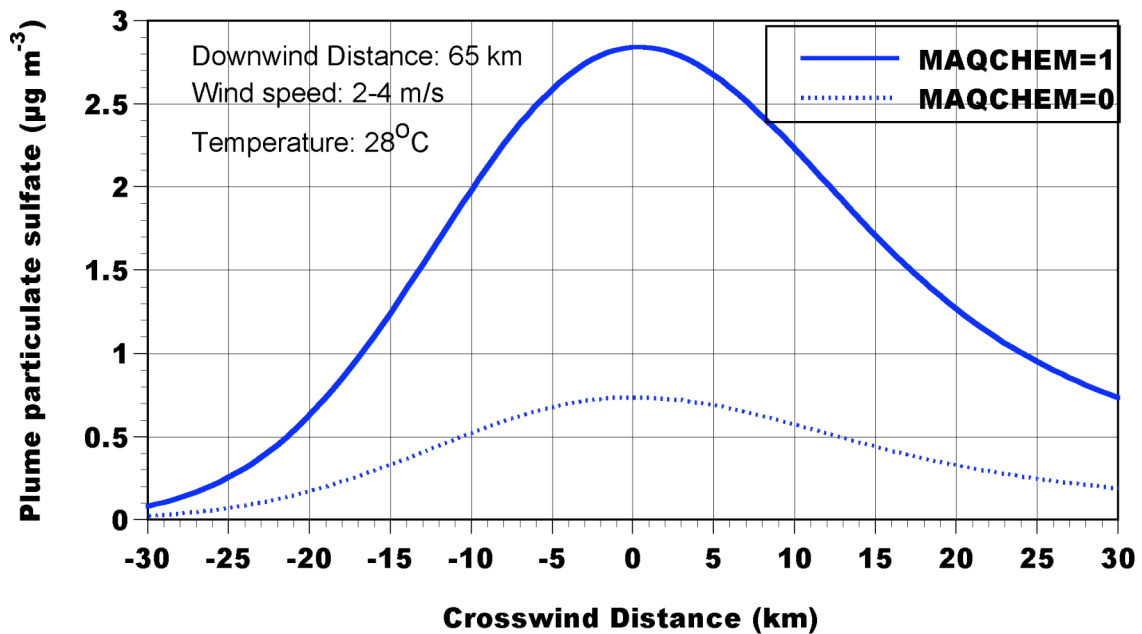
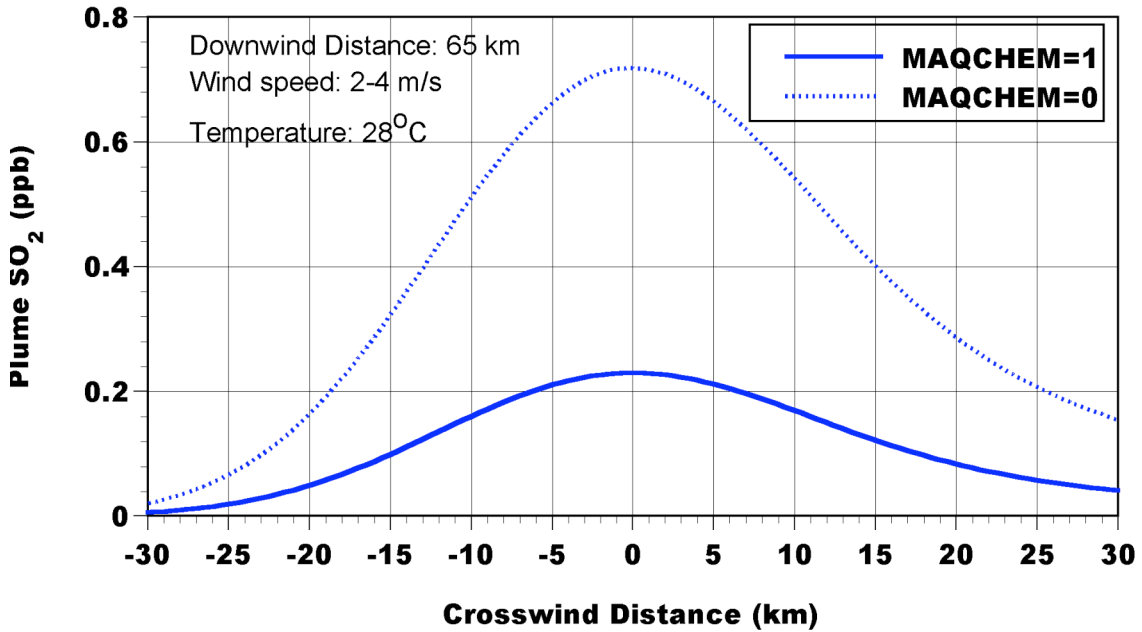


Figure 3-18. Effect of aqueous-phase chemistry on SO₂ and sulfate concentrations for plume traverse 187010. MAQCHEM=0 refers to the case with no aqueous-phase chemistry, while MAQCHEM=1 refers to the case with aqueous-phase chemistry.

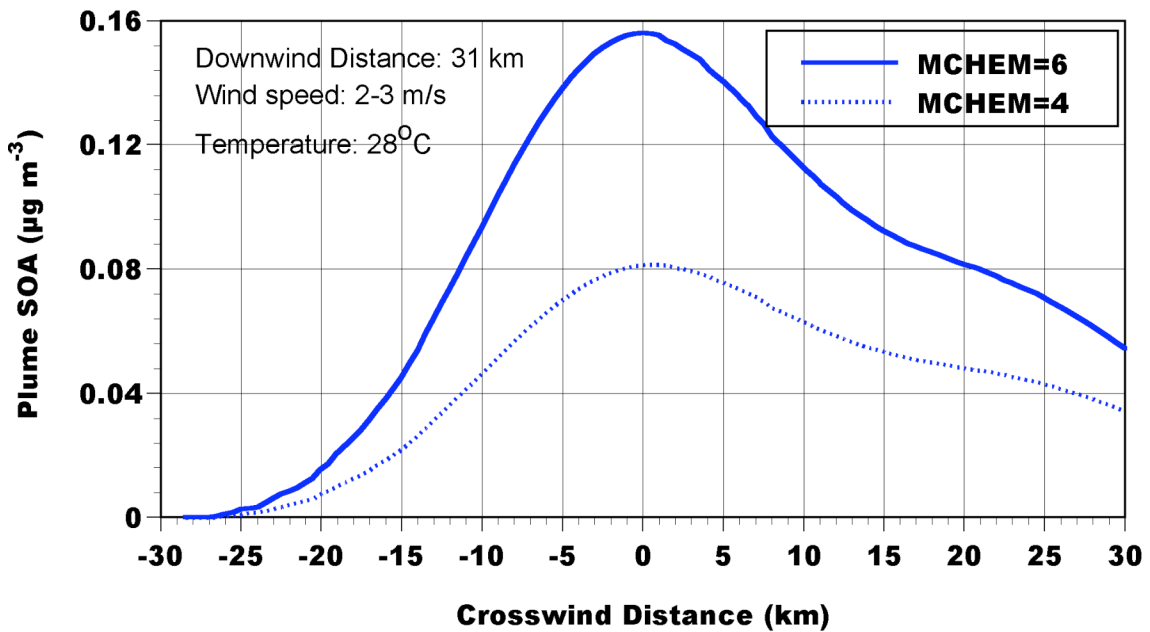
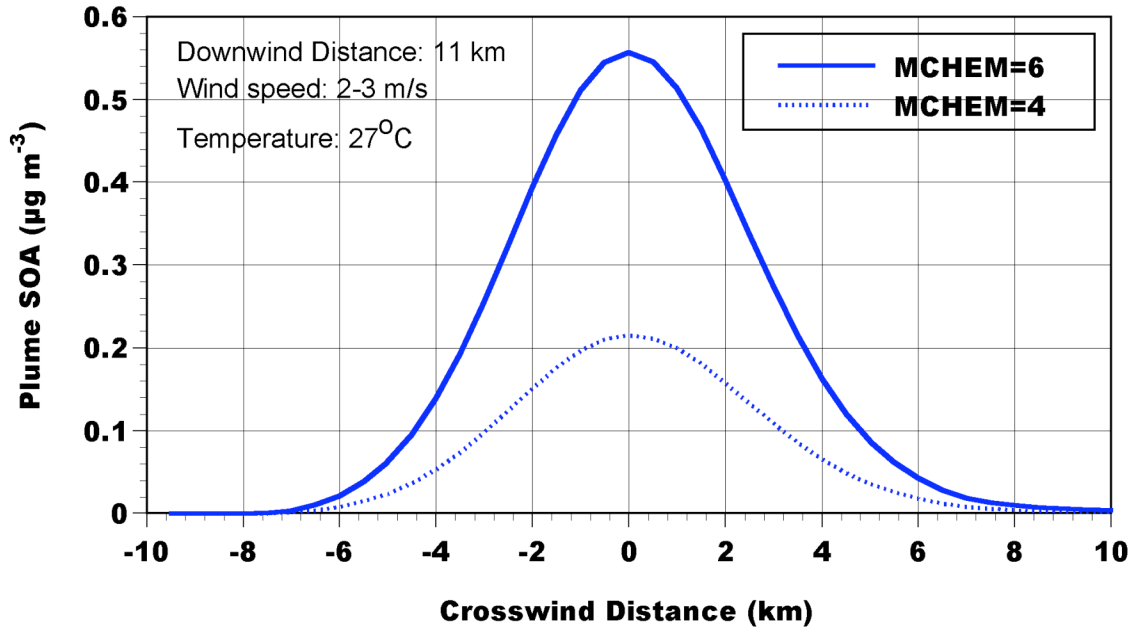


Figure 3-19. Total SOA concentrations from the original and new CALPUFF SOA formulations for plume traverses 187003 (top) and 187006 (bottom). MCHEM=4 refers to the original CALPUFF SOA treatment, while MCHEM=6 refers to the new treatment.

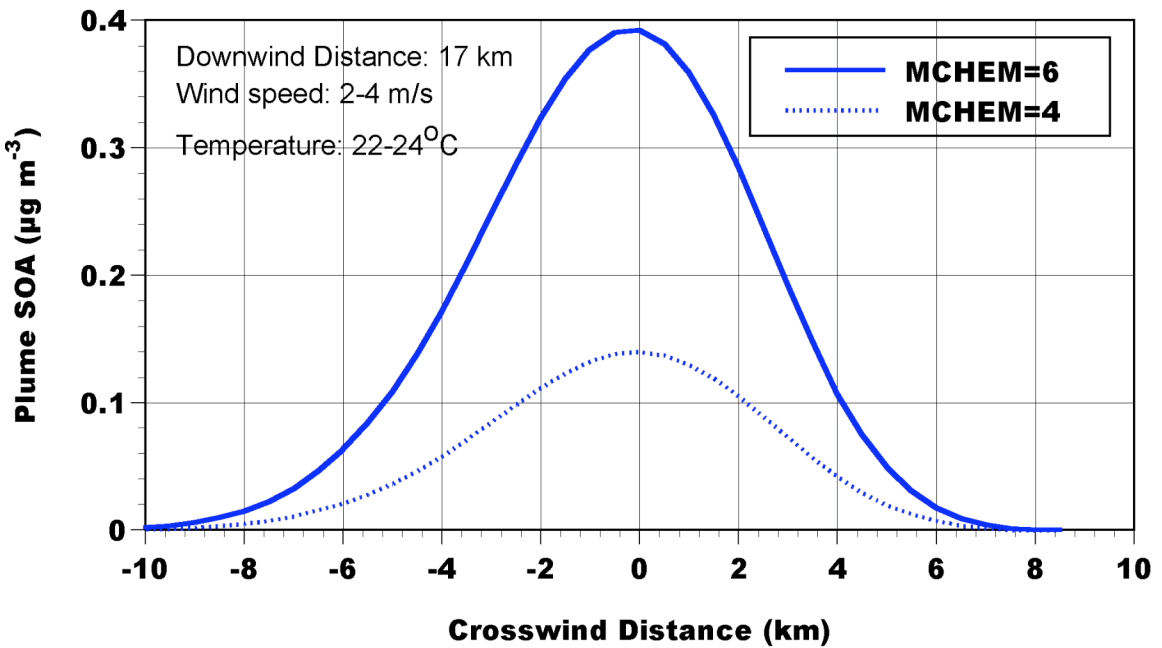
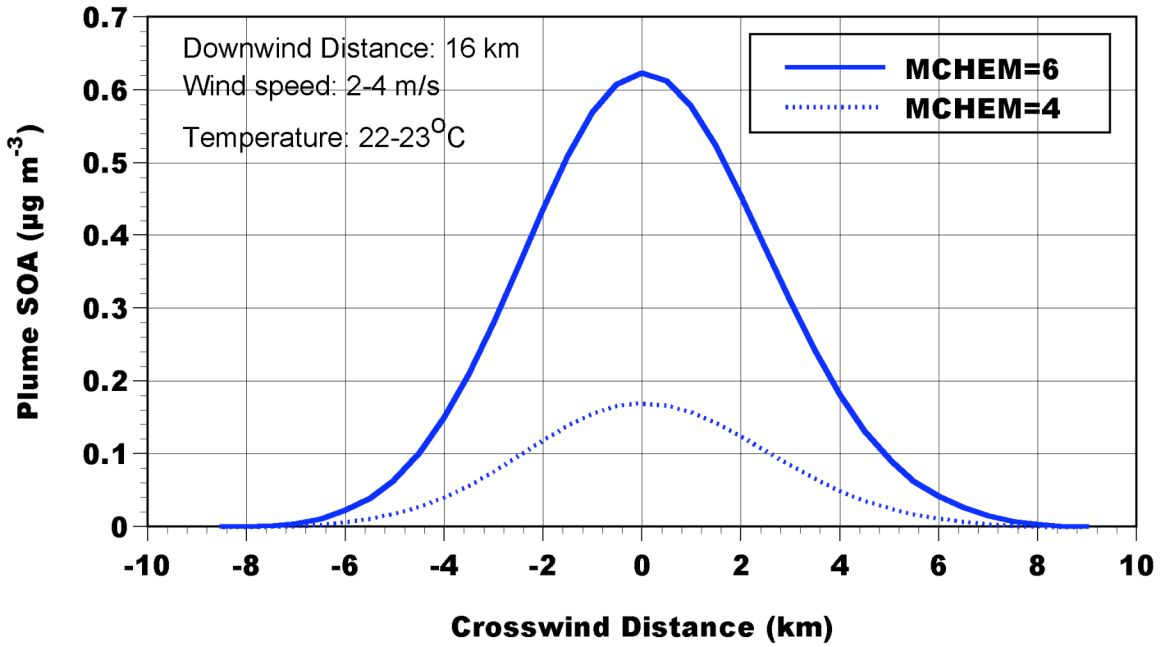


Figure 3-20. Total SOA concentrations from the original and new CALPUFF SOA formulations for plume traverses 194004 (top) and 196001 (bottom). MCHEM=4 refers to the original CALPUFF SOA treatment, while MCHEM=6 refers to the new treatment.

4. SENSITIVITY STUDIES

In this section, we describe the results of sensitivity studies to investigate the response of the different chemistry treatments in CALPUFF to ambient conditions. These sensitivity studies focused on the formation of particulate nitrate. We conducted two sets of sensitivity studies. The first set consisted of a number of CALPUFF simulations for July 6, 1999 with different values of relative humidity, temperature, and background NH₃ concentration. These simulations were conducted with the 2007 official release of CALPUFF (Version 5.8). For the second set of sensitivity studies, we constructed box-model implementations of the inorganic aerosol modules in CALPUFF. The box-models were then applied for different values of relative humidity, temperature, background NH₃ concentration, background sulfate concentration, and initial nitric acid concentration (representing total nitrate in the system). We describe the results from the sensitivity studies below.

4.1 CALPUFF Sensitivity Studies

We conducted sensitivity studies with CALPUFF for the three chemistry options (MESOPUFF II, original RIVAD, and improved RIVAD) by varying relative humidity, temperature and background NH₃ concentration one at a time from their baseline values of 70%, 25°C, and 1 ppb, respectively. The range of values investigated in the sensitivity studies were 20 to 90% for relative humidity, -10 to 35°C for temperature, and 0.1 to 10 ppb for background NH₃ concentration.

4.1.1 Effect of relative humidity

Figure 4-1 shows the HNO₃ and particulate nitrate concentrations as a function of downwind distance for July 6, 1999 for a relative humidity of 20% with all other parameters at their baseline values. For such dry conditions, the partitioning of total nitrate to the particle phase is very small (less than 0.3 µg/m³) for both the MESOPUFF II and original RIVAD options and negligible for the improved RIVAD option.

When the relative humidity is increased to 50% and 70% (Figures 4-2 and 4-3, respectively), we see that the particulate nitrate formation is still less than 0.5 µg/m³ for the original CALPUFF chemistry options and negligible for the improved RIVAD option. At a relative humidity of 80% (Figure 4-4) the original RIVAD option predicts greater than 0.5 µg/m³ of particulate nitrate, while the maximum nitrate concentration from the MESOPUFF II option is about a factor of two lower than the original RIVAD option. The particulate nitrate concentration predictions from the revised RIVAD option are still negligible.

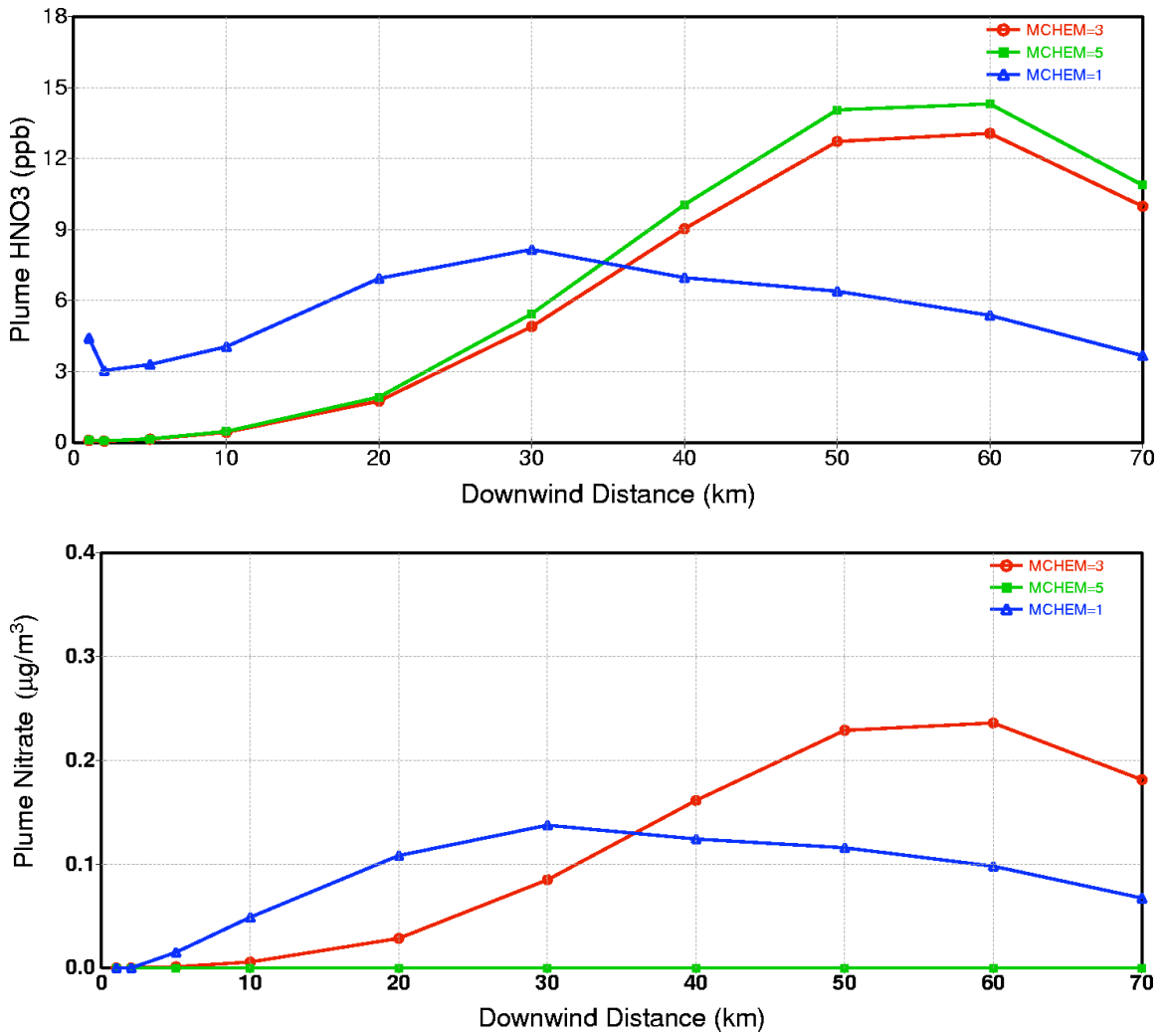


Figure 4-1. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a relative humidity of 20%. MCHEM=1 refers to the MESOPUFF II option, while MCHEM=3 refers to the original RIVAD treatment, and MCHEM=5 refers to the new RIVAD treatment (ISORROPIA).

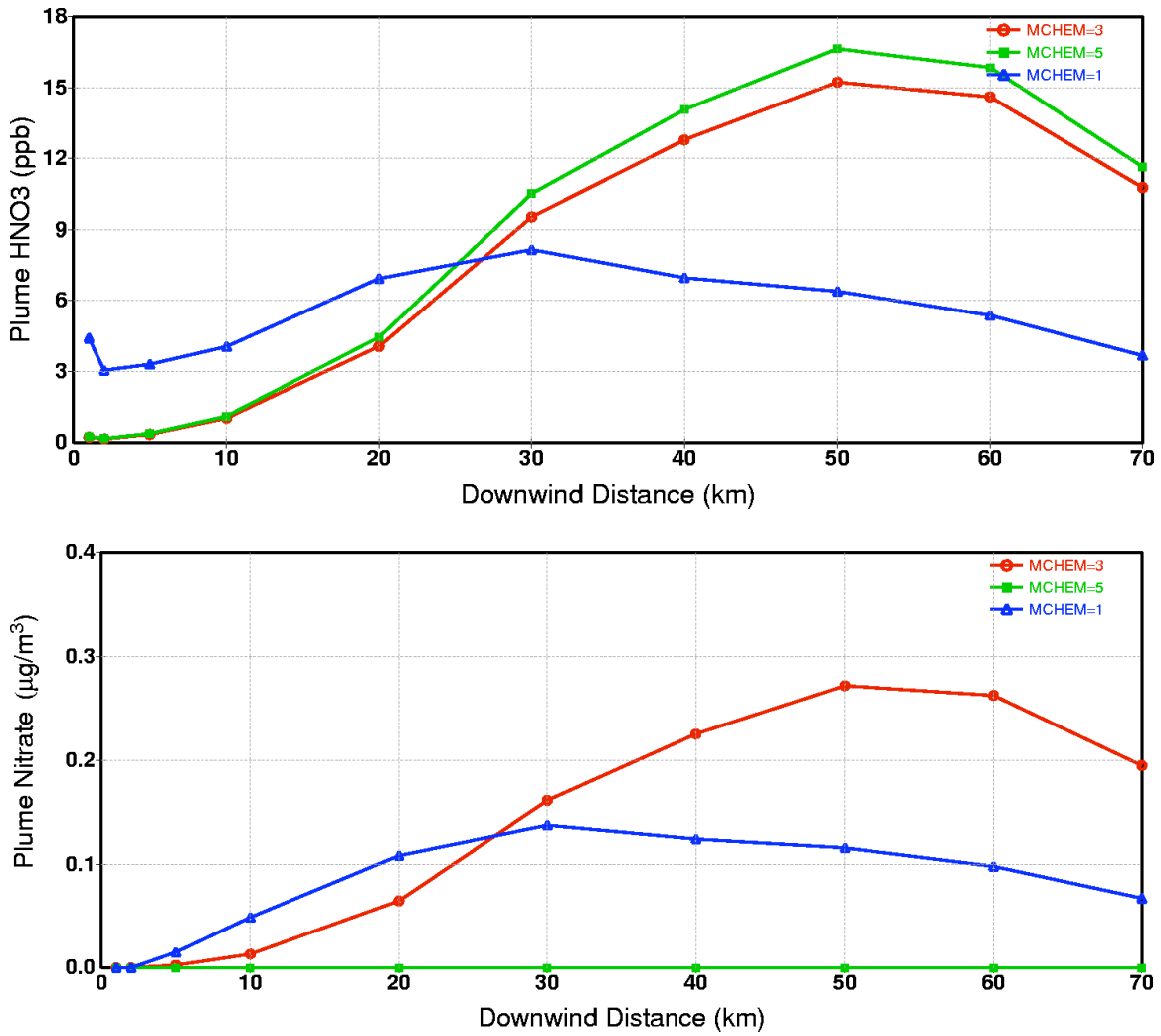


Figure 4-2. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a relative humidity of 50%. MCHEM=1 refers to the MESOPUFF II option, while MCHEM=3 refers to the original RIVAD treatment, and MCHEM=5 refers to the new RIVAD treatment (ISORROPIA).

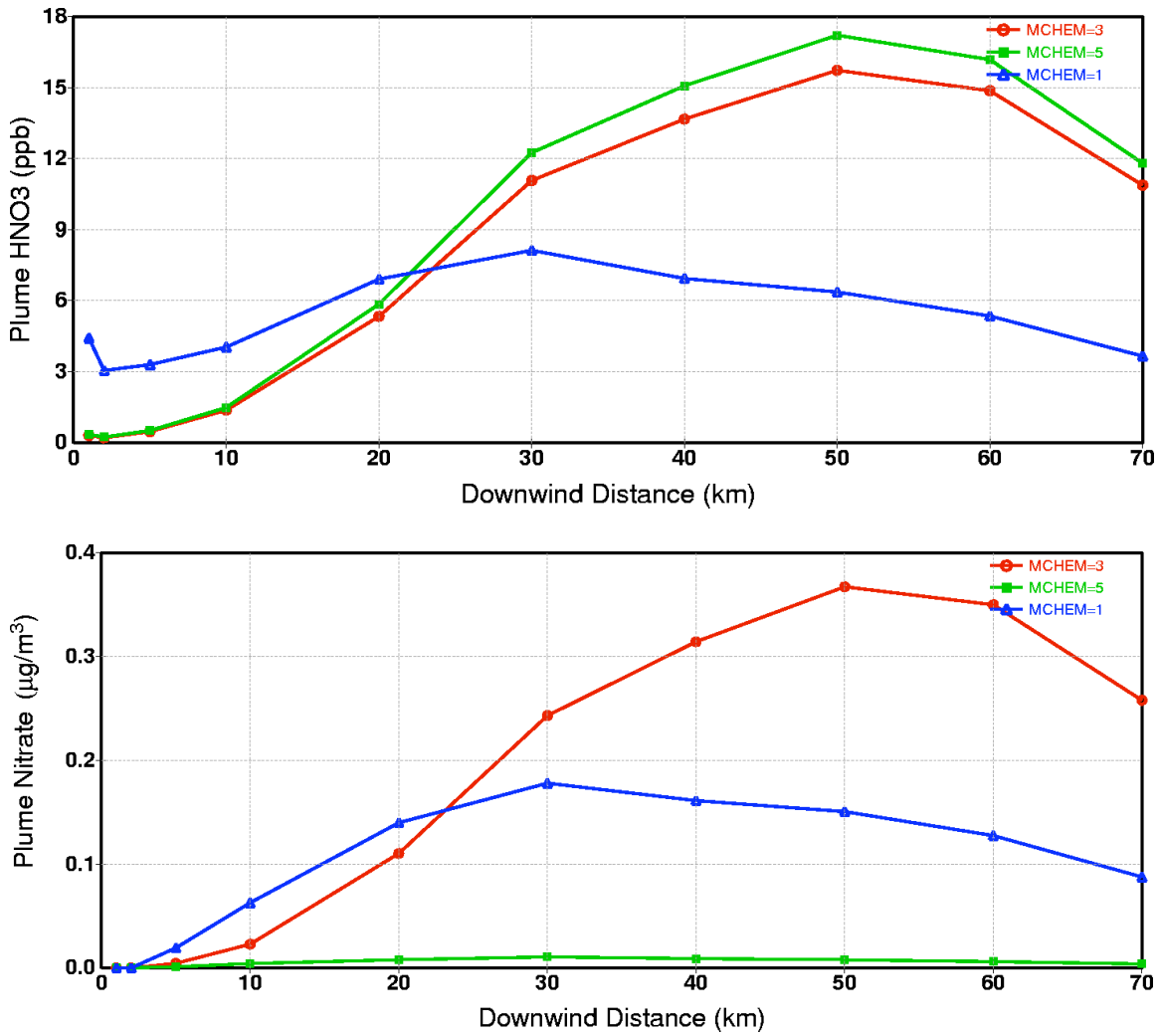


Figure 4-3. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a relative humidity of 70%. MCHEM=1 refers to the MESOPUFF II option, while MCHEM=3 refers to the original RIVAD treatment, and MCHEM=5 refers to the new RIVAD treatment (ISORROPIA).

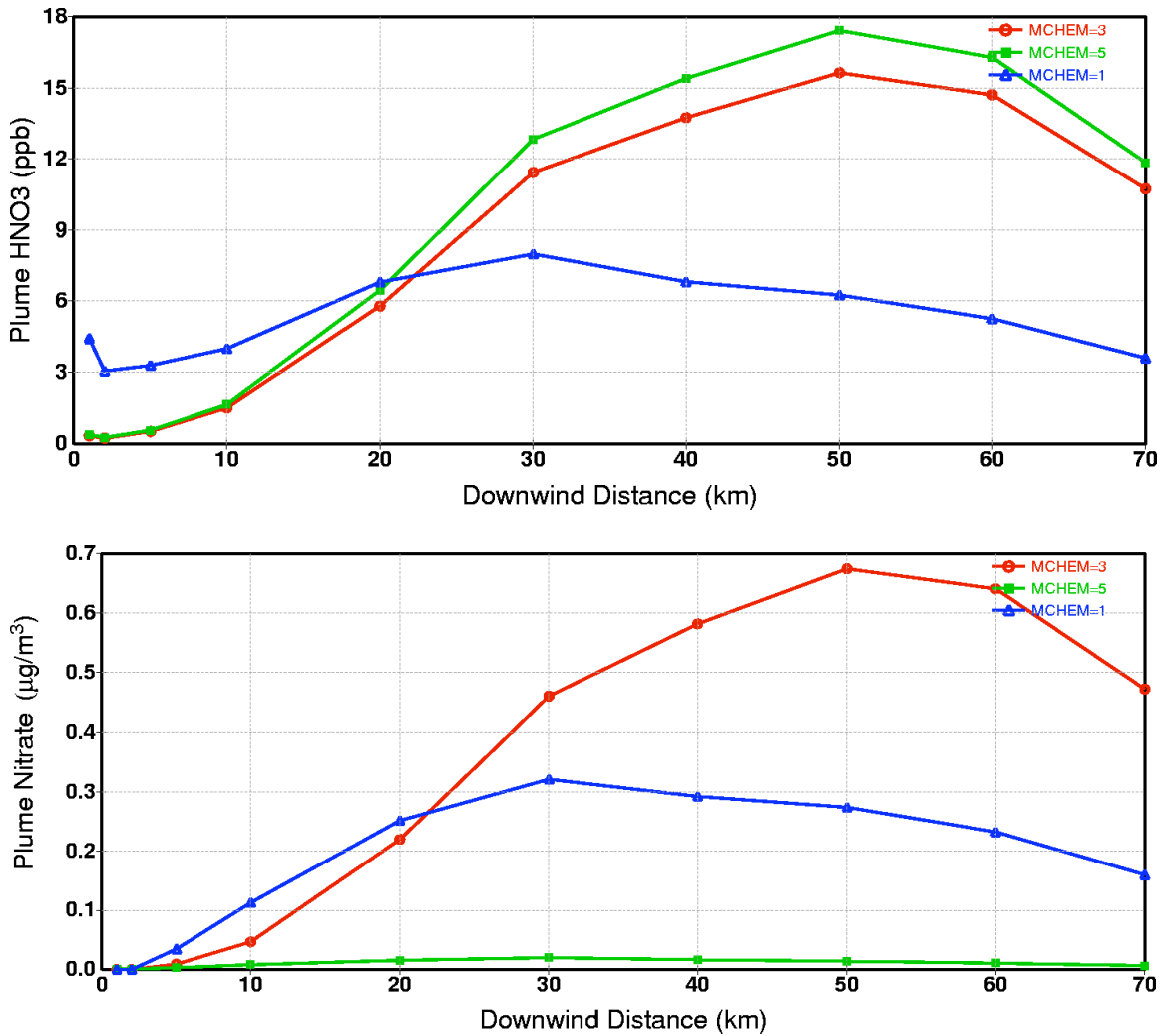


Figure 4-4. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a relative humidity of 80%. MCHM=1 refers to the MESOPUFF II option, while MCHM=3 refers to the original RIVAD treatment, and MCHM=5 refers to the new RIVAD treatment (ISORROPIA).

Figure 4-5 shows that when the relative humidity is increased to 90%, the maximum downwind particulate nitrate concentration predicted with the original RIVAD option is nearly $2 \mu\text{g}/\text{m}^3$, while the maximum concentration predicted with the MESOPUFF II option is about a factor of two lower. With the revised RIVAD option, there is some formation of particulate nitrate but the maximum nitrate concentration is an order of magnitude or more lower than the two original CALPUFF options.

4.1.2 Effect of temperature

Figure 4-6 shows the HNO_3 and particulate nitrate concentrations as a function of downwind distance for July 6, 1999 for a temperature of -10°C with all other parameters at their baseline values (i.e., relative humidity at 70% and background NH_3 concentration at 1 ppb). At such low temperatures, all three chemistry options show significant formation of particulate nitrate. The highest downwind particulate nitrate concentration (over $12 \mu\text{g}/\text{m}^3$) is predicted by the revised RIVAD chemistry option, followed by the original RIVAD option (nearly $10 \mu\text{g}/\text{m}^3$) and the MESOPUFF II option (nearly $8 \mu\text{g}/\text{m}^3$). For all three options, we see that most of the total nitrate is present in the particulate phase.

Note that all three chemistry options predict a particulate nitrate concentration that is much higher than the theoretical maximum of about $2.7 \mu\text{g}/\text{m}^3$, corresponding to 1 ppb of NH_3 (assuming that all the ammonia is bound to particulate nitrate). This is due to a shortcoming of CALPUFF that limits ammonia on a per puff basis rather than over all puffs that contribute to the composite concentration calculation at a given receptor location. One method of treating this shortcoming is to use the inorganic aerosol thermodynamic module in a post-processing step before calculating receptor concentrations. Using a box model (see Section 4.2) as a post-processor, we find that the $12 \mu\text{g}/\text{m}^3$ predicted by the revised RIVAD chemistry option at -10°C should actually be about $2.3 \mu\text{g}/\text{m}^3$.

When the temperature is increased to 0°C (Figure 4-7), we see that the revised RIVAD option produces lower particulate nitrate concentrations than the original RIVAD option, but both RIVAD options predict higher nitrate concentrations than the MESOPUFF II option. The particulate nitrate concentrations are still significantly higher than the theoretical maximum corresponding to 1 ppb of available NH_3 .

Figure 4-8 shows the results for an ambient temperature of 10°C . We see that, even at this relatively low temperature, the revised RIVAD option produces significantly lower particulate nitrate concentrations than either the MESOPUFF II or original RIVAD options. For the revised RIVAD option, substantially all the total nitrate is present in the gaseous phase, while for both the MESOPUFF II and original RIVAD options, a non-negligible amount of the total nitrate is present in the particulate phase. For the MESOPUFF II and original RIVAD options, the maximum particulate nitrate concentrations are over 3 and $6 \mu\text{g}/\text{m}^3$, respectively, higher than the theoretical maximum corresponding to 1 ppb of available NH_3 .

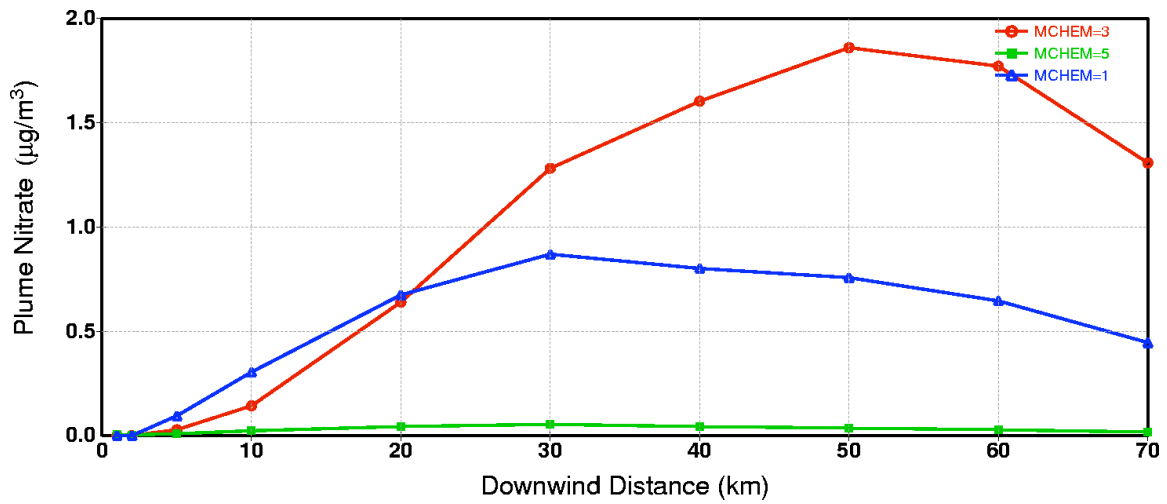
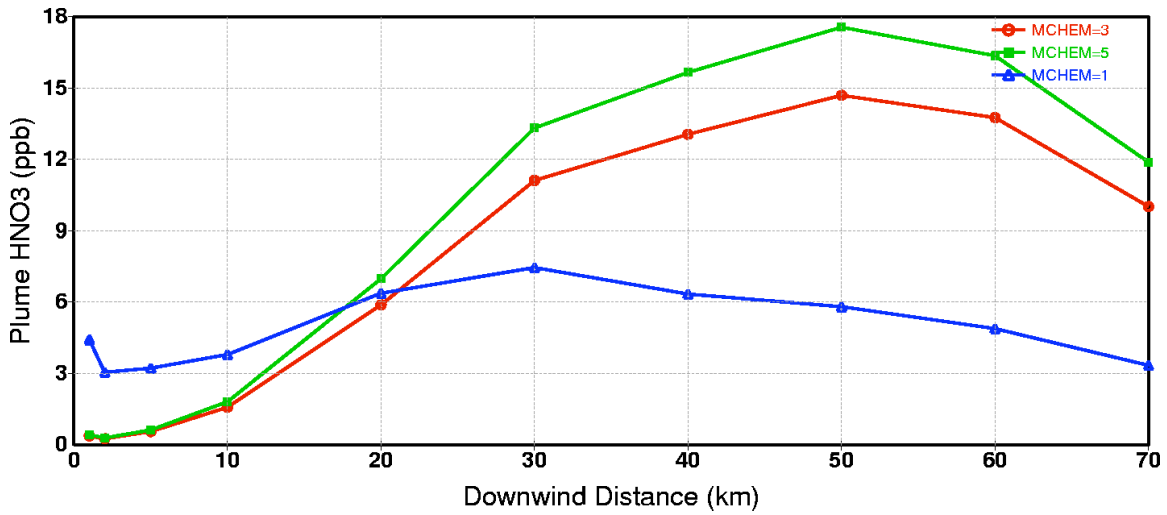


Figure 4-5. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a relative humidity of 90%. MCHM=1 refers to the MESOPUFF II option, while MCHM=3 refers to the original RIVAD treatment, and MCHM=5 refers to the new RIVAD treatment (ISORROPIA).

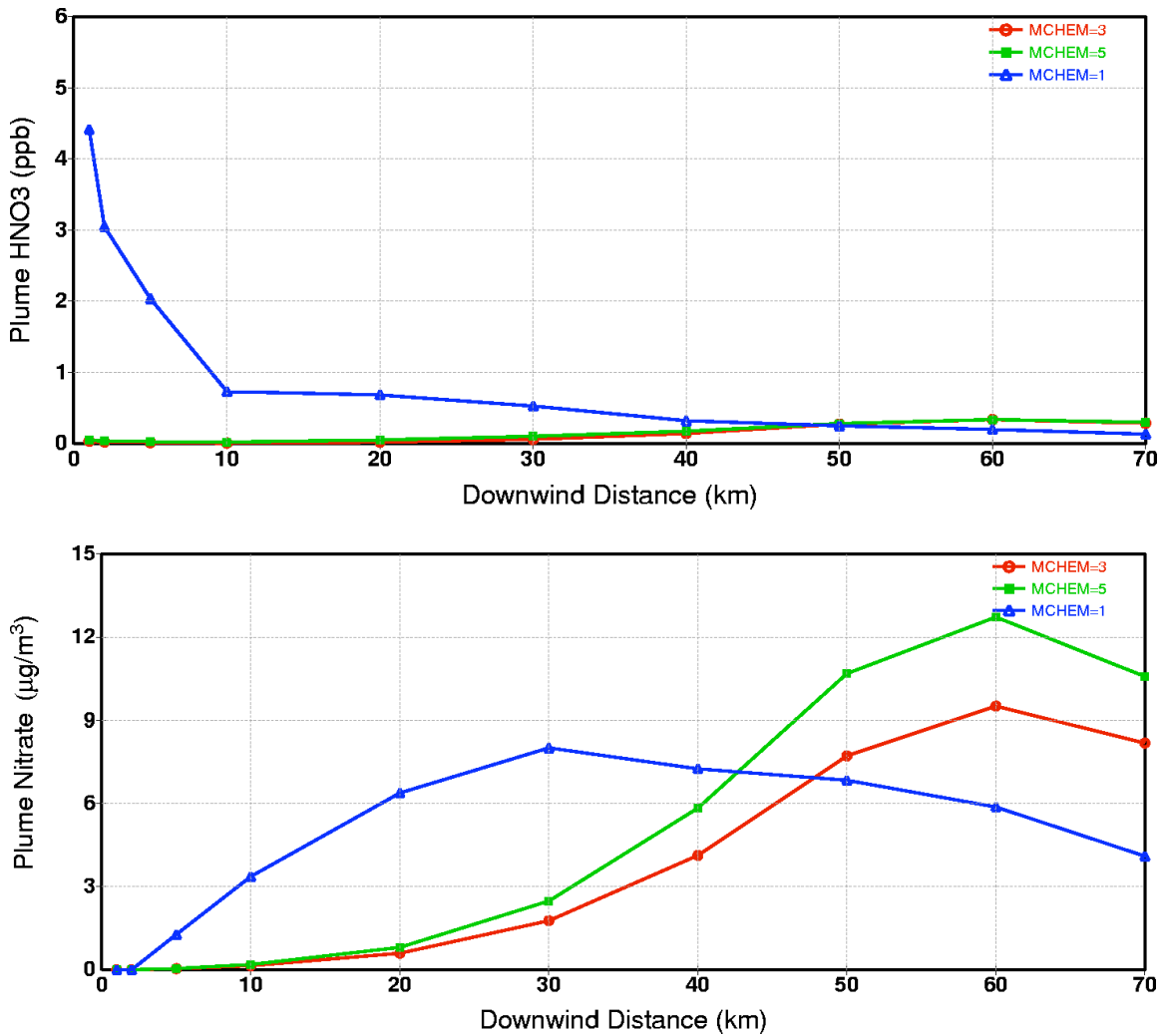


Figure 4-6. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a temperature of -10°C. MCHM=1 refers to the MESOPUFF II option, while MCHM=3 refers to the original RIVAD treatment, and MCHM=5 refers to the new RIVAD treatment (ISORROPIA).

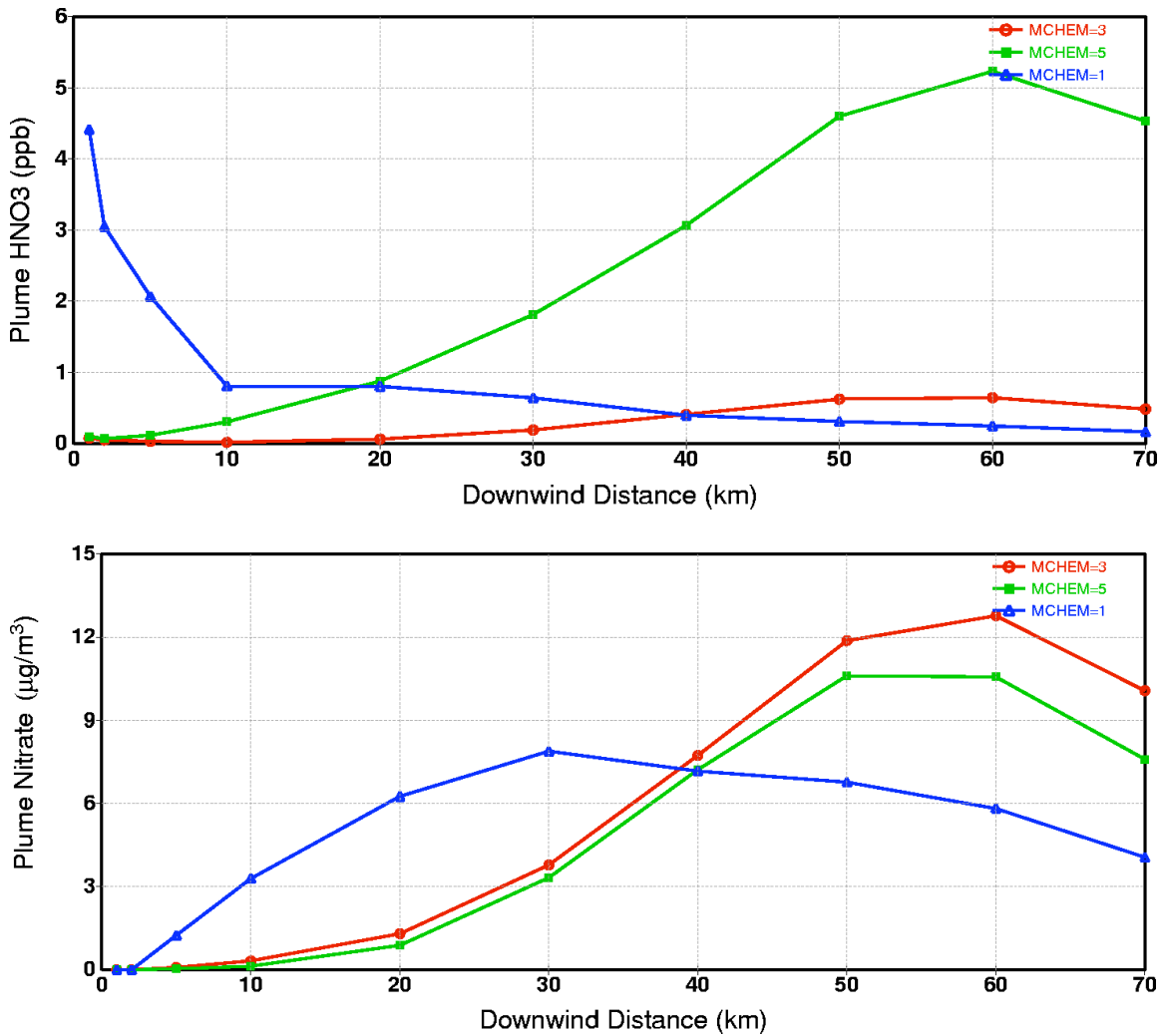


Figure 4-7. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a temperature of 0°C. MCHM=1 refers to the MESOPUFF II option, while MCHM=3 refers to the original RIVAD treatment, and MCHM=5 refers to the new RIVAD treatment (ISORROPIA).

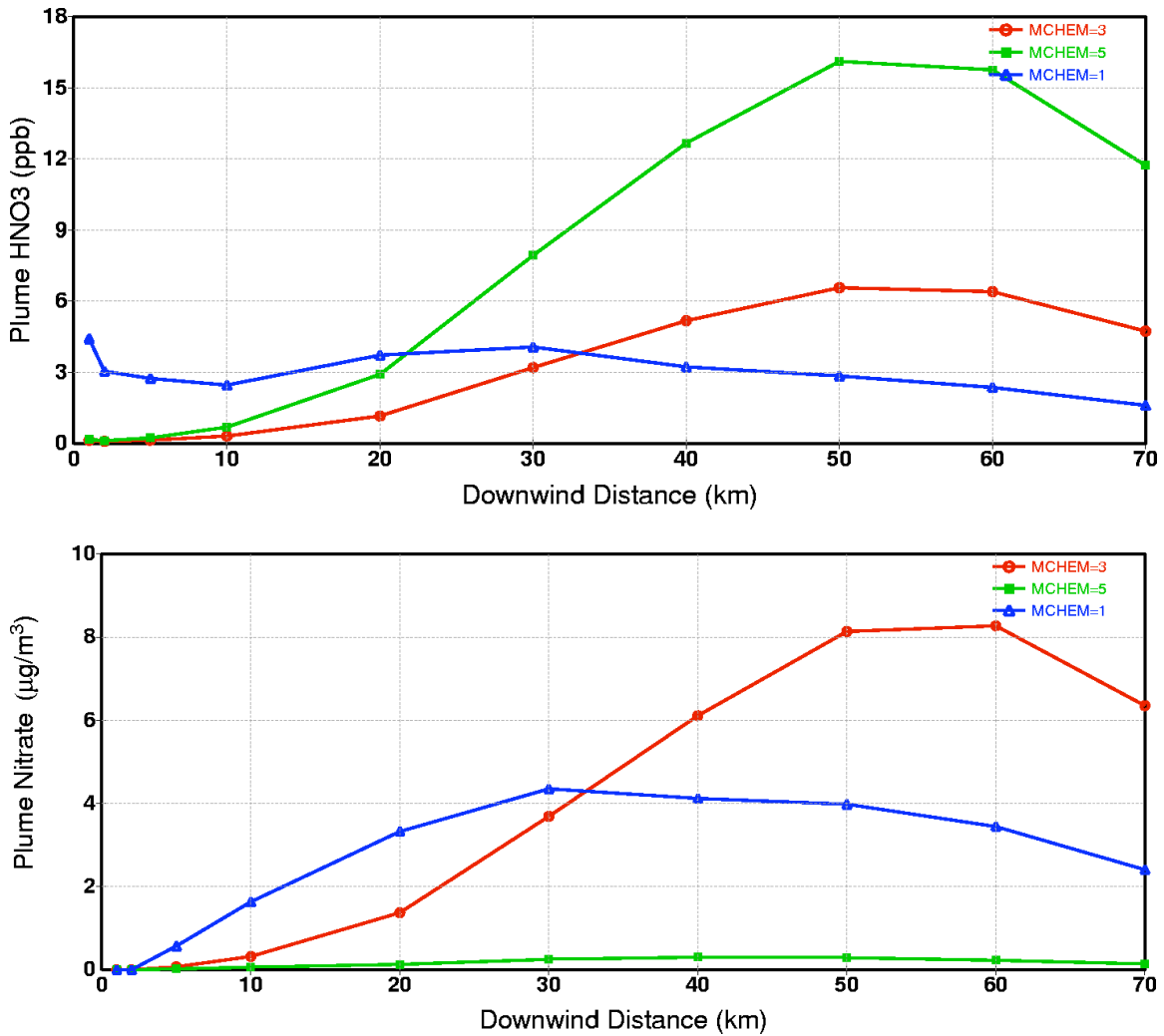


Figure 4-8. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a temperature of 10°C. MCHEM=1 refers to the MESOPUFF II option, while MCHEM=3 refers to the original RIVAD treatment, and MCHEM=5 refers to the new RIVAD treatment (ISORROPIA).

The results for an ambient temperature of 15°C are qualitatively similar (Figure 4-9) to those for 10°C, but with more of the total nitrate present in the gaseous phase for all three chemistry options. We see that the original RIVAD option still predicts a maximum particulate nitrate concentration that is higher than the theoretical maximum.

At higher temperatures of 25°C, 30°C, and 35°C (Figures 4-10 through 4-12), we see that all three chemistry options partition most of the total nitrate into the gaseous phase, and particulate nitrate formation is negligible.

4.1.3 Effect of background NH₃ concentration

Figure 4-13 shows the HNO₃ and particulate nitrate concentrations as a function of downwind distance for July 6, 1999 for a background ammonia concentration of 0.1 ppb with all other parameters at their baseline values (i.e., relative humidity at 70% and temperature at 25°C). The system is ammonia-limited, and we see that there is negligible particulate nitrate formation with all three (MESOPUFF II, original RIVAD and revised RIVAD) chemistry options.

Figure 4-14 shows that when the background NH₃ concentration is increased to 0.5 ppb (the FLAG recommended value for forests) there is some small production of particulate nitrate with the MESOPUFF II and original RIVAD options, but the revised RIVAD option again shows negligible particulate nitrate. The results for a background NH₃ concentration of 1 ppb (the FLAG recommended value for arid land), shown in Figure 4-15, are qualitatively similar to those for a background concentration of 0.5 ppb.

At a background NH₃ concentration of 2 ppb, the original RIVAD option produces nearly 1 µg/m³ of particulate nitrate while the MESOPUFF II option produces less than 0.5 µg/m³ of particulate nitrate, as shown in Figure 4-16. The particulate nitrate concentration from the revised RIVAD option is still negligible. Finally, Figure 4-17 shows that when the background NH₃ concentration is increased to 10 ppb (the FLAG recommended value for grassland), the original RIVAD option predicts a maximum downwind particulate nitrate concentration of over 3 µg/m³, while the MESOPUFF II values are about a factor of 2 lower. A small amount of particulate nitrate (about 0.2 µg/m³) is produced with the revised RIVAD option.

4.2 Box-Model Sensitivity Studies

We now describe the results of sensitivity studies conducted with box-model implementations of the inorganic aerosol equilibrium modules implemented in the original and improved CALPUFF. The original module is used with the MESOPUFF II and original RIVAD chemistry options and will be referred to as MESOPUFF in the results presented below, while the new module, ISORROPIA, is used with the improved RIVAD chemistry option.

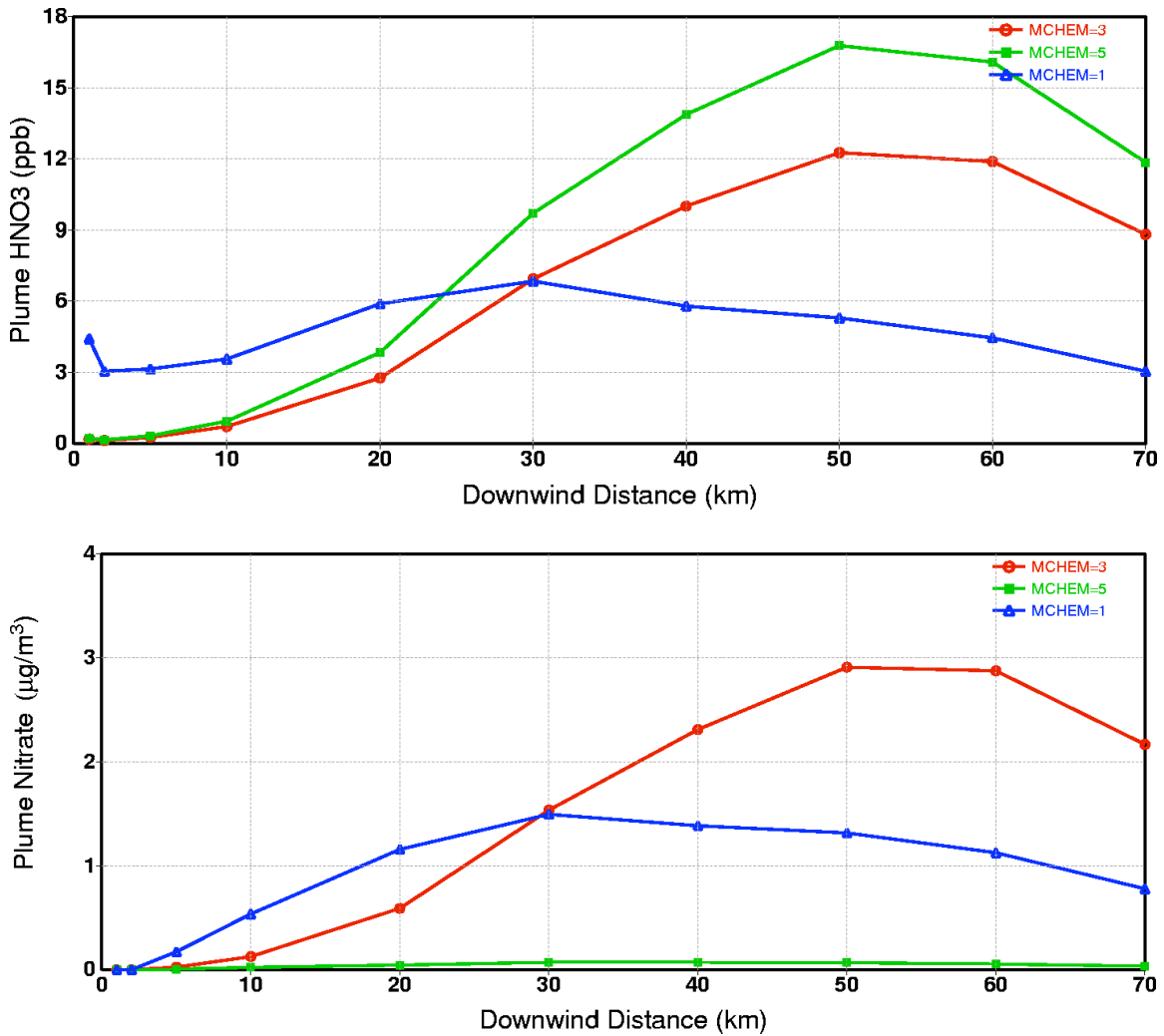


Figure 4-9. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a temperature of 15°C. MCHEM=1 refers to the MESOPUFF II option, while MCHEM=3 refers to the original RIVAD treatment, and MCHEM=5 refers to the new RIVAD treatment (ISORROPIA).

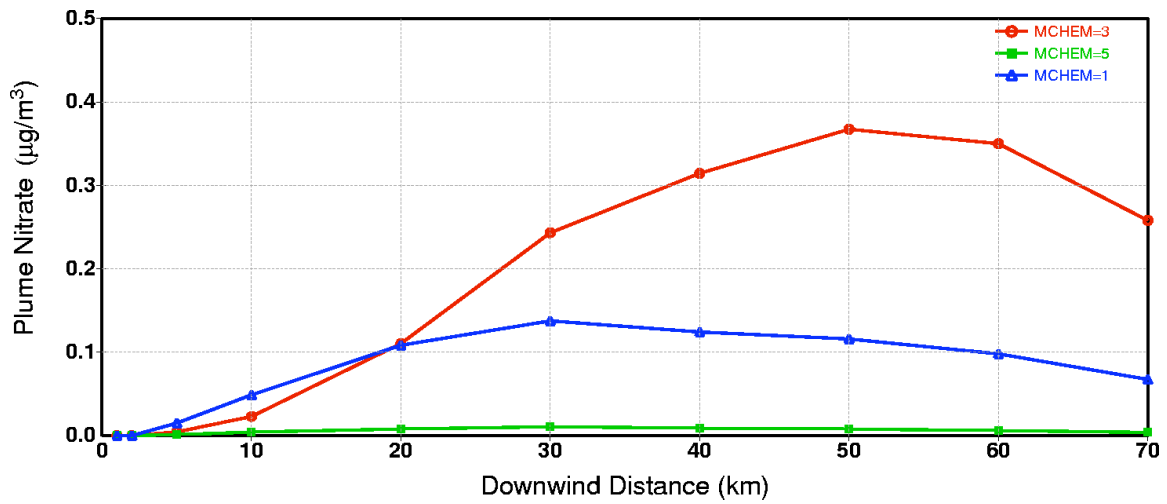
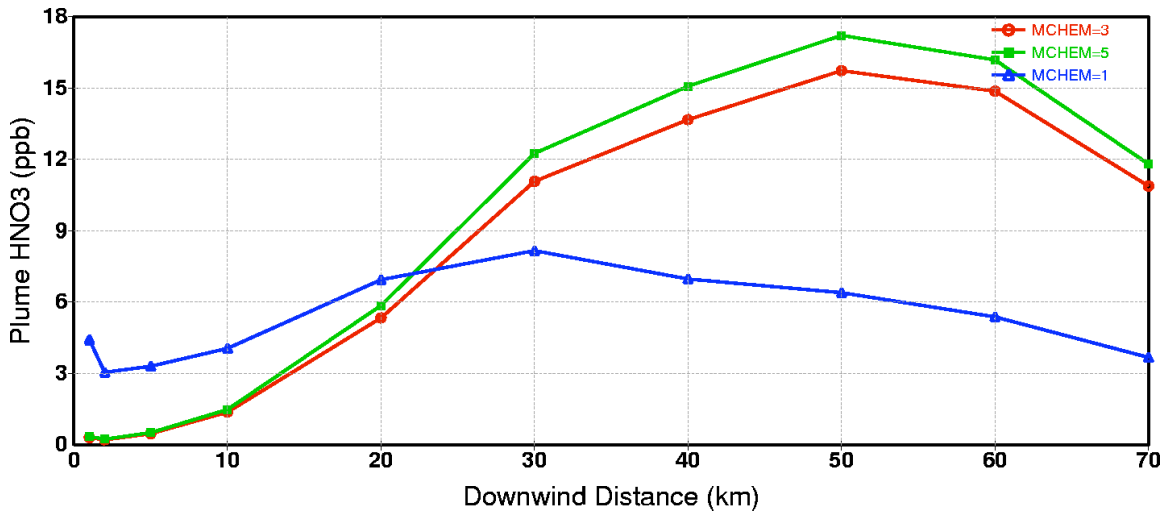


Figure 4-10. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a temperature of 25°C. MCHEM=1 refers to the MESOPUFF II option, while MCHEM=3 refers to the original RIVAD treatment, and MCHEM=5 refers to the new RIVAD treatment (ISORROPIA).

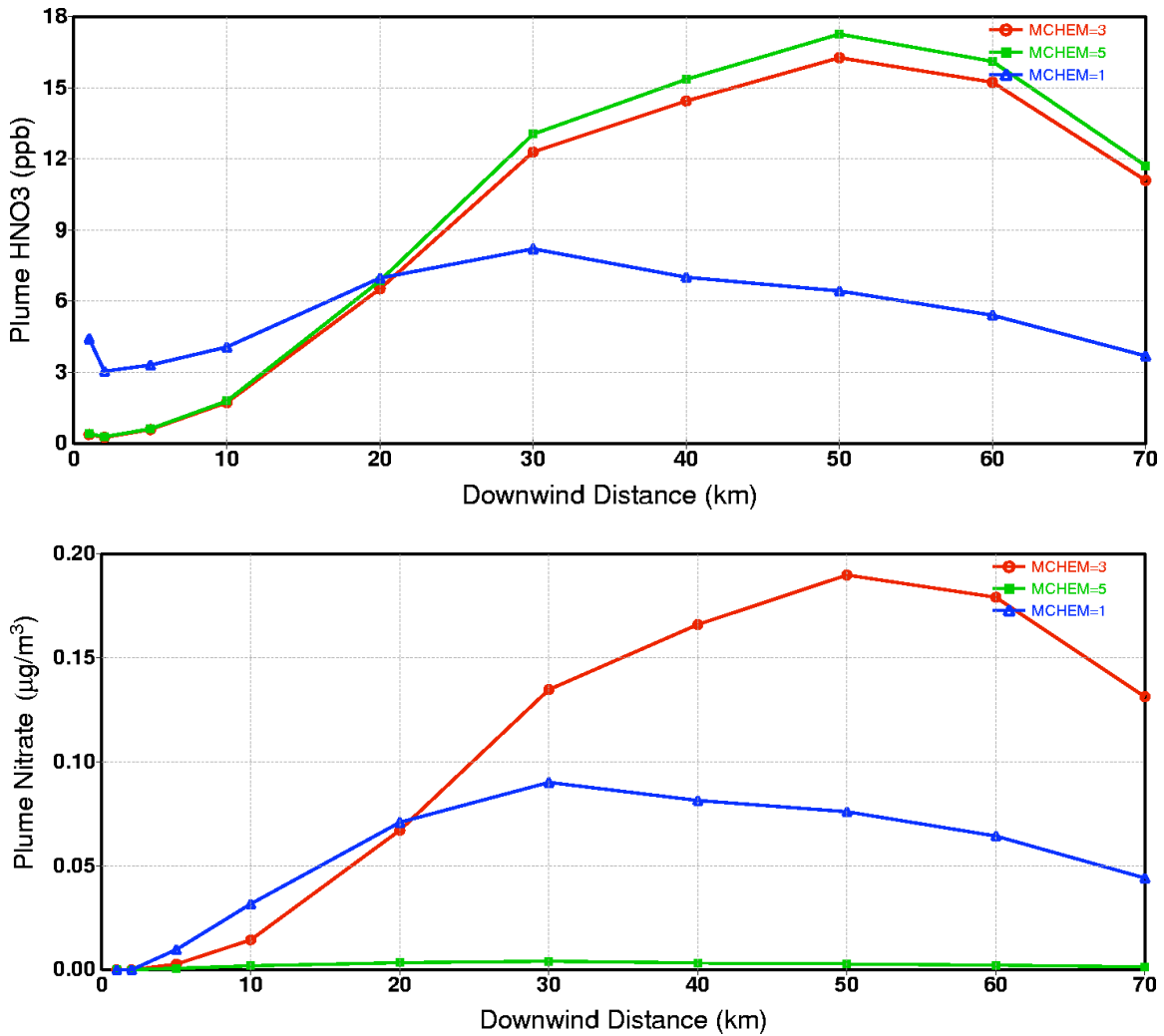


Figure 4-11. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a temperature of 30°C. MCHEM=1 refers to the MESOPUFF II option, while MCHEM=3 refers to the original RIVAD treatment, and MCHEM=5 refers to the new RIVAD treatment (ISORROPIA).

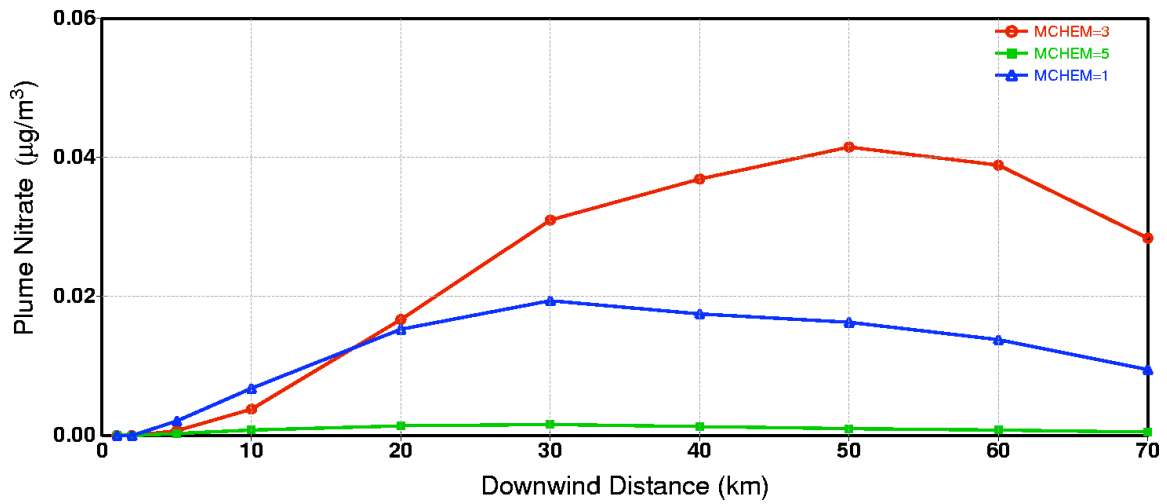
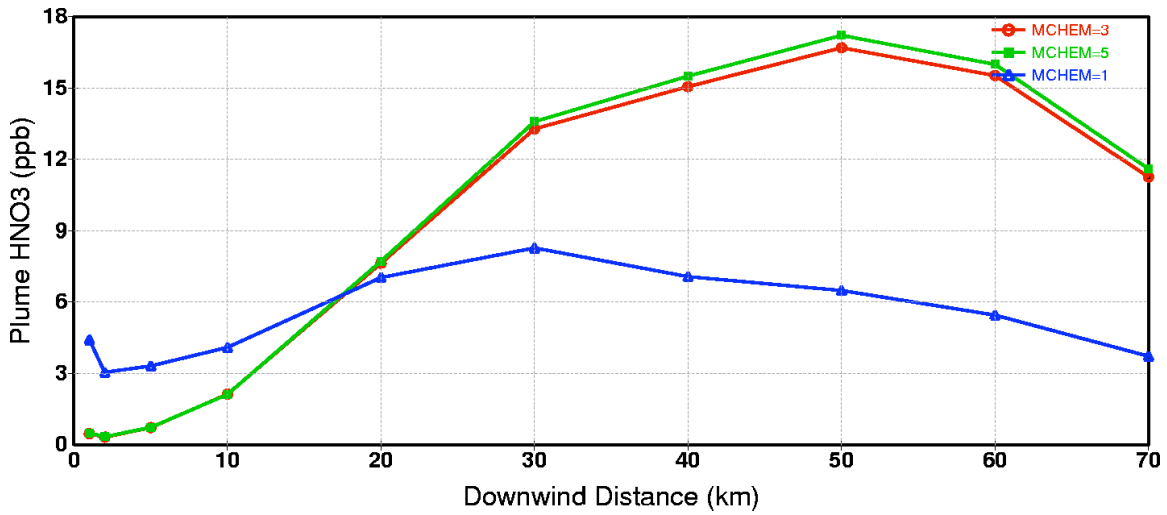


Figure 4-12. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a temperature of 35°C. MCHEM=1 refers to the MESOPUFF II option, while MCHEM=3 refers to the original RIVAD treatment, and MCHEM=5 refers to the new RIVAD treatment (ISORROPIA).

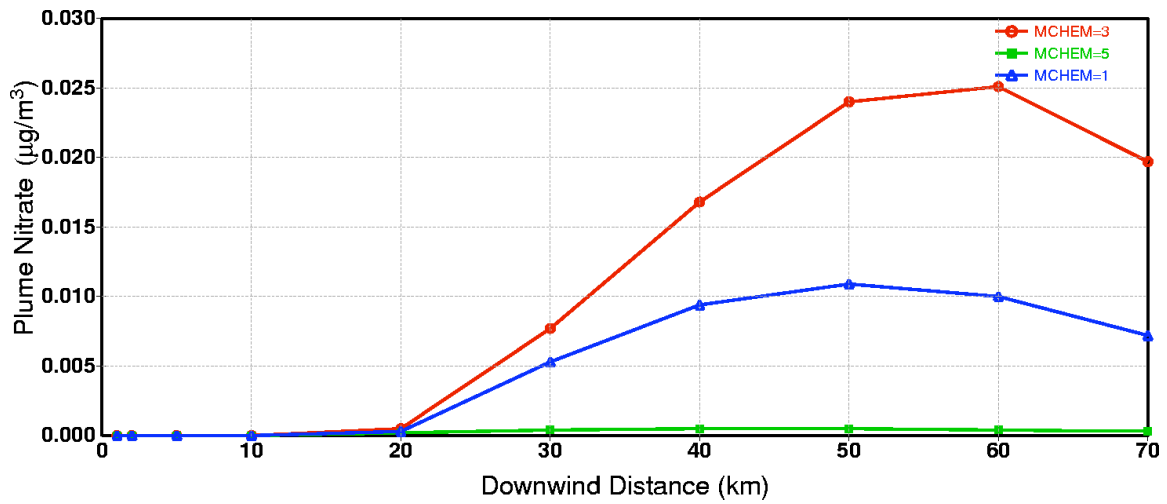
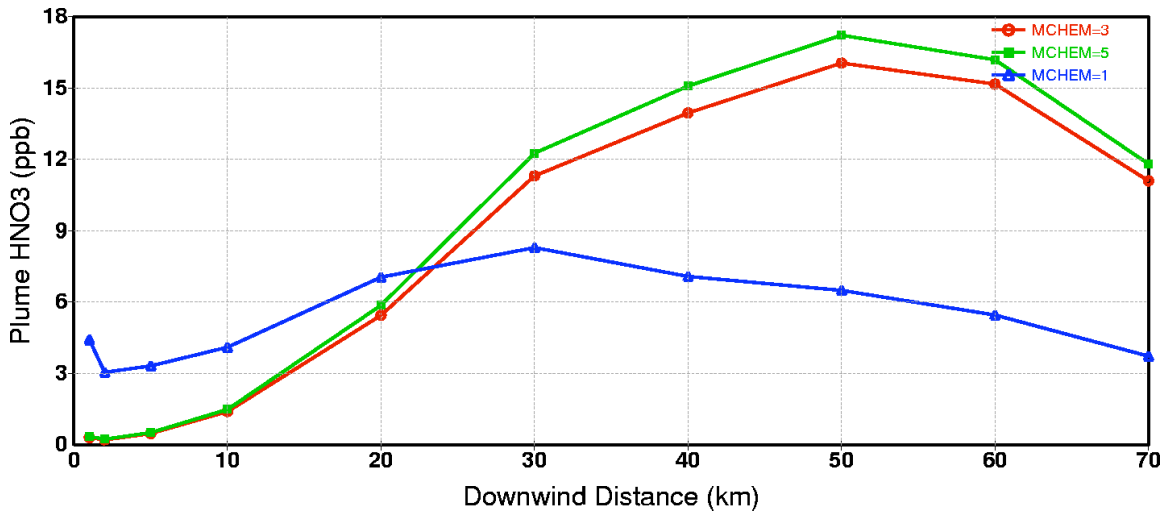


Figure 4-13. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a background NH₃ concentration of 0.1 ppb. MCHEM=1 refers to the MESOPUFF II option, while MCHEM=3 refers to the original RIVAD treatment, and MCHEM=5 refers to the new RIVAD treatment (ISORROPIA).

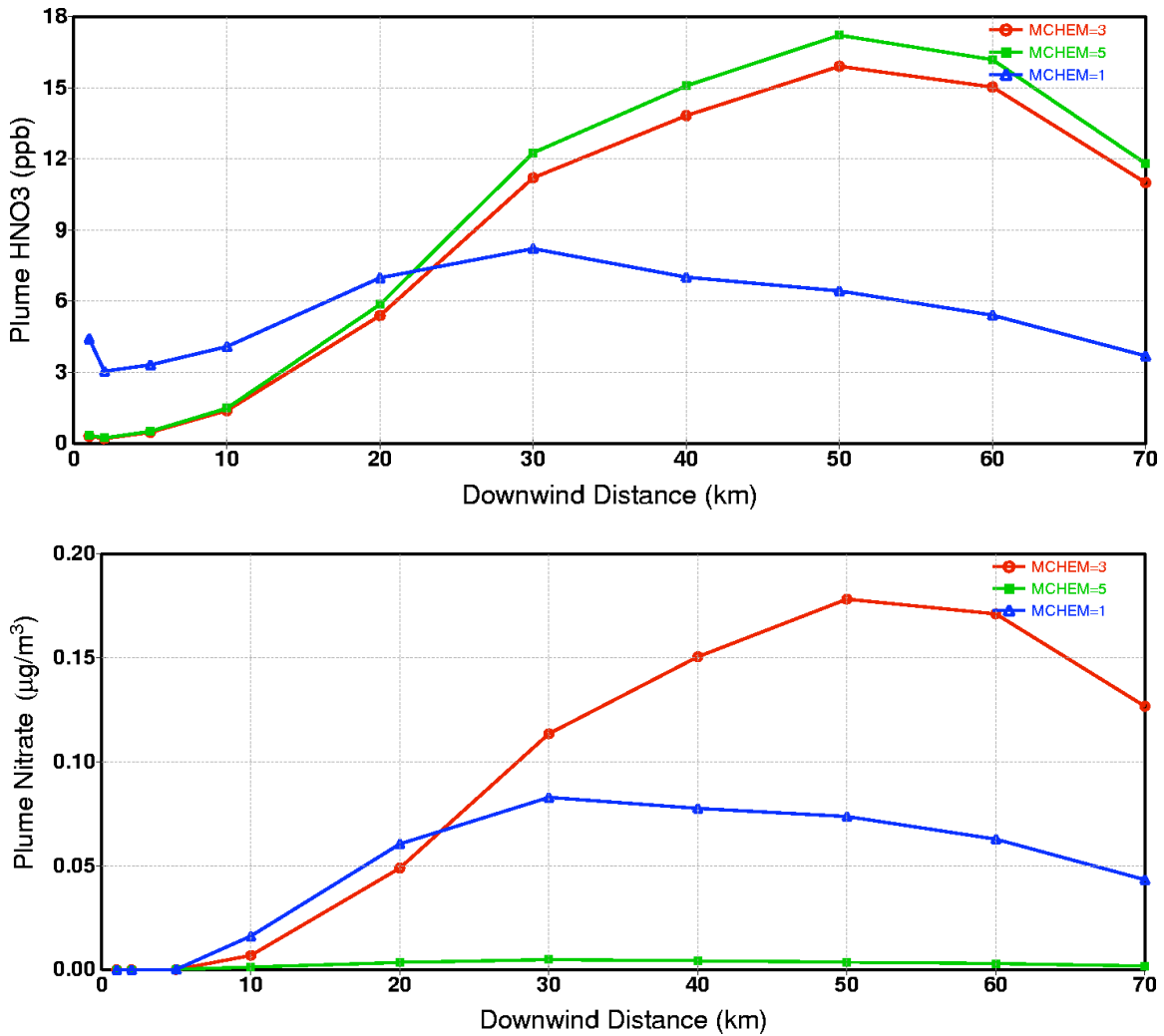


Figure 4-14. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a background NH₃ concentration of 0.5 ppb. MCHEM=1 refers to the MESOPUFF II option, while MCHEM=3 refers to the original RIVAD treatment, and MCHEM=5 refers to the new RIVAD treatment (ISORROPIA).

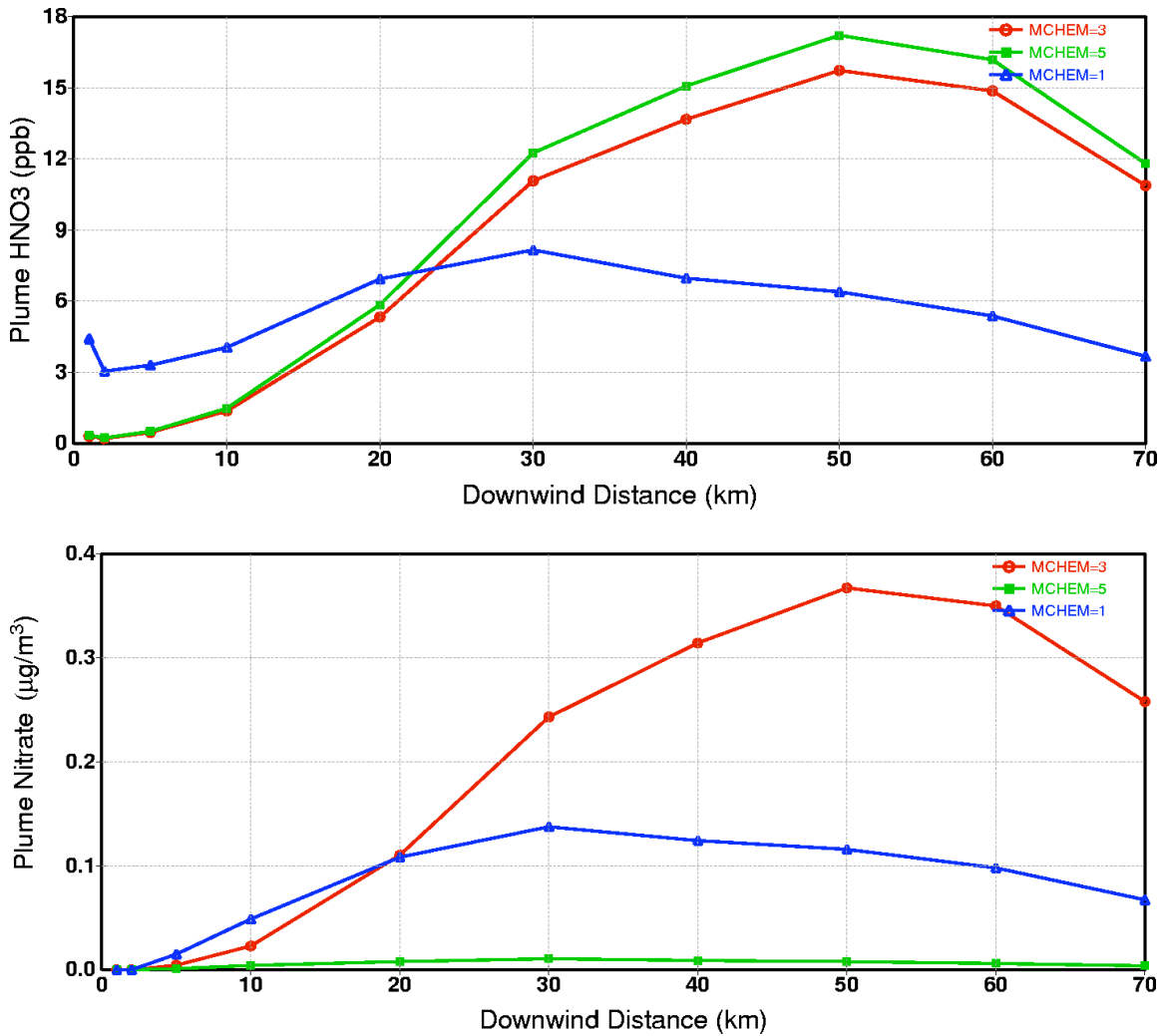


Figure 4-15. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a background NH₃ concentration of 1.0 ppb. MCHM=1 refers to the MESOPUFF II option, while MCHM=3 refers to the original RIVAD treatment, and MCHM=5 refers to the new RIVAD treatment (ISORROPIA).

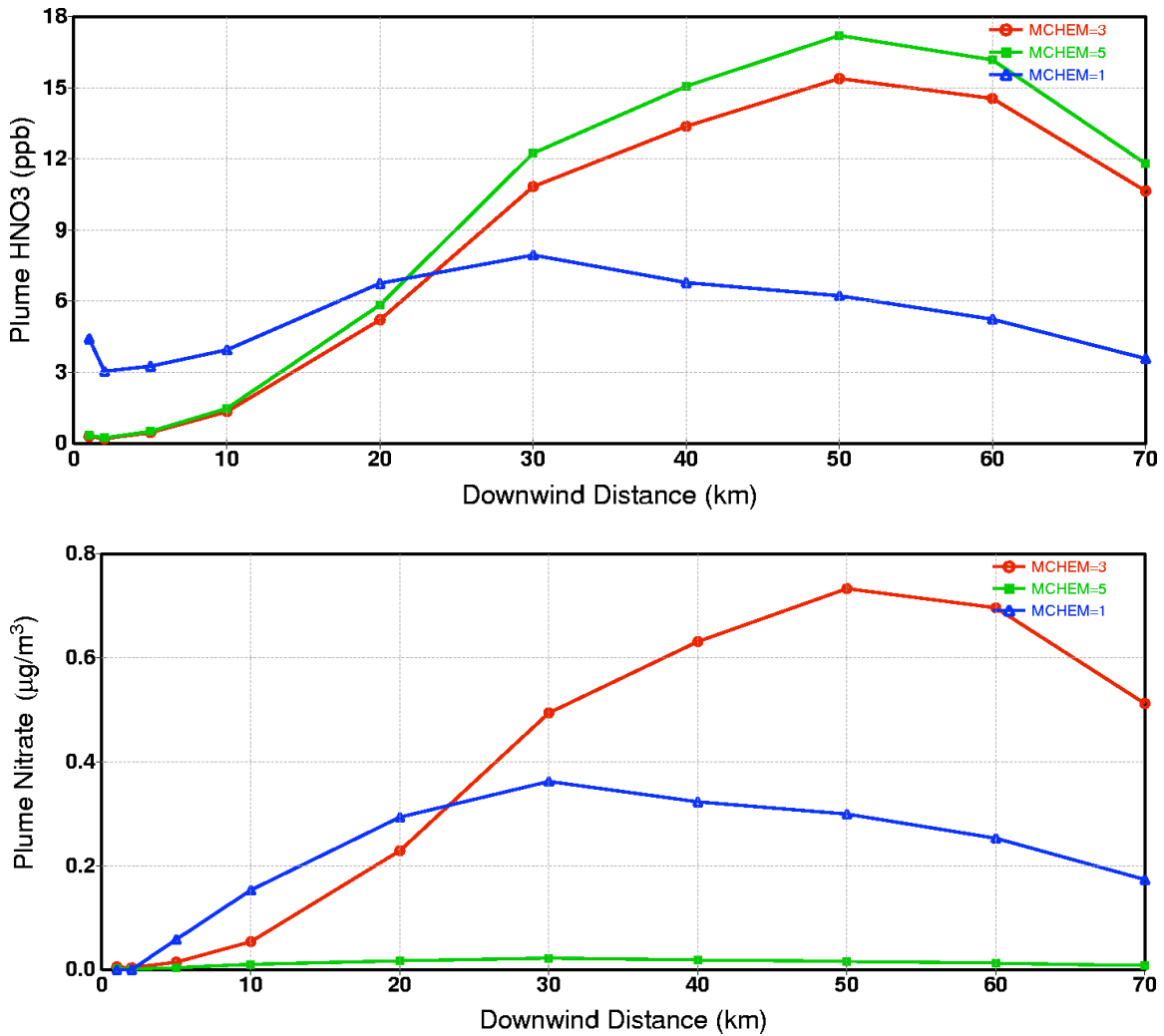


Figure 4-16. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a background NH₃ concentration of 2.0 ppb. MCHM=1 refers to the MESOPUFF II option, while MCHM=3 refers to the original RIVAD treatment, and MCHM=5 refers to the new RIVAD treatment (ISORROPIA).

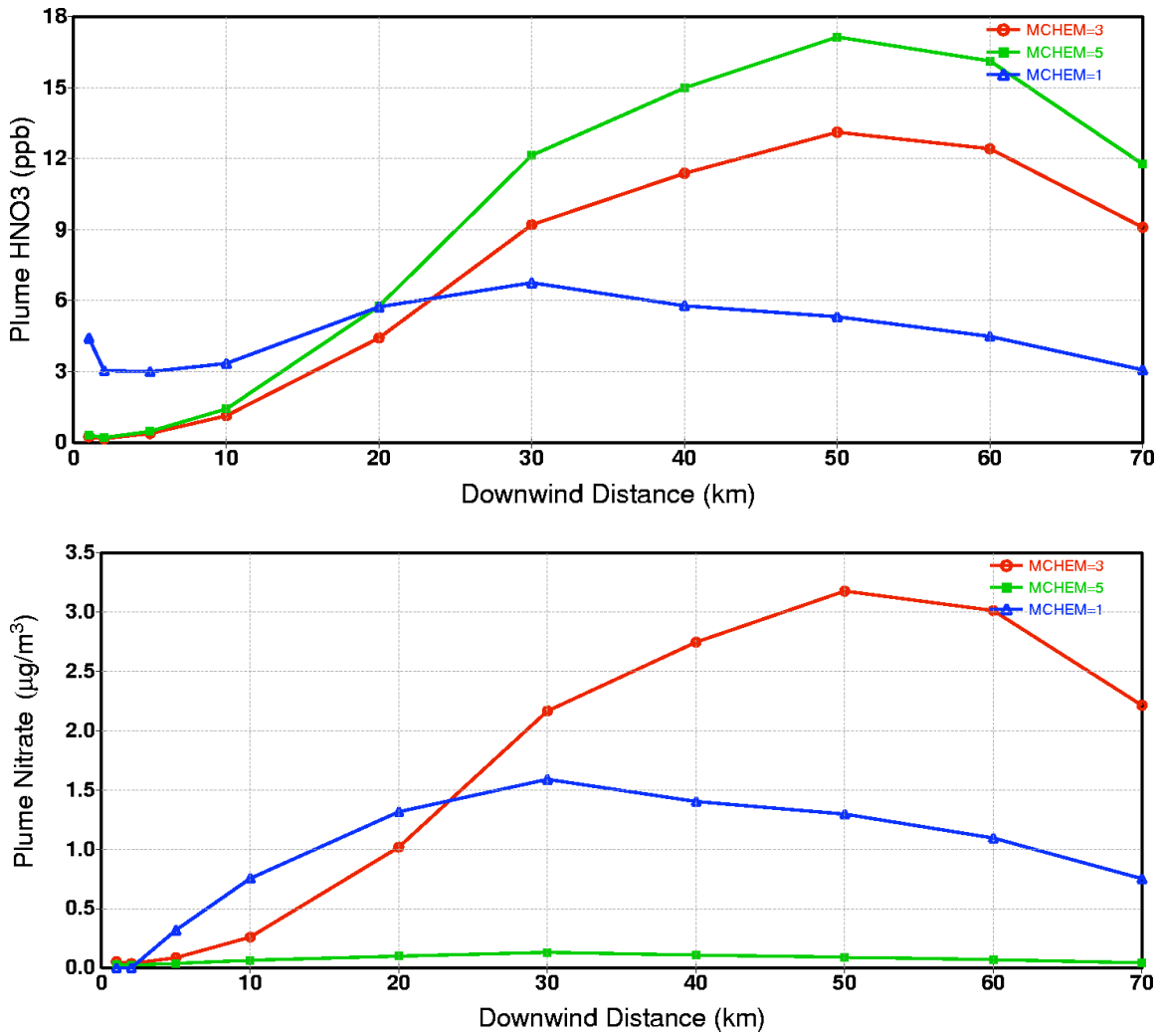


Figure 4-17. Plume centerline HNO₃ and particulate nitrate concentrations as a function of downwind distance for a background NH₃ concentration of 10.0 ppb. MCHM=1 refers to the MESOPUFF II option, while MCHM=3 refers to the original RIVAD treatment, and MCHM=5 refers to the new RIVAD treatment (ISORROPIA).

We investigated the responses of the two modules to variations in the following parameters:

- Relative humidity
- Temperature
- Background NH_3 concentration
- Background $\text{SO}_4^{=}$ concentration
- Total nitrate concentration

Each of the parameters above was varied one at a time while the other parameters were fixed at their baseline values. These baseline values are 70% for relative humidity, 25°C for temperature, 1 ppb for background NH_3 , 1 $\mu\text{g}/\text{m}^3$ for background $\text{SO}_4^{=}$, and 1 ppb for initial total nitrate. The results are presented as final concentrations of the initial total nitrate in the gas and particle phases, as well as the fraction of the total nitrate that is condensed to the particle phase.

Figure 4-18a shows the final HNO_3 and particulate nitrate concentrations predicted by the MESOPUFF and ISORROPIA modules as a function of relative humidity. We see that the MESOPUFF module always predicts higher particulate nitrate concentrations than the ISORROPIA module. The latter predicts negligible particulate nitrate at relative humidity below 60% while the former predicts a small but non-negligible particulate nitrate concentration. At higher relative humidities, the ISORROPIA module also predicts some particulate nitrate formation, but its prediction is a factor of two to three lower than the prediction from the MESOPUFF module. These results are consistent with the CALPUFF sensitivity studies described in Section 4.1. From Figure 4-18b, we see that for relative humidity less than 60%, the MESOPUFF module predicts that slightly less than 1% of the total nitrate is in the particle phase, while there is no particle phase nitrate predicted by the ISORROPIA module. At a relative humidity of 90%, the particle phase nitrate predicted by the MESOPUFF module is nearly 6% of the total nitrate, while the corresponding value for the ISORROPIA module is about 2%.

Figure 4-19 shows the effect of temperature on box-model predictions of the partitioning of total nitrate into the gas and particle phases. Figure 4-19a shows the gas-phase HNO_3 and particulate phase nitrate concentrations, while Figure 4-19b shows the fraction of total nitrate that is in the particle phase. We see that at the colder temperatures, a large fraction of the total nitrate condenses to the particle phase. For example, at -10°C, both modules predict that more than 50% of the total nitrate is present in the particle phase. As the temperature increases, the gas-phase fraction of total nitrate increases. At temperatures greater than 30°C, essentially all of the nitrate is present as gaseous nitric acid. These results are consistent with our expectations. Furthermore, we see from Figure 4-19a that the ISORROPIA scheme predicts a slightly higher particulate nitrate concentration than the MESOPUFF scheme at -10°C. However, at all temperatures higher than -10°C, the ISORROPIA module predicts much lower particulate nitrate concentrations than the MESOPUFF module.

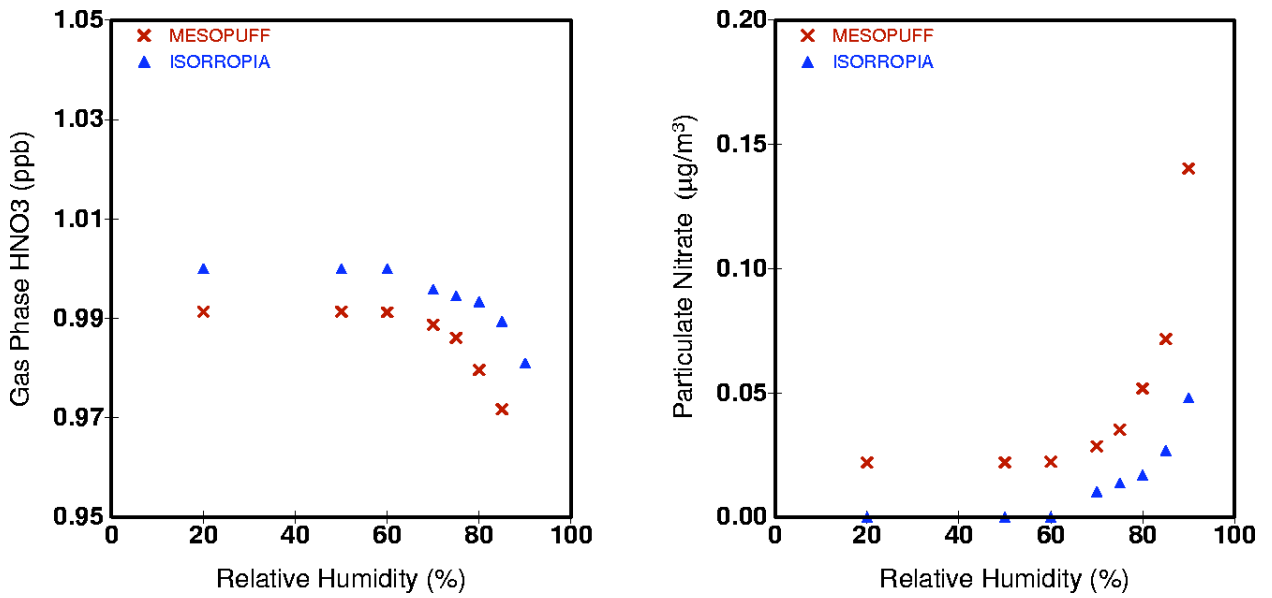


Figure 4-18a. Box-model predictions of HNO₃ and particulate nitrate concentrations as a function of relative humidity.

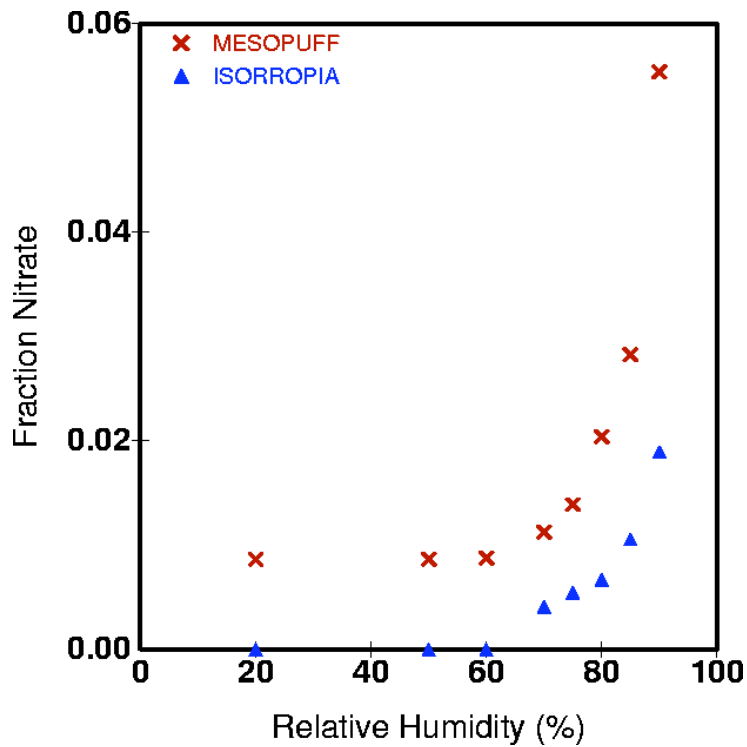


Figure 4-18b. Fraction of total initial nitrate in the particle phase as a function of relative humidity.

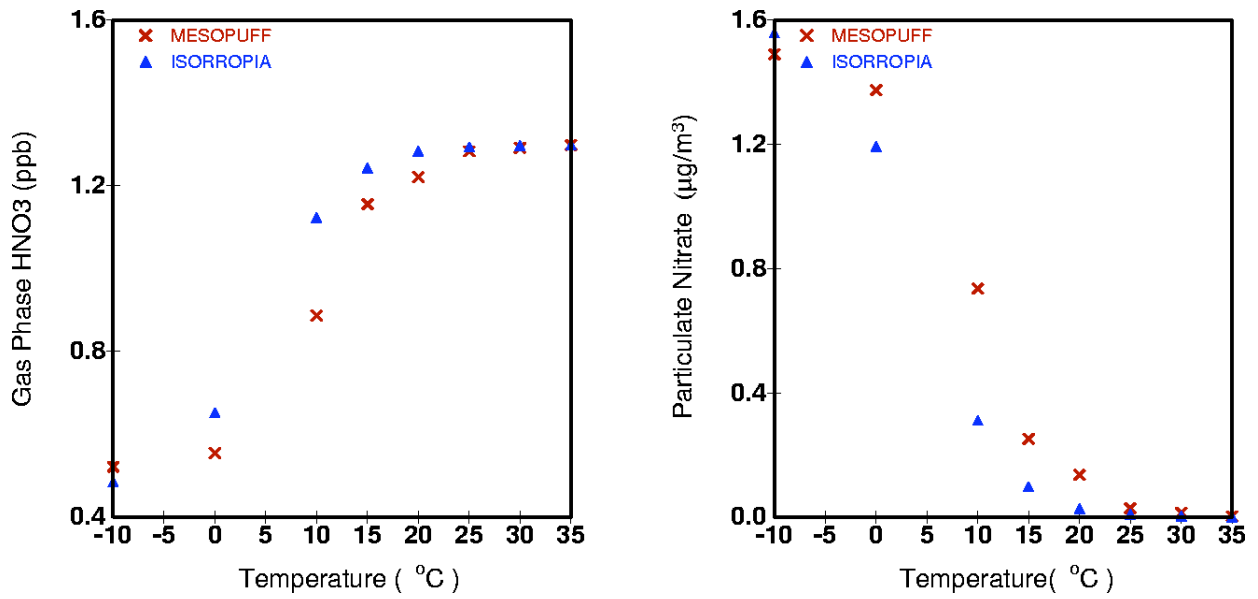


Figure 4-19a. Box-model predictions of HNO₃ and particulate nitrate concentrations as a function of temperature.

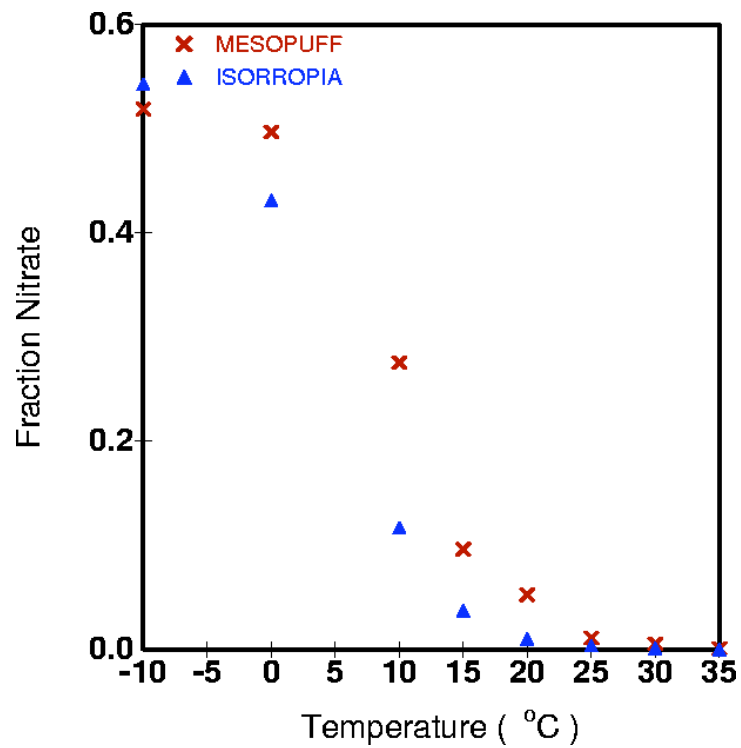


Figure 4-19b. Fraction of total initial nitrate in the particle phase as a function of temperature.

The box-model results for variations in background ammonia concentrations are shown in Figures 4-20a and 4-20b. As expected, background NH_3 concentrations have a strong effect on the partitioning of total nitrate to the gas and particle phases. At low NH_3 concentrations, all of the nitrate is present in the gas phase. As NH_3 concentrations are increased, both modules predict an increase in the particulate nitrate fraction. The ISORROPIA module predicts lower particulate nitrate fractions than the MESOPUFF module. For a background NH_3 concentration of 10 ppb, the MESOPUFF module predicts nearly 20% fractionation of total nitrate to the particle phase, while the ISORROPIA module prediction is about a factor of two lower. These results are consistent with the earlier CALPUFF sensitivity study results presented in Section 4.1.

The effects of variations in background sulfate concentrations, keeping all other parameters at their baseline values, are shown in Figure 4-21. The results are consistent with the expected behavior of the sulfate-nitrate-ammonium system. Sulfate preferentially consumes the available ammonia to form ammonium sulfate and ammonium bisulfate. As sulfate concentrations are increased, there is less ammonia available to form ammonium nitrate, and more of the total nitrate remains in the gas-phase. We see that the ISORROPIA module again predicts lower fractions of particulate nitrate than the MESOPUFF module.

Finally, Figure 4-22 shows the effect of variations in total nitrate concentrations. From Figure 4-22a, we see that both modules predict increases in gas-phase nitric acid and particulate phase nitrate as total nitrate concentrations are increased. The ISORROPIA module predictions of particulate nitrate concentrations are lower than the MESOPUFF module predictions. The fraction of total nitrate that is in the particle phase is not very sensitive to the initial total nitrate concentration for either module. Figure 4-22b shows that the MESOPUFF prediction of the fraction of nitrate that is in the particle phase decreases from about 1.2% at low initial total nitrate concentrations to slightly less than 1% at higher total nitrate concentrations. The ISORROPIA prediction of fractional particulate nitrate is fairly constant at about 0.4% for all but the lowest total nitrate concentration.

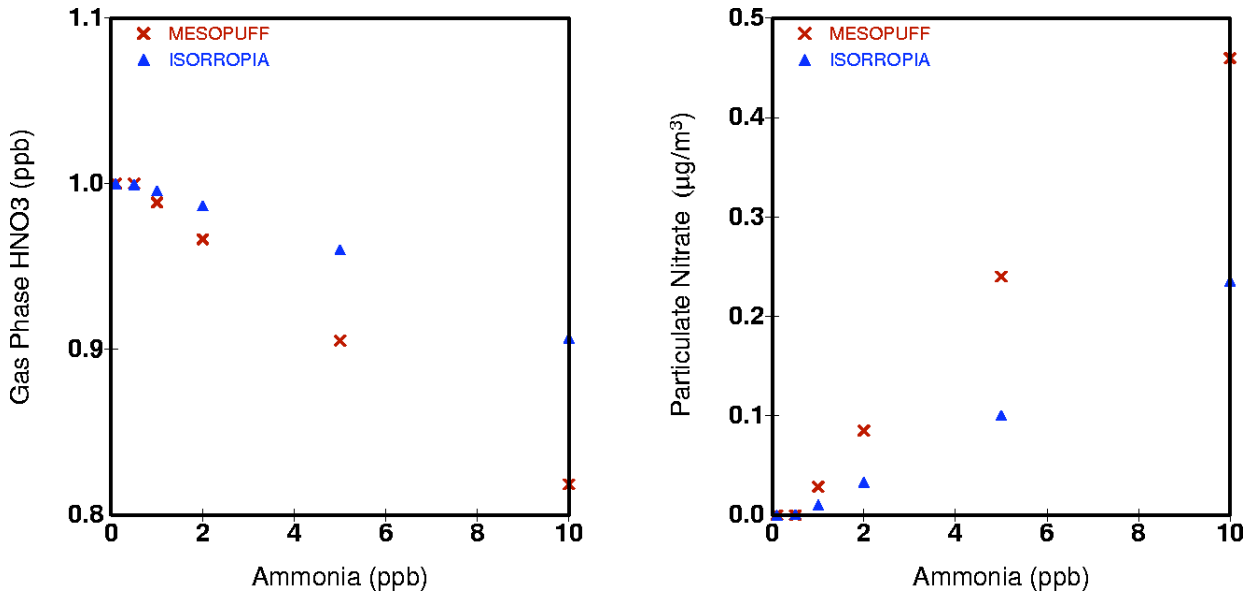


Figure 4-20a. Box-model predictions of HNO₃ and particulate nitrate concentrations as a function of background NH₃ concentration.

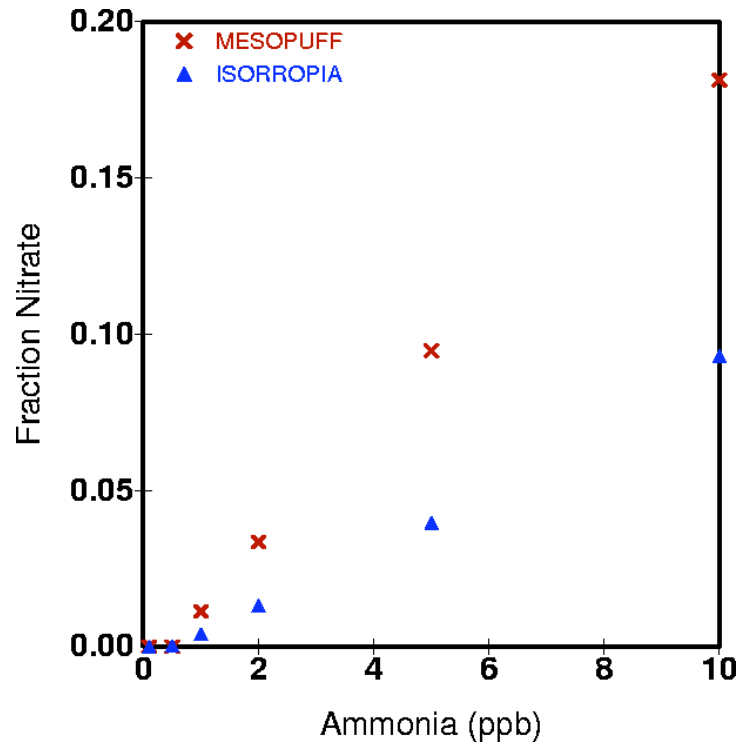


Figure 4-20b. Fraction of total initial nitrate in the particle phase as a function of background NH₃ concentration.

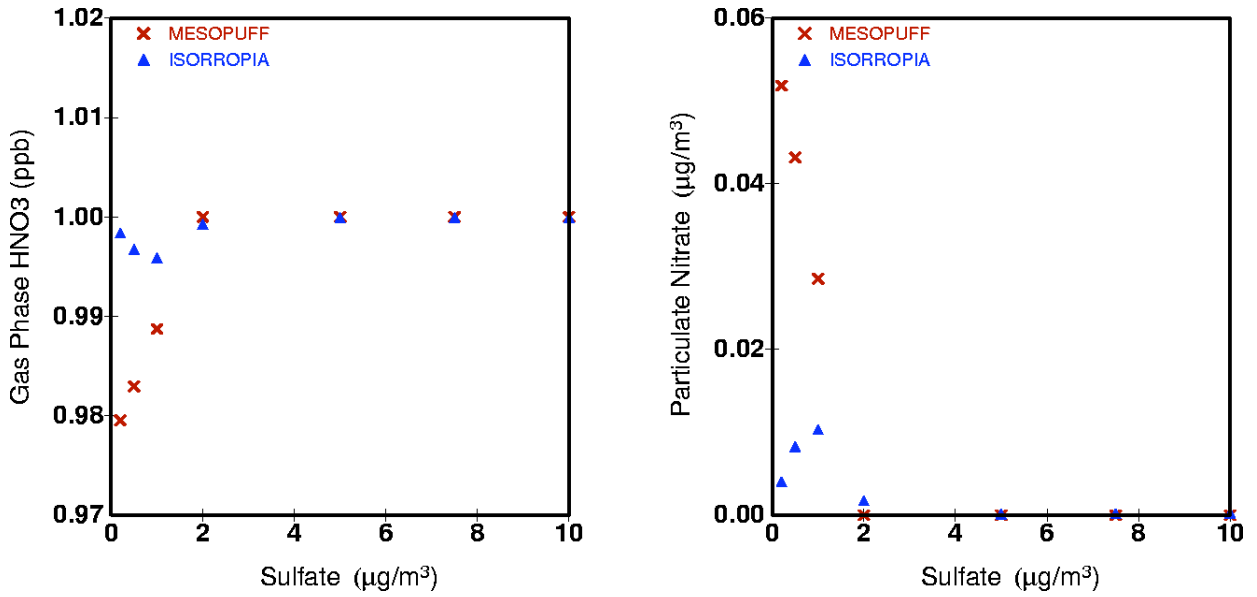


Figure 4-21a. Box-model predictions of HNO₃ and particulate nitrate concentrations as a function of background SO₄⁼ concentration.

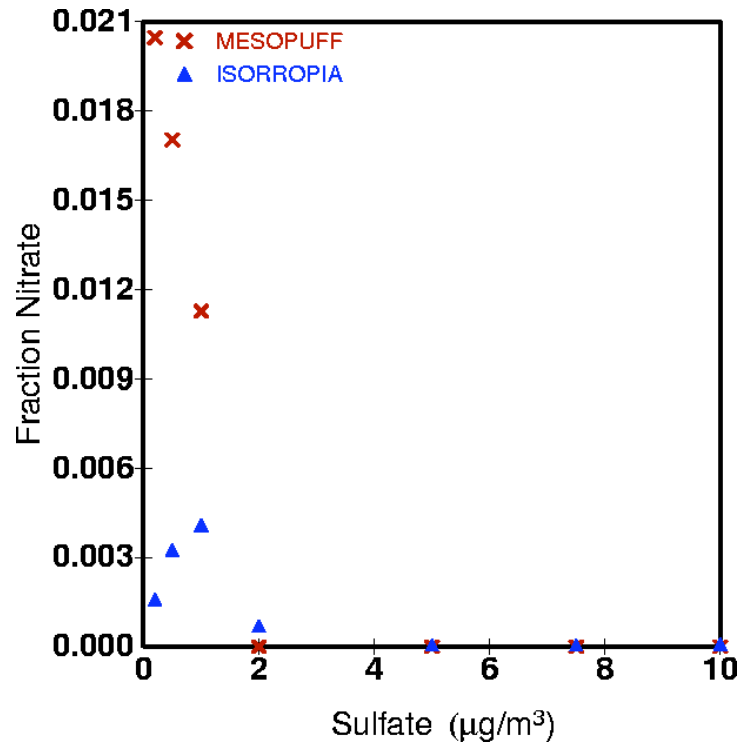


Figure 4-21b. Fraction of total initial nitrate in the particle phase as a function of background SO₄⁼ concentration.

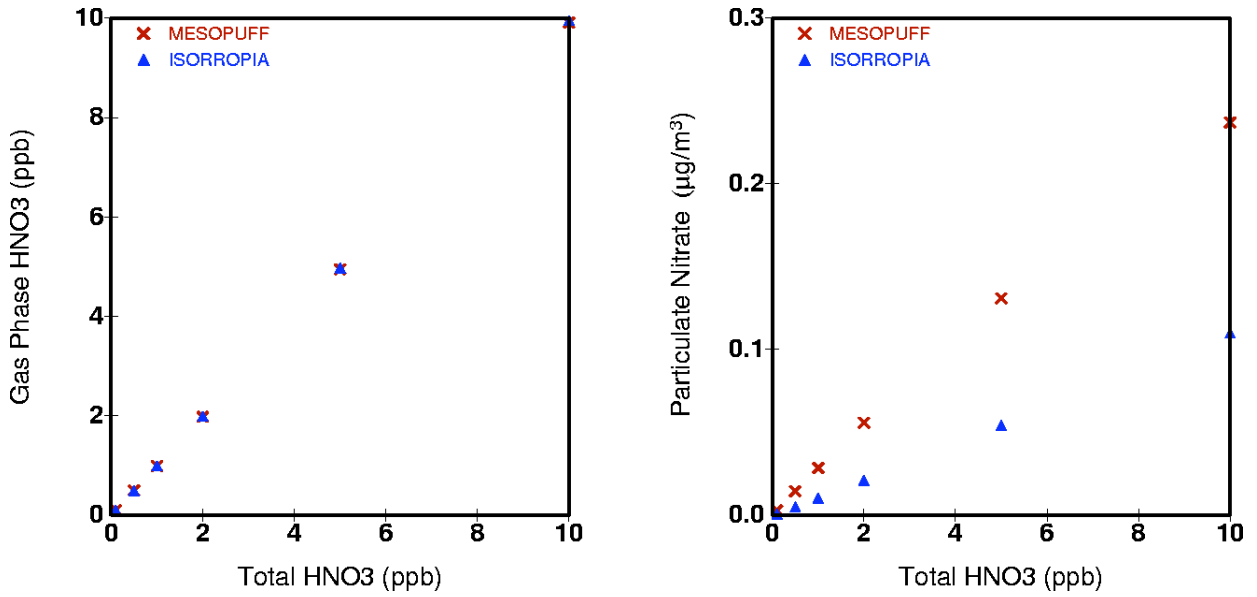


Figure 4-22a. Box-model predictions of HNO₃ and particulate nitrate concentrations as a function of total nitrate concentration.

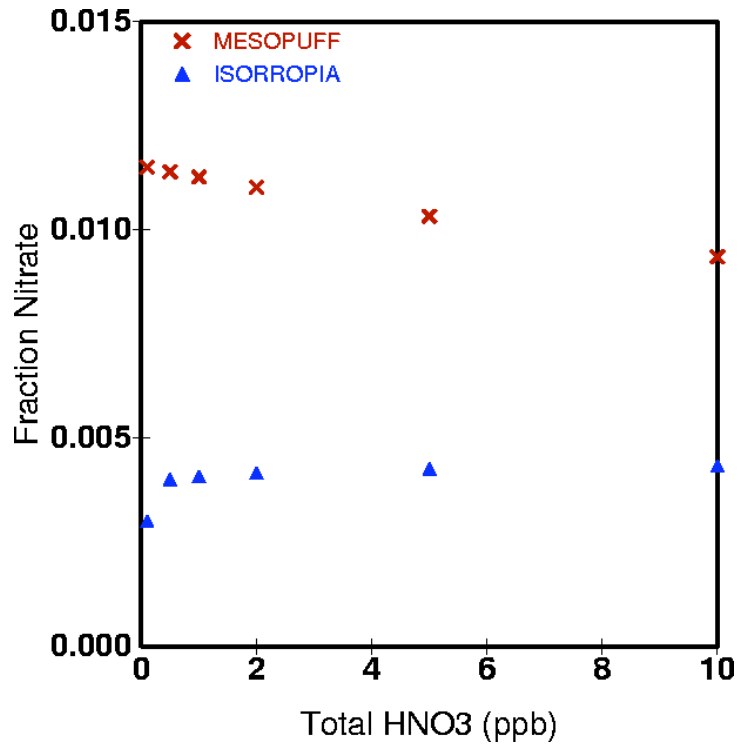


Figure 4-22b. Fraction of total initial nitrate in the particle phase as a function of total nitrate concentration.

5. CONCLUSIONS AND RECOMMENDATIONS

Several improvements were made to CALPUFF for this study. These include:

1. A correction to an error in the RIVAD/ARM3 gas-phase chemistry scheme
2. Implementation of a new inorganic aerosol equilibrium module as an alternative to the original treatment in CALPUFF
3. Implementation of a new secondary organic aerosol module as an alternative to the original treatment in CALPUFF
4. Implementation of a new aqueous-phase chemistry module as an enhancement to the model

The first improvement is a correction of an error in the original CALPUFF and does not include any scientific improvements (except for updates to the rate constants for SO₂ and NO₂ oxidation). The remaining three improvements increase the scientific credibility of CALPUFF by incorporating science modules that are also implemented in a number of air quality models that are currently in widespread use.

The above improvements were made to the two latest available versions of CALPUFF. The first version was the unofficial April 2006 release (Version 6), available from the model developers, while the second version is the official EPA June 2007 release (Version 5.8).

The improvements to CALPUFF were tested using a plume chemistry database that AER has used in previous studies with CALPUFF and SCICHEM. Both baseline and sensitivity studies were conducted with the revised versions of CALPUFF to determine the effects of the changes to the code. We also conducted box-model sensitivity studies to test the changes to the inorganic aerosol thermodynamic equilibrium module.

The correction of the RIVAD/ARM3 gas-phase chemistry scheme, while necessary, showed the smallest effect on model results for the case studies simulated in this work. This correction involved the implementation of a scheme in which a history of puff ozone concentrations is saved so that the ozone concentration at a given time step is calculated as a weighted average of the puff concentration from the previous time step and the background concentration. A similar correction was applied to calculate puff H₂O₂ concentrations, required for the new aqueous-phase chemistry module.

The new inorganic aerosol module implemented in this study is based on the ISORROPIA model of Nenes et al. (1999). This model is implemented in models such as CMAQ, CMAQ-MADRID, SCICHEM, REMSAD and CAMx. As compared to the original inorganic aerosol module in CALPUFF, which is based on a simplified parameterization, the new module predicts significantly lower PM nitrate formation for a wide range of conditions, except at very low (sub-zero) temperatures. The low temperature sensitivity studies highlighted another important shortcoming of CALPUFF, namely, its lack of treatment of ammonia limitation for multiple or overlapping puffs. This leads to substantial overestimation of particulate nitrate formation at downwind

receptors. This shortcoming can be addressed by a post-processing step to recalculate inorganic aerosol equilibrium at receptor locations. In addition, an upper limit for particulate nitrate formation that is based on the amount of ammonia available in the background can be implemented in CALPUFF to prevent the output of particulate ammonium nitrate concentrations that are physically unrealistic.

The new secondary organic aerosol module is based on the scheme used in CMAQ-MADRID (Pun et al., 2005) and SCICHEM. The module includes SOA formation from anthropogenic VOCs, such as aromatics, PAH, and long-chain alkanes. It does not include SOA formation from biogenics, such as terpenes and isoprene, because these are emitted from vegetation and are not typically treated in a puff model. The original CALPUFF SOA scheme included SOA formation from aromatics and biogenics, and had an error in its calculation of the temperature dependence of the partitioning of condensable species between the gas and particulate phases. The new SOA module in CALPUFF predicts about 2 to 3 times higher SOA formation than the original SOA module.

The new aqueous-phase chemistry module was implemented to overcome a shortcoming of CALPUFF, which did not include an explicit aqueous-phase chemistry module. The module is based on the model of Walcek and Taylor (1986), which is also used in CMAQ, CMAQ-MADRID, SCICHEM and CAMx. The tests of this module showed the expected result that reaction in the aqueous-phase is a major pathway for SO₂ oxidation.

The improvements to the inorganic aerosol equilibrium module, the SOA module, and the aqueous-phase chemistry module have the largest impact on model results. Thus, we recommend that future studies be designed to more rigorously evaluate these components. However, recall that these modules, although new to CALPUFF, are currently being used in operational air quality models, such as CMAQ and CMAQ-MADRID, which have undergone substantial evaluation. The Southwest Wyoming Technical Air Forum (SWWYTAF) data base, which includes a complete CALPUFF modeling data base for 1995, as well as monitoring data from IMPROVE, CASTNET and NADP, is a possible candidate for conducting a model performance evaluation with the revised version of CALPUFF.

We also recommend that CALPUFF be adapted to use the outputs of three-dimensional air quality models, such as CMAQ, as background concentrations. This would improve the chemistry calculations in CALPUFF. This improvement would require both changes to CALPUFF as well as the development of processors to create the input background concentration files. These are relatively straightforward tasks, and AER has previously developed similar interfaces between CMAQ and SCICHEM.

It is also recommended that the new SOA scheme in CALPUFF be updated as new data become available. There are still many uncertainties in our understanding of secondary organic aerosol formation and it is a subject of intensive research. For example, scientists at Caltech have reported new data for SOA formation from aromatics

(Ng et al., 2007). Once their work has been incorporated in regional air quality models, the CALPUFF SOA module should be updated accordingly.

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