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CALPUFF Chemistry Improvements

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Reactive Plume Models

- Two major reactive plume models currently available for impact assessments:
  - CALPUFF (recommended by EPA for PSD and BART analyses)
  - SCIPUFF/SCICHEM (alternative model)

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CALPUFF vs. SCICHEM

- CALPUFF
  - 1st order closure diffusion
  - Simple chemistry
  - Computationally efficient
  - Regulatory model with prescribed options for typical applications
- SCICHEM
  - 2nd order closure diffusion
  - Comprehensive chemistry
  - Computationally demanding
  - Alternative model

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CALPUFF Chemistry Upgrade-Issues

- Gas-phase chemistry highly simplified but difficult to replace with comprehensive chemistry:
  - Significant development effort to implement non-linear chemistry
  - Increases complexity of model
  - Alternative puff models with detailed chemistry already available (e.g., SCICHEM)

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CALPUFF Chemistry Upgrade-Approach

- Correct an existing error in the RIVAD gas-phase chemistry option and update RIVAD chemistry rate constants
- Focus on improving treatments for PM formation and cloud chemistry
- All new modules added as new options – none of the previous CALPUFF chemistry options modified

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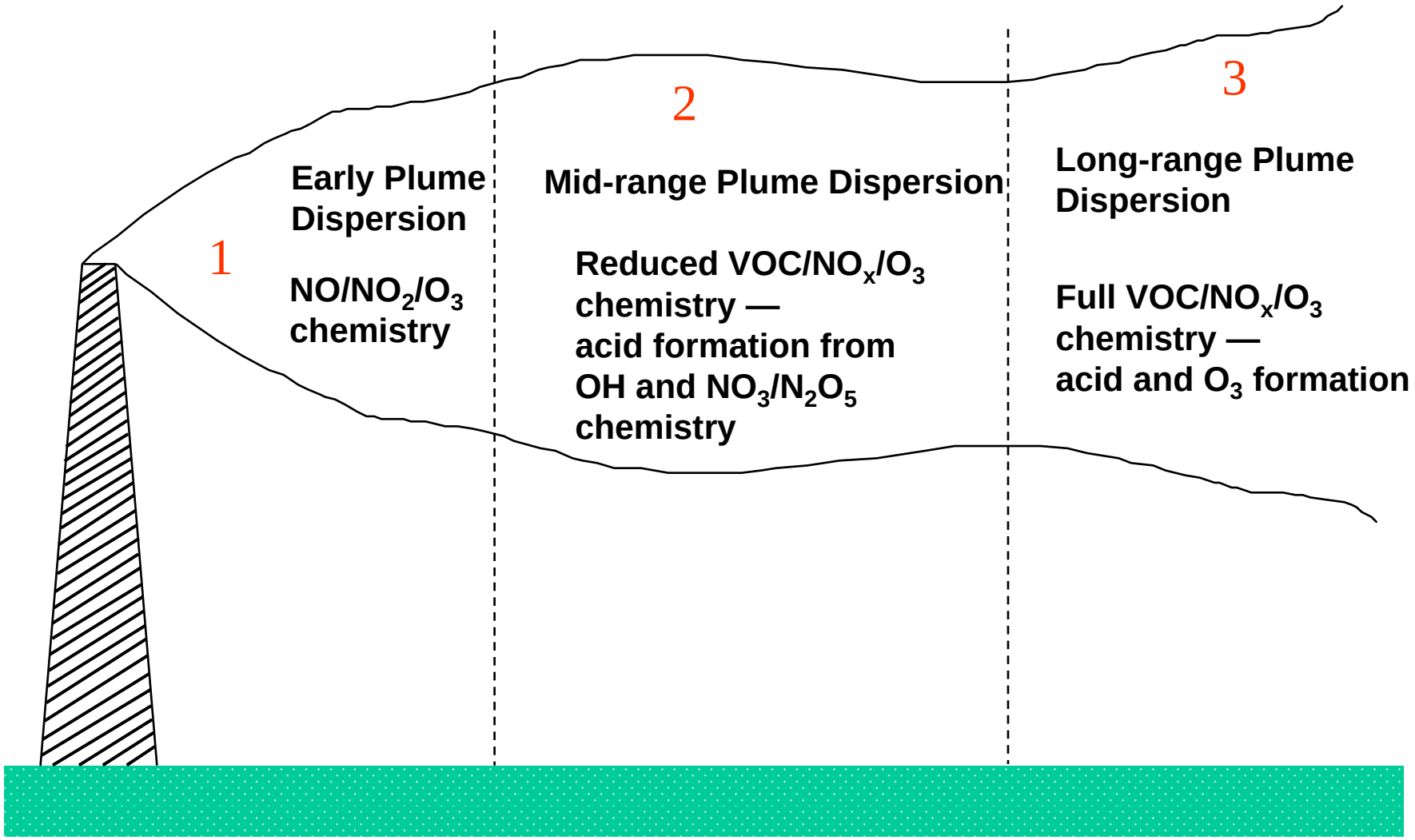
Chemistry of NO_x Plumes



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RIVAD Chemistry Option in CALPUFF

- The RIVAD chemistry option in CALPUFF uses Stage 1 chemistry for $NO/NO_2/O_3$ and part of Stage 2 chemistry for OH and the formation of H_2SO_4 and HNO_3
- O_3 puff concentration in CALPUFF is replenished to its background value at each time step; the code must be corrected to account for the O_3 depletion in the puff in the early stages of plume dispersion
- Correction: Store puff O_3 history and calculate new puff O_3 concentration at each time step

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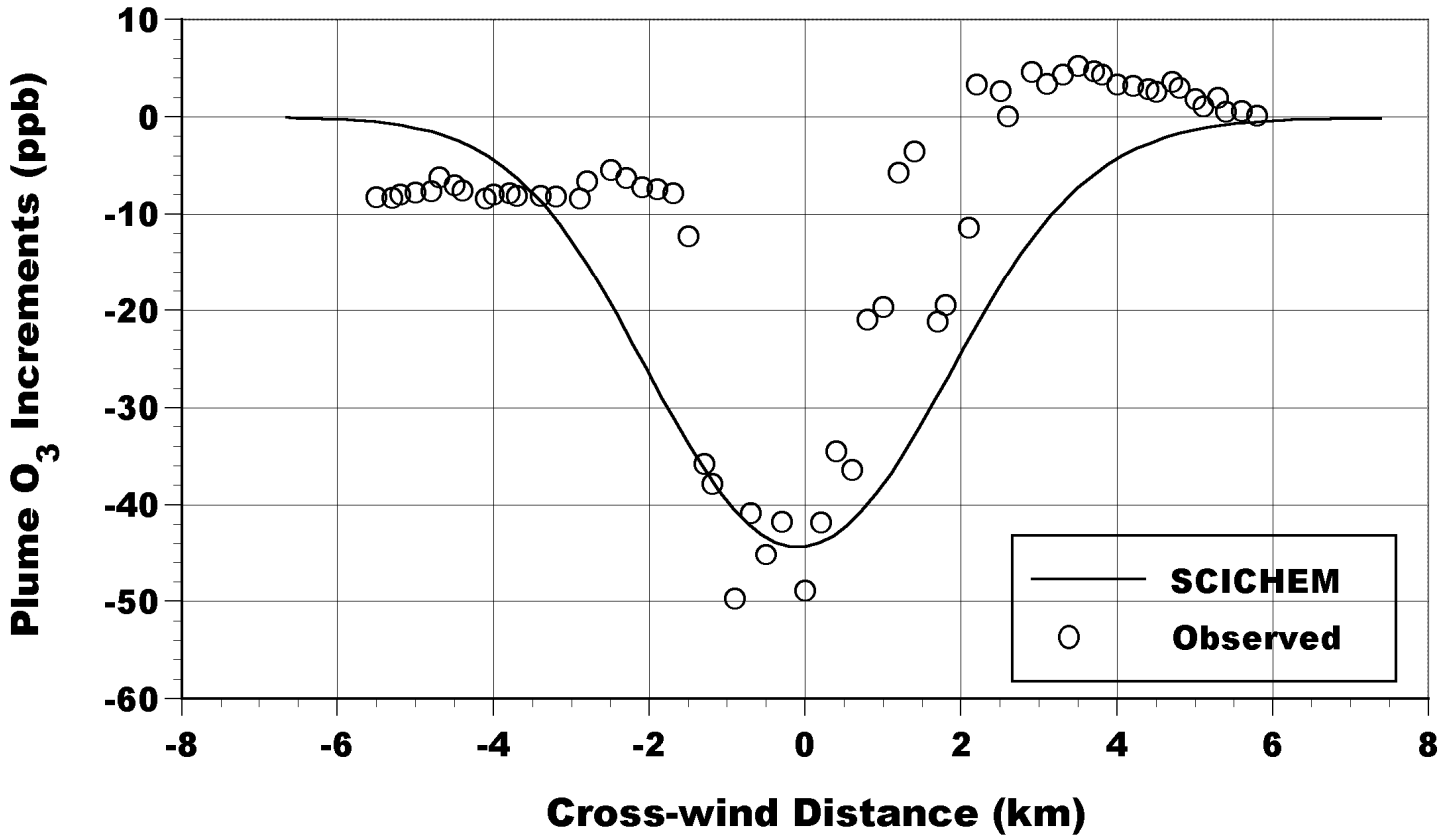
Ozone Depletion in a Fresh Plume

Helicopter measurements of Cumberland power plant plume, July 6, 1999; downwind distance = 11 km



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Original PM Chemistry in CALPUFF

- PM chemistry includes formation of inorganic species (sulfate, nitrate and ammonium) and organic species (secondary organic aerosols, SOA)
- H_2SO_4 and HNO_3 lead to the formation of ammonium sulfate and ammonium nitrate according to a simple gas/particle algorithm that uses a constant NH_3 concentration
- Includes a treatment for the formation of SOA from anthropogenic and biogenic VOCs (developed for Wyoming DEQ)
  - simplified treatment
  - only includes toluene and xylene as anthropogenic SOA precursors

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New PM Chemistry in CALPUFF

- Formation of ammonium sulfate and ammonium nitrate is treated with the thermodynamic equilibrium model ISORROPIA
- Inorganic PM formation that is now consistent with that of other operational models (e.g., CMAQ) while retaining computational efficiency
- Formation of SOA includes oxidation of anthropogenic VOCs (aromatics, long-chain alkanes and PAH) by OH to form condensable products, which are partitioned according to Pankow's absorption algorithm (based on MADRID formulation)

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Original CALPUFF Cloud Chemistry

- No explicit treatment of aqueous-phase chemistry

- MESOPUFF-II chemistry option uses a simple parameterization to approximate the increased oxidation of SO_2 in presence of clouds or fog:
  - function of relative humidity (RH)
  - may significantly underestimate SO_2 oxidation rates when clouds are present
  - may overestimate SO_2 oxidation when clouds are not present but RH is high

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New Cloud Chemistry in CALPUFF

- Based on CMAQ treatment
- Includes SO_2 oxidation by hydrogen peroxide and ozone as well as iron and manganese catalyzed oxidation by oxygen
- Includes gas-aqueous equilibria to calculate liquid-phase concentrations and cloud pH

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CALPUFF Upgrade & Testing

- Gas-phase chemistry corrections and new PM and aqueous-phase chemistry modules incorporated into 2 versions of CALPUFF
  - Unofficial Version 6 (April 2006 release)
  - EPA-approved Version 5.8 (June 2007 release)

- Box-model sensitivity studies with old and new inorganic PM modules

- Original (MCHEM options = 3,4) and new (MCHEM options = 5,6) CALPUFF codes tested using a power plant plume database used in previous SCICHEM/CALPUFF studies

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Box-Model Sensitivity Studies with Inorganic PM Modules

- Sensitivity of original CALPUFF module (MESOPUFF) and new CALPUFF module (ISORROPIA) to
  - Relative humidity
  - Temperature
  - Background ammonia
  - Background sulfate
  - Total nitrate

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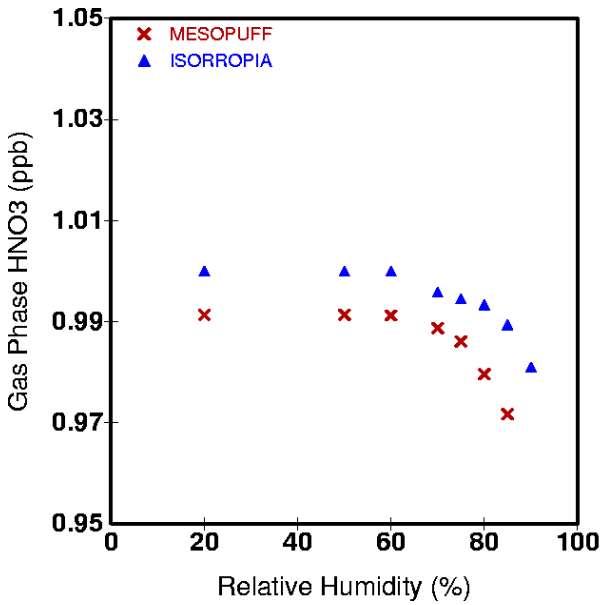
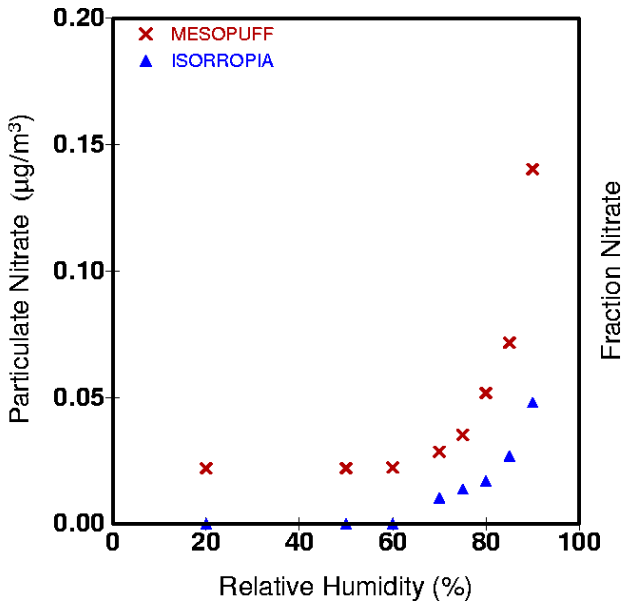
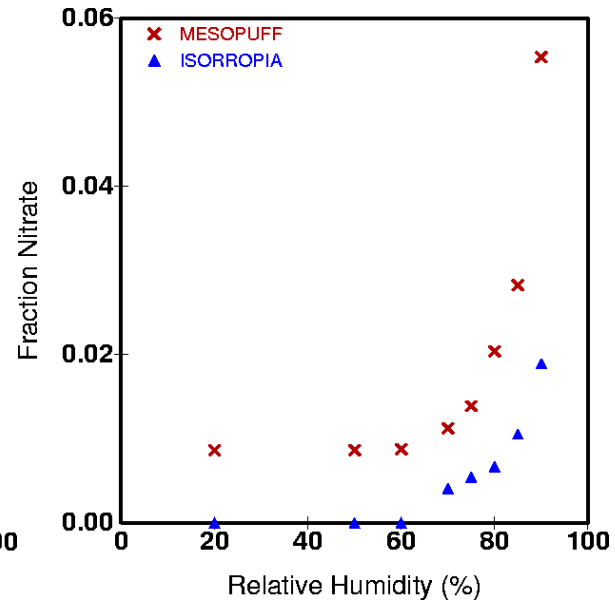
Sensitivity to Relative Humidity







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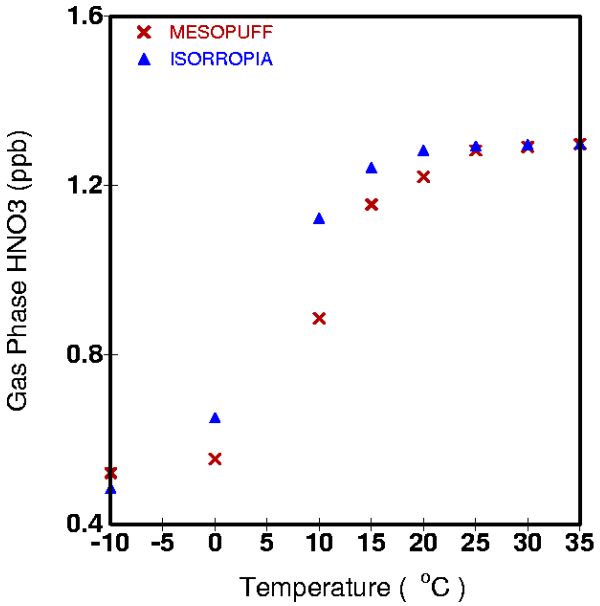
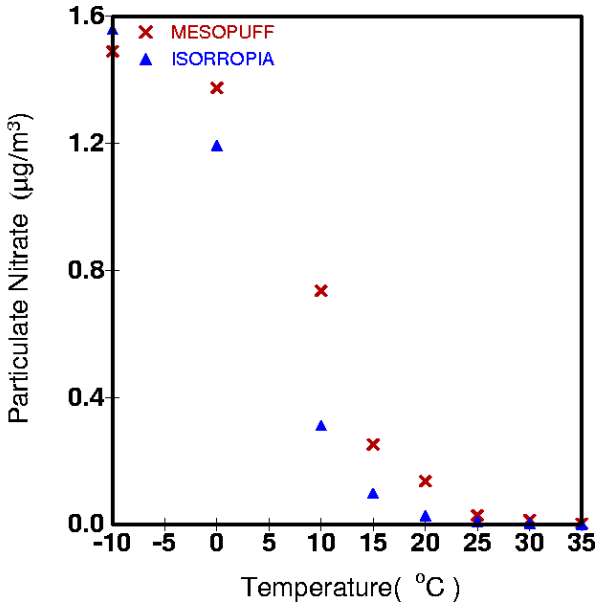
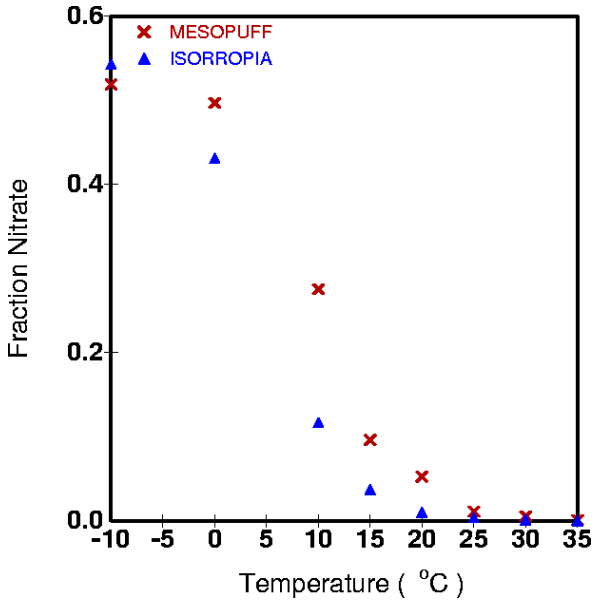
Sensitivity to Temperature







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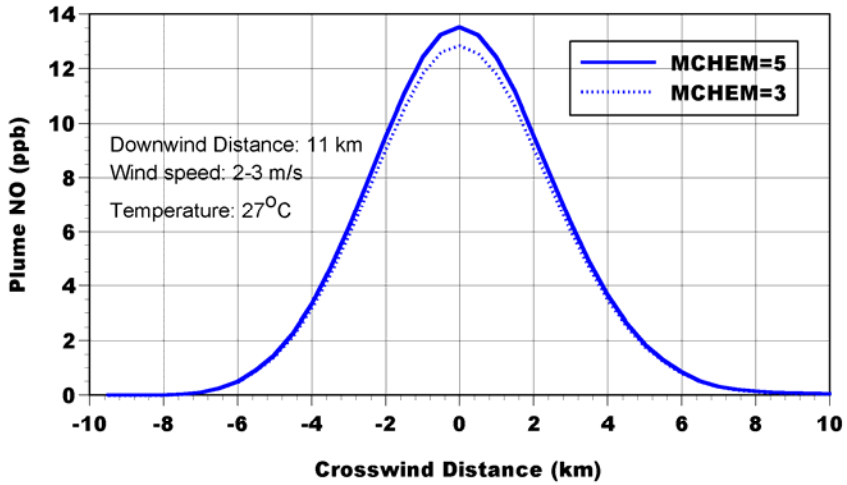
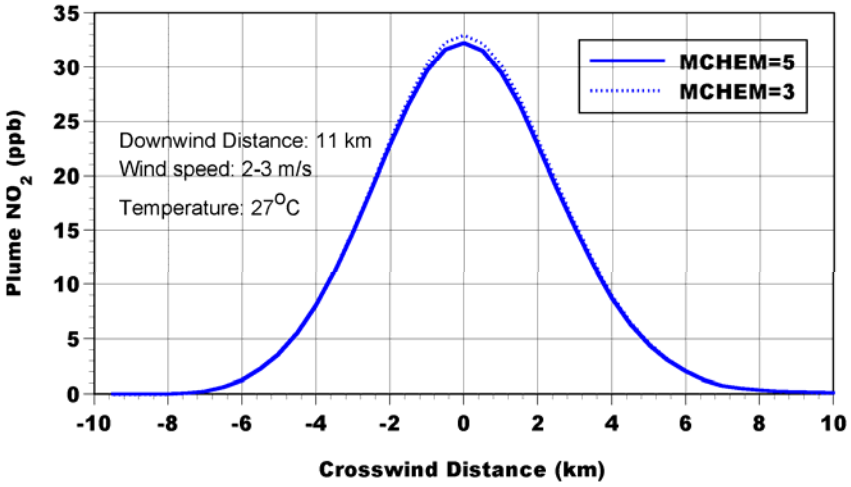
CALPUFF Results
Effect of O_3 Correction





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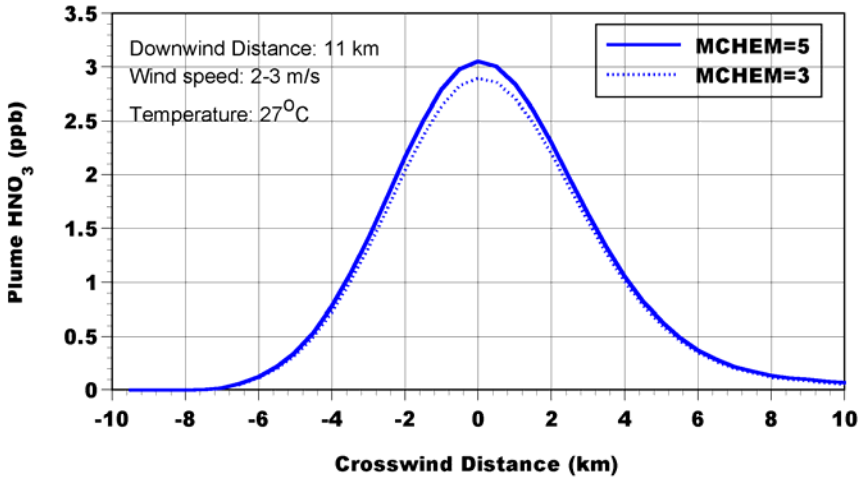
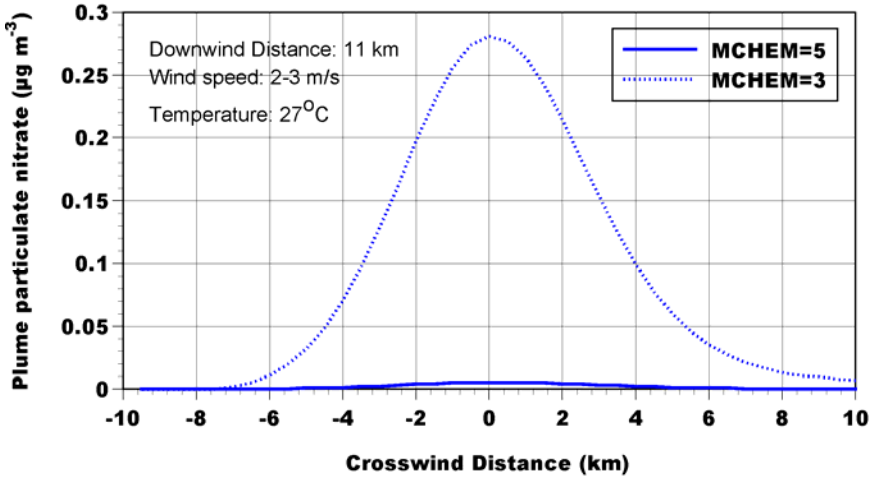
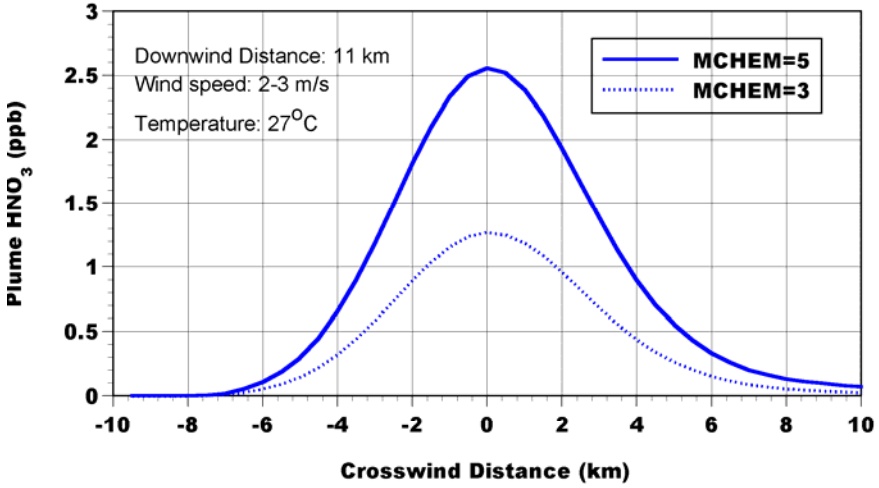
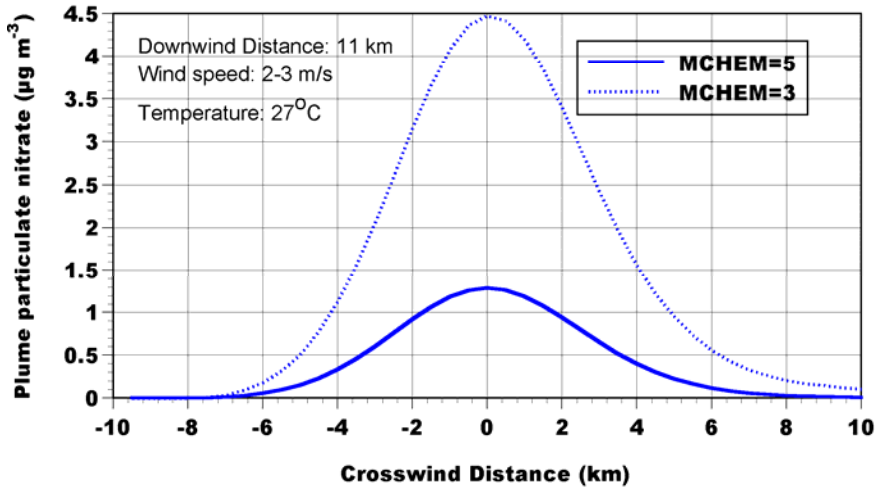
CALPUFF Results - Inorganic PM Module Comparison





CALPUFF Results - Inorganic PM Module Comparison at High RH (95%)





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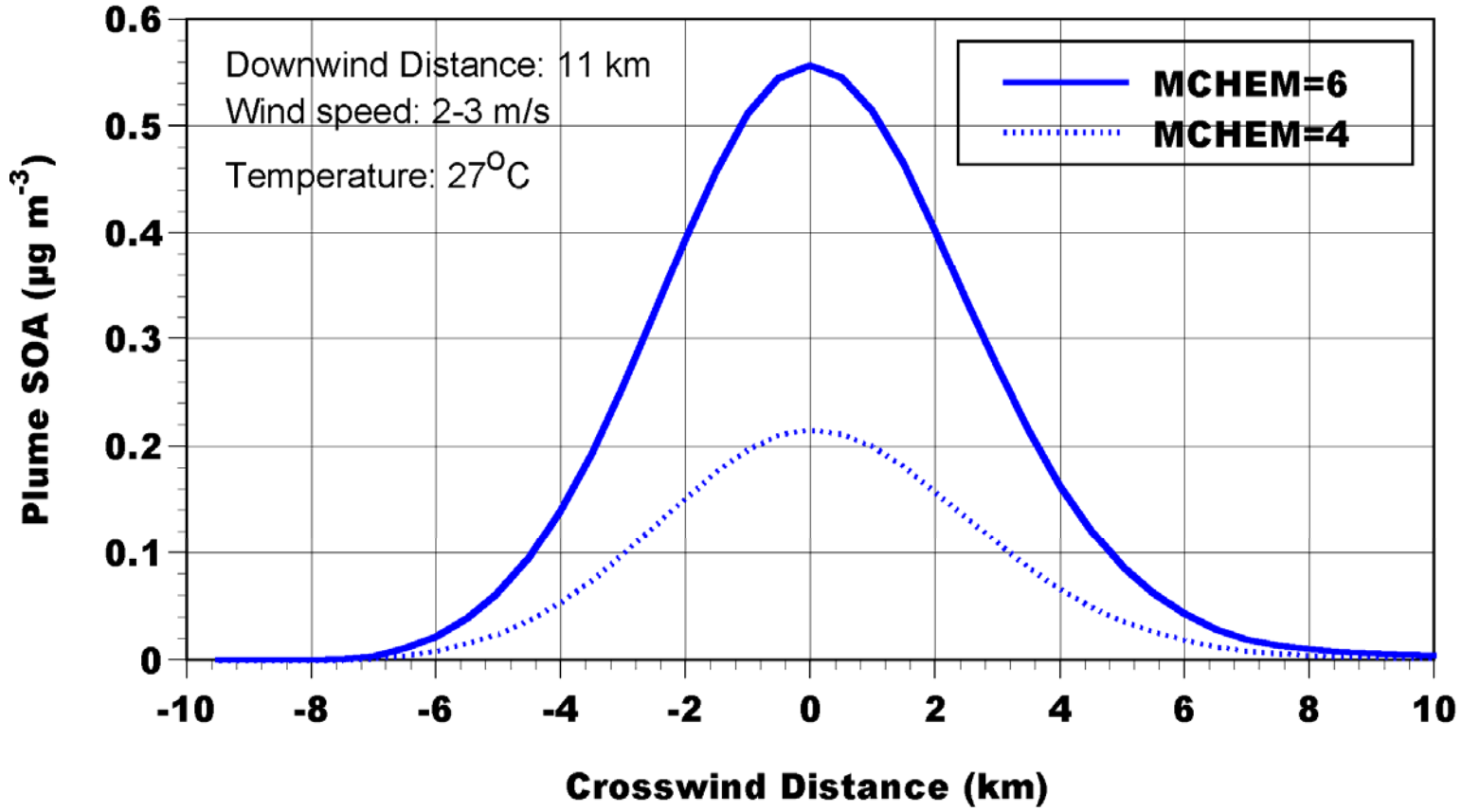
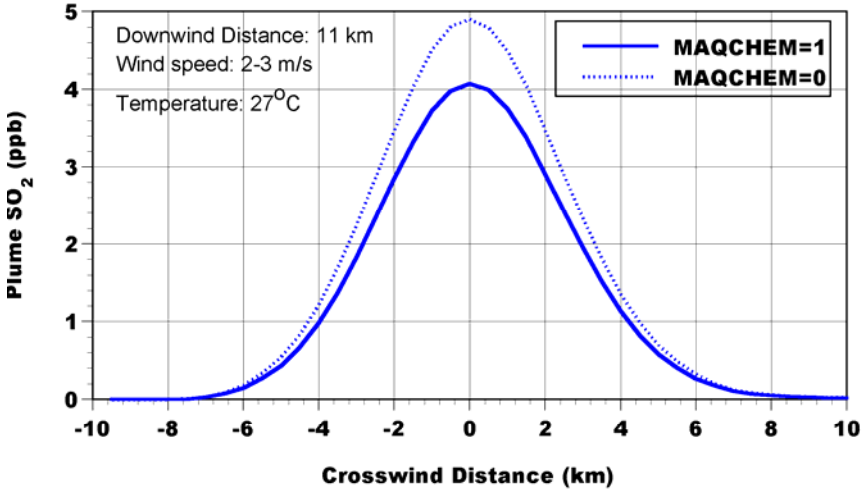
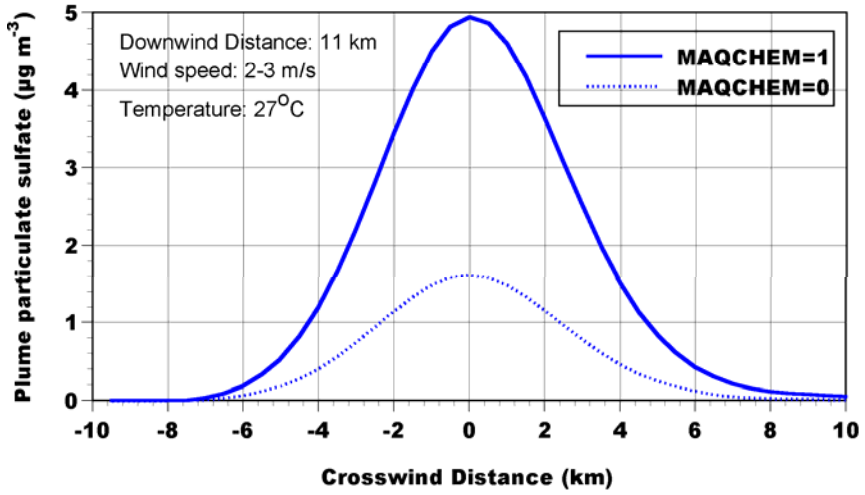
CALPUFF Results - Organic PM (SOA) Module Comparison



CALPUFF Results
Aqueous-Phase Chemistry





Cloud cover and liquid water content hard-coded for testing aqueous-phase chemistry option

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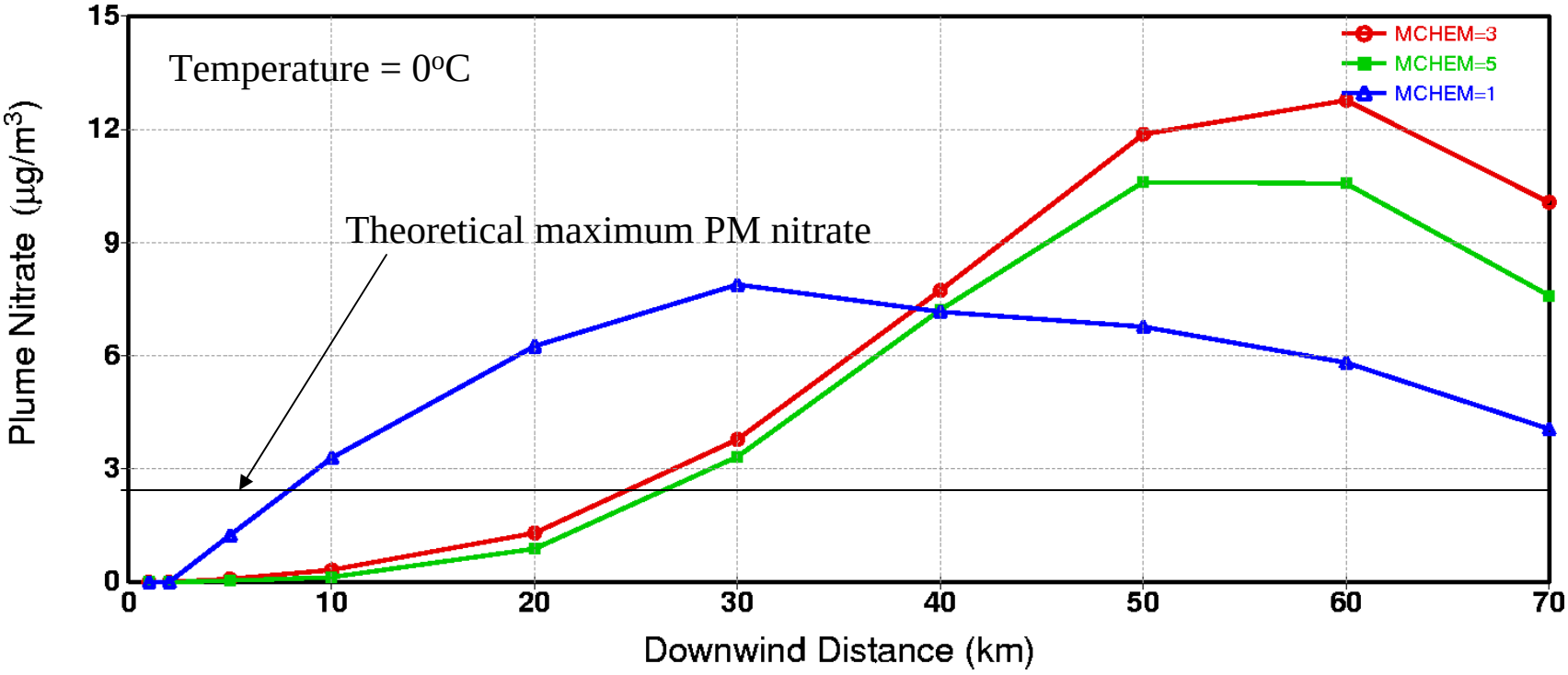
Shortcoming in CALPUFF Ammonia Treatment



Ammonia limitation handled in POSTUTIL (optional CALPUFF post-processing program)

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Ongoing Work

- Model is currently being evaluated with the Southwest Wyoming Technical Air Forum (SWWYTAF) data base
- Additional model updates:
  - Update ammonia limitation method in POSTUTIL to use ISORROPIA algorithm
  - Allow vertical profiles in input ammonia concentrations

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Recommendations

- Modify CALPUFF to read 3-D grid model outputs
  - More realistic specification of oxidant (OH, O_3, H_2O_2) and ammonia concentrations
  - Temporal and spatial variability
- Include cloud fields in CALMET and CALPUFF for using the aqueous-phase chemistry option
- Additional testing and evaluation of new chemistry options with other data bases

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Acknowledgments

- API:
  - Provided funding for this study and ongoing CALMET/CALPUFF evaluation study with SWWYTAF data base

- Wyoming Department of Environmental Quality:
  - Provided SWWYTAF data base for model application and evaluation for ongoing evaluation study