New Developments and Evaluations of the CALPUFF Model

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- **Work performed by CALPUFF model authors while at TRC (Phase I) and now at Exponent, Inc. (Phase II)**
- **Original implementation of modules conducted by AER (Karamchandani et al., 2008, 2009) under sponsorship of the American Petroleum Institute (API)**

Overview of Changes

- **CALPUFF v6.42b Chemical Module Updates**
  - ISORROPIA II (v2.1) used for nitric acid/nitrate aerosol partition
    - ISORROPIA used in Eulerian models such as CMAQ and CAMx
  - Aqueous-phase chemical transformation (adapted from RADM cloud module in CMAQ/SCICHEM)
    - Oxidation of SO_2 in cloud water and rain water
    - V6.42b couples CALPUFF with MM5/WRF liquid water content
    - Tracks location of plume and overlap with cloud layer
  - New RIVAD module tracks depleted O_3 and H_2O_2 in each puff
  - Anthropogenic secondary organic aerosol (SOA) formation (from CalTech SOA routines implemented in CMAQ-MADRID)

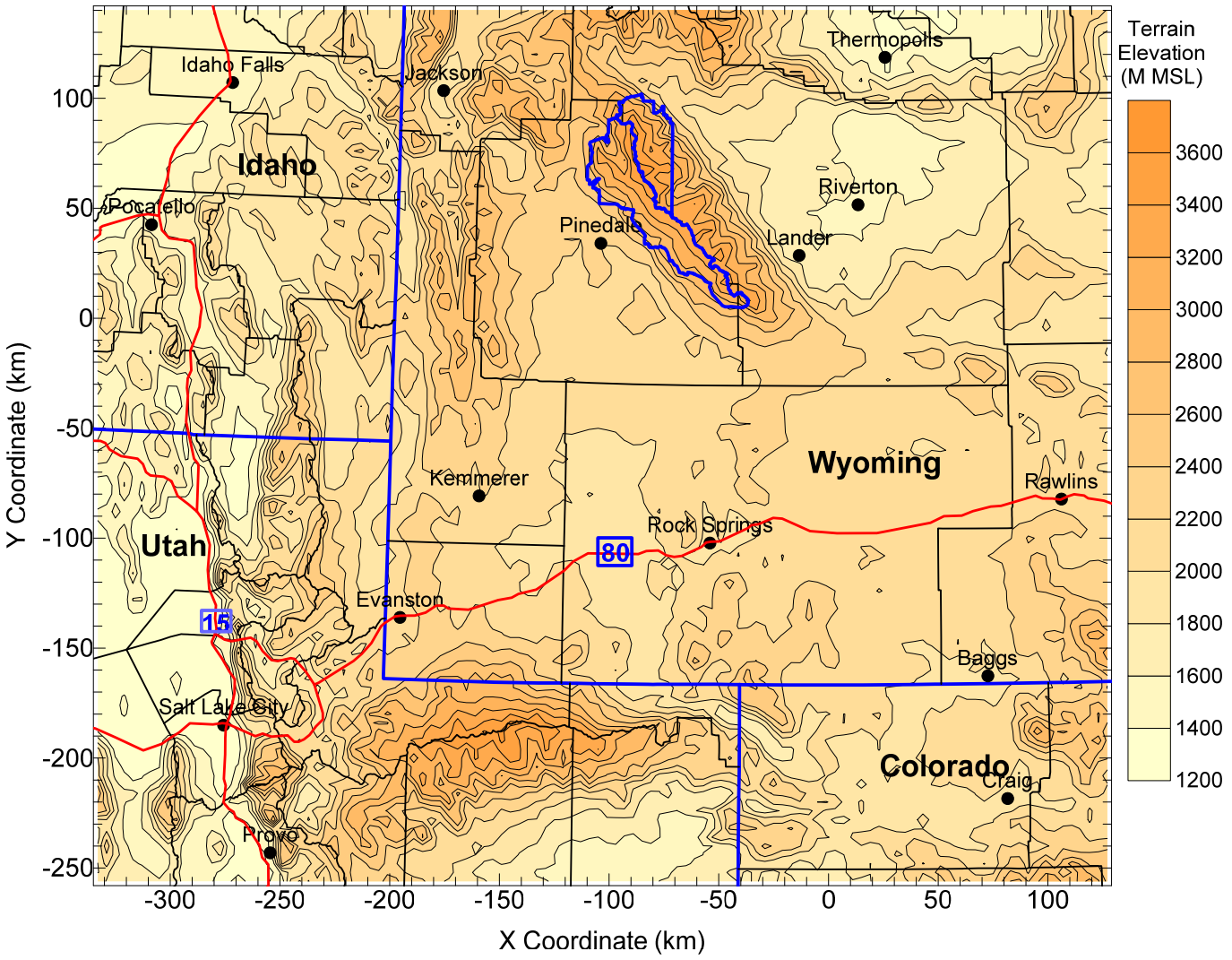
Evaluation and Testing of v6.42b

- **SWWYTAF 1995 dataset**
  - Evaluation of actual emissions in SW Wyoming and surrounding area
  - Large-scale, long range transport for a full year (1995)
  - Concentrations at Bridger IMPROVE and Pinedale CASTNet monitors
- **Cumberland Plume Study Dataset (1999)**
  - In-plume/single-event
- **Intercomparison tests with ISORROPIA II in CMAQ v5.0**
  - Over three million Monte Carlo cases evaluated for a wide range of conditions

SWWYTAF Model Evaluation

- **Meteorological Data:**
  - MM5 4-km data
  - CALMET run in no-observations mode for all scenarios
  - 24 vertical layers
- **Total sources: 1776**
  - Point, area, and boundary sources
  - Constant annual, monthly variable sources
  - Time variable (CEM) sources
- **Air Quality Data:**
  - Bridger IMPROVE and Pinedale CASTNet Sites
  - NADP Deposition Sites

SWWYTAF CALMET Domain

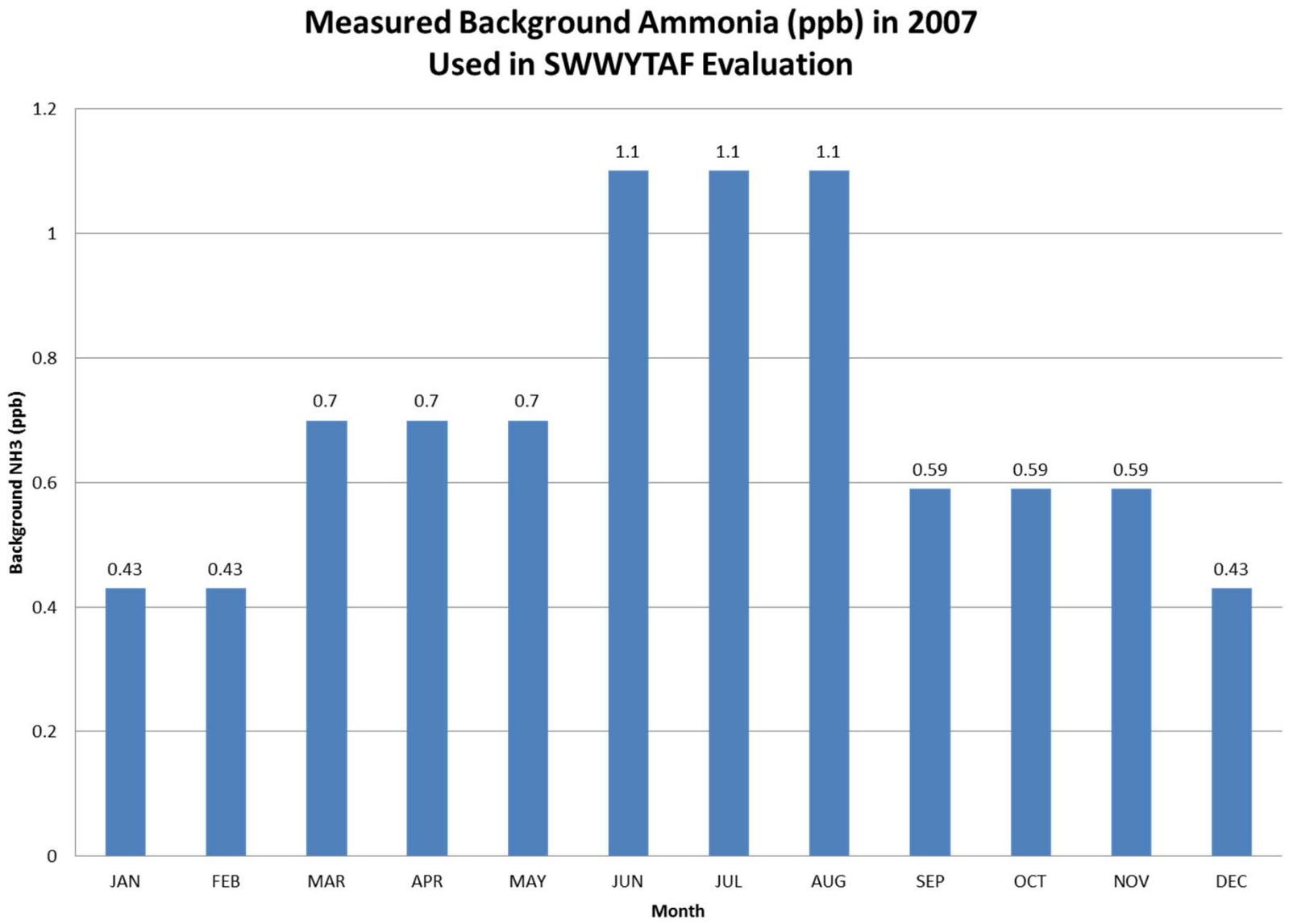


SWWYTAF Scenarios

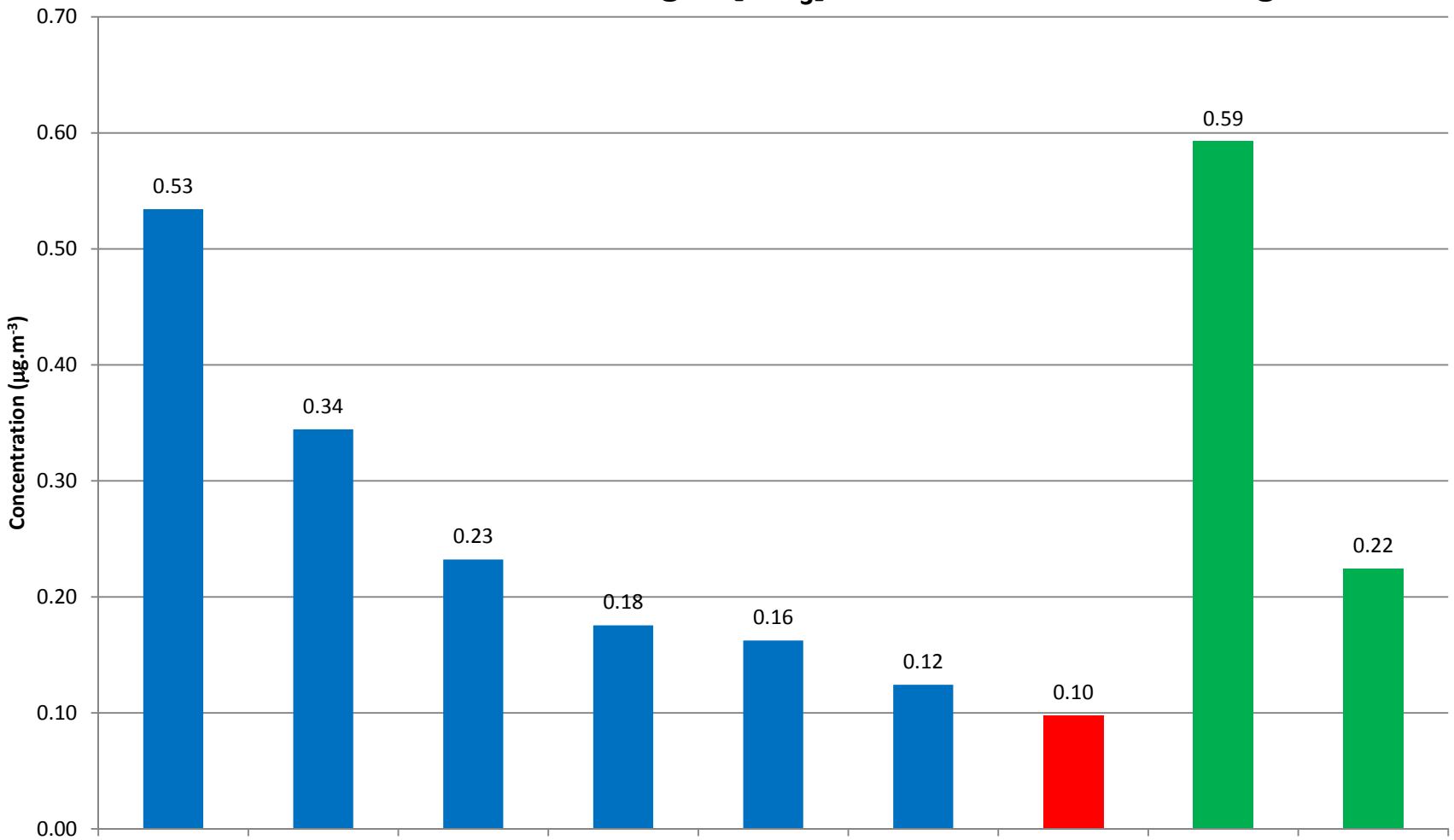
- **Gas phase chemistry**
  - MESOPUFF II scheme
  - Modified RIVAD (API chemistry)
  - With and without Ammonia Limited Method (ALM) applied in postprocessing step
- **Aerosol chemistry**
  - Original CALPUFF (CHEMEQ) method (Stelson & Seinfeld, 1982)
  - ISORROPIA II (Nenes, Pandis & Pilinis, 1998)
- **Background Ammonia**
  - Constant (1 ppb) background NH_3
  - Seasonally-varying 2007 measured background
- **Wet scavenging/Aqueous phase chemistry**
  - Scavenging coefficient/ No AQ chemistry
  - Aqueous phase chemistry (surrogate and 3D liquid water)

Aqueous-Phase: Cloud Water

- **Cloud Liquid Water Content Option MLWC=0**
  - Surrogate cloud-cover and precipitation data
  - LWC = 0.1 g/kg for non-precipitating clouds
  - LWC = 0.5 g/kg for precipitating clouds
  - In-cloud SO_2 conversion rate apportioned to puff mass by cloud-cover fraction
  - Vertical distribution of cloud water is not addressed
  - Cloud-cover observations are spatially sparse
- **Cloud Liquid Water Content Option MLWC=1**
  - MM5/WRF 3D LWC provides detailed vertical and horizontal resolution
  - CALMET modified to pass 3D LWC data to CALPUFF via CALMET.AUX file
  - CALPUFF uses only LWC that overlaps puff mass distribution

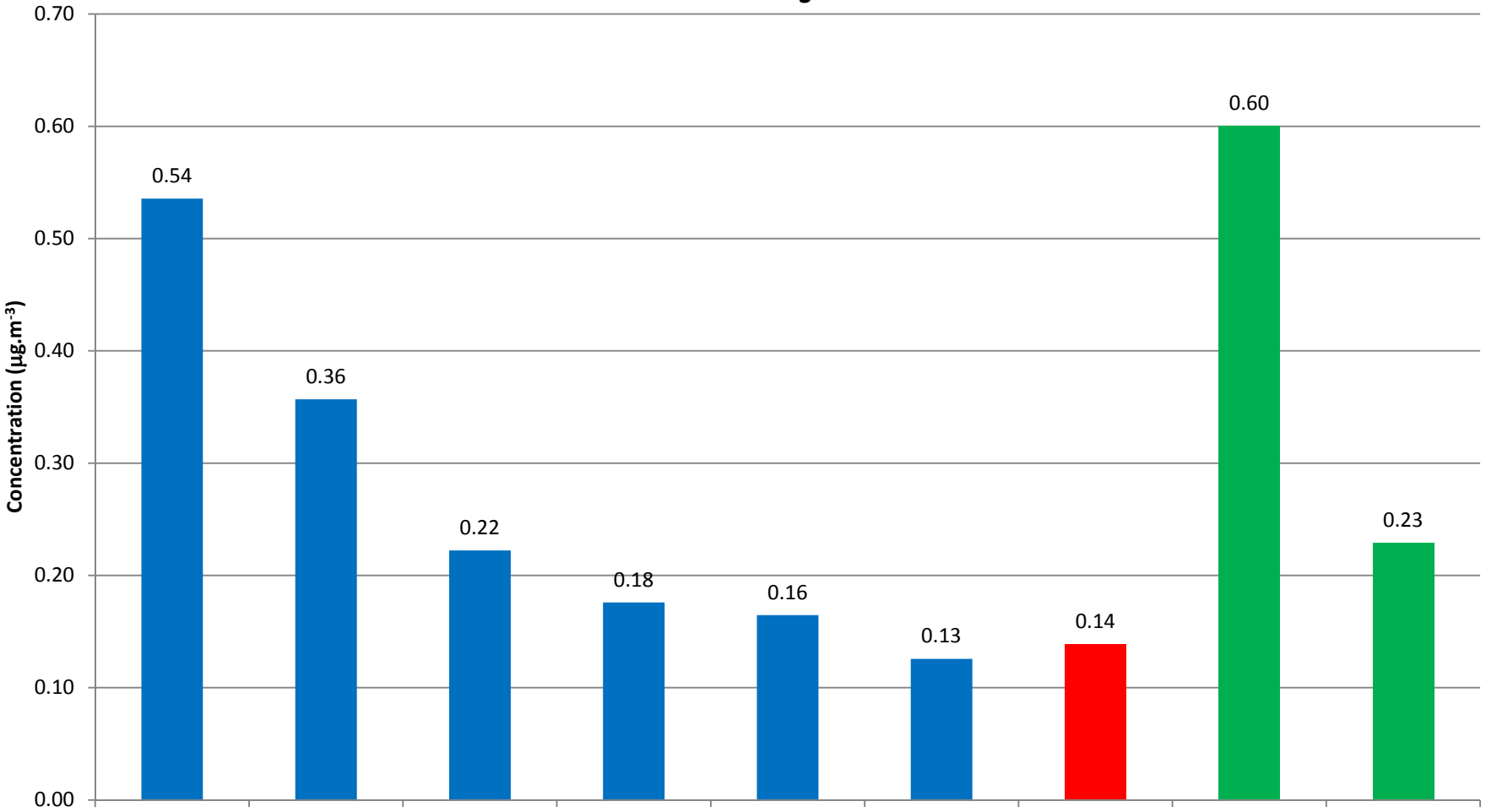

Measured Background Ammonia (ppb) in 2007
Used in SWWYTAF Evaluation
Background NH3 (ppb)
1.2
1
0.8
0.6
0.4
0.2
0
0.43
0.43
0.7
0.7
0.7
1.1
1.1
1.1
0.59
0.59
0.59
0.43
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
Month

Observed and Predicted Averaged [NO_3] in Different Cases at Bridger



Scenario:	Base	Base + ALM	Run A	Run B	Run C	Run C + ALM	Observed	Base2	Run C2
Chemistry:	MESOPUFF II CHEMEQ	MESOPUFF II CHEMEQ/ALM	Modified RIVAD ISORROPIA	Modified RIVAD ISORROPIA	Modified RIVAD ISORROPIA	Modified RIVAD ISORROPIA/ALM		MESOPUFF II CHEMEQ	Modified RIVAD ISORROPIA
Aqueous chem:	No	No	No	Yes	Yes	Yes		No	Yes
Wet dep:	Scav coef.	Scav coef.	Scav coef.	Default LWC	MM5 LWC	MM5 LWC		Scav coef	MM5 LWC
Background NH3	2007 OBS	2007 OBS	2007 OBS	2007 OBS	2007 OBS	2007 OBS		1 ppb	1 ppb

Observed and Predicted Averaged [NO_3] in Different Cases at Pinedale



Scenario:	Base	Base + ALM	Run A	Run B	Run C	Run C + ALM	Observed	Base2	Run C2
Chemistry:	MESOPUFF II CHEMEQ	MESOPUFF II CHEMEQ/ALM	Modified RIVAD ISORROPIA	Modified RIVAD ISORROPIA	Modified RIVAD ISORROPIA	Modified RIVAD ISORROPIA/ALM		MESOPUFF II CHEMEQ	Modified RIVAD ISORROPIA
Aqueous chem:	No	No	No	Yes	Yes	Yes		No	Yes
Wet dep:	Scav coef.	Scav coef.	Scav coef.	Default LWC	MM5 LWC	MM5 LWC		Scav coef	MM5 LWC
Background NH3	2007 OBS	2007 OBS	2007 OBS	2007 OBS	2007 OBS	2007 OBS		1 ppb	1 ppb

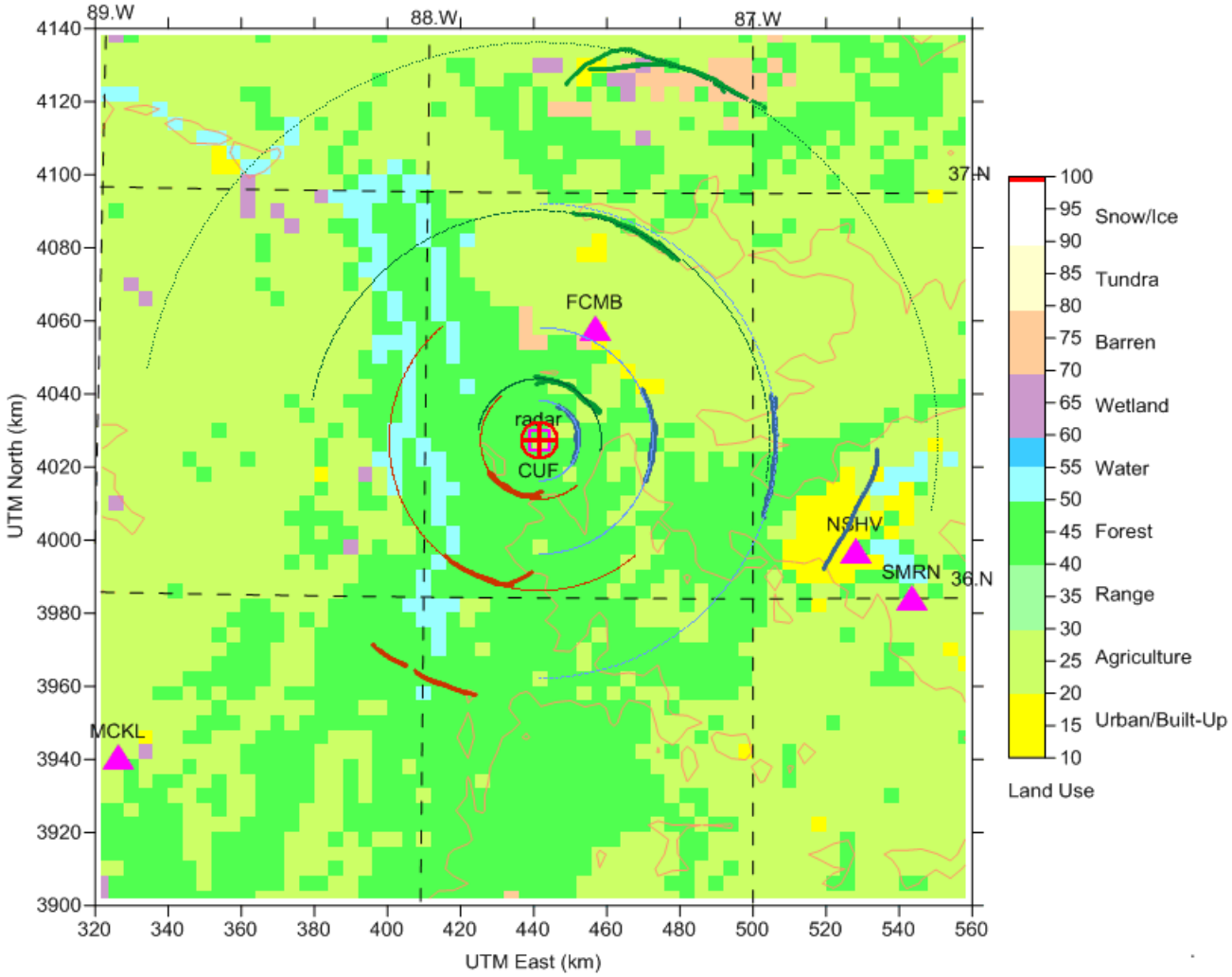
SWWYTAF Summary

- **CALPUFF using constant ammonia with old chemistry overpredicts nitrate by about 4-6x at Bridger and Pinedale, WY**
- **ISORROPIA-v2.1 in CALPUFF-v6.42b substantially improves performance of the model**
- **Use of seasonally-varying ammonia, which shows substantial variability improves performance**
- **Use of aqueous phase chemistry with MM5 3D cloud data produces the overall best results**
- **ALM is important with MESOPUFF II chemistry but results with ISORROPIA are less sensitive to ALM**

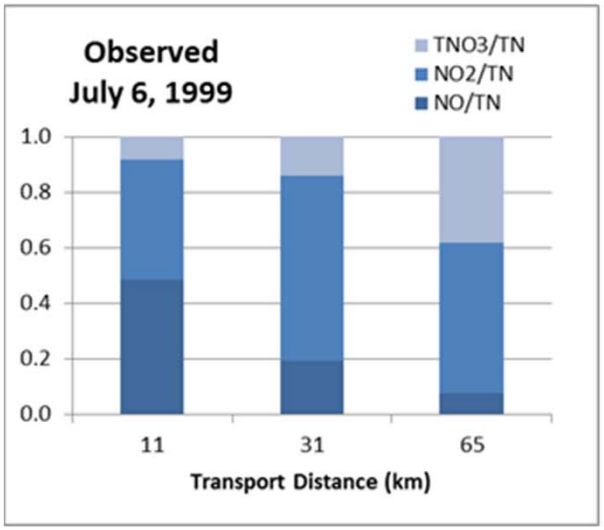
July 1999 Cumberland Plume Study

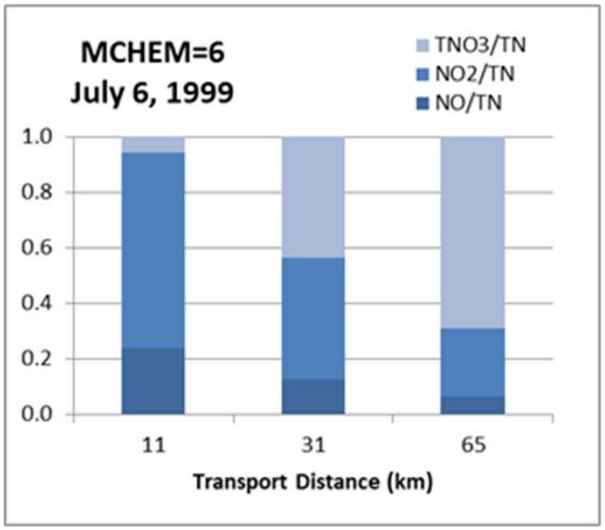
- **Modules Tested**
  - MCHEM=6: Updated RIVAD implementation with ISORROPIA V2.1 gas-particle phase equilibrium
  - MCHEM=3: Original RIVAD implementation with CHEMEQ gas-particle phase equilibrium
  - MCHEM=1: MESOPUFF II transformation with CHEMEQ gas-particle phase equilibrium
- **Data**
  - Plume chemistry measurements (aerial sampling)
  - Hourly emissions (SO_2, SO_4, NO, NO_2)
  - RADAR wind profiles at the source
  - Tabulated hi-vol data from study report (Tanner et al., 2002)
  - Hourly WMO surface met. reports, 2/day Nashville radiosondes

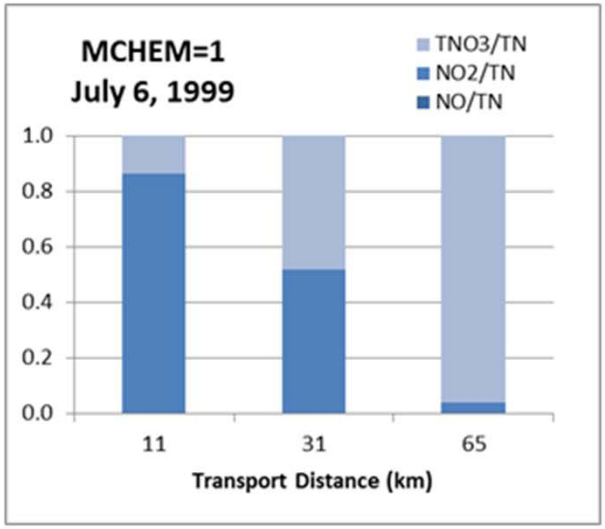
RADAR Wind Profiler at Stack (CUF)
Hourly Surface Meteorology at Triangles, 2/day RAOB Profiles Near NSHV (Nashville)
Aircraft Sampling Locations (blue-grey [E] = July 6; red [SSW] = July 13; green [NNE] = July 15)
High-Resolution CALPUFF Receptors Along Arcs

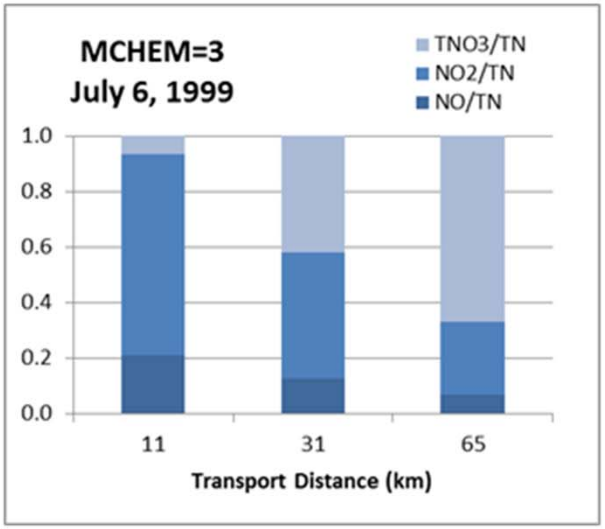


July, 1999 Cumberland Plume Study

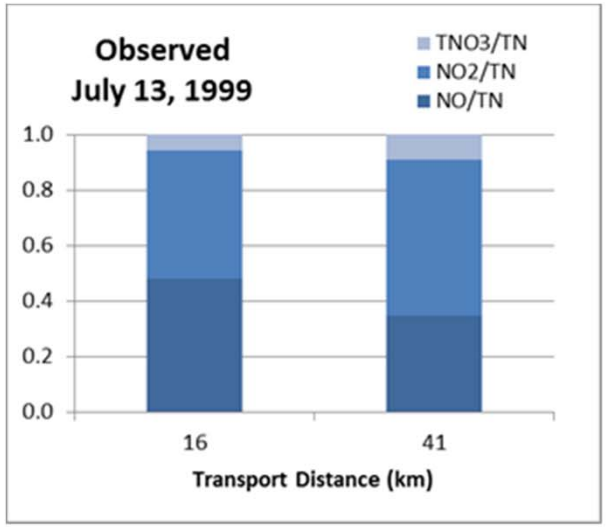


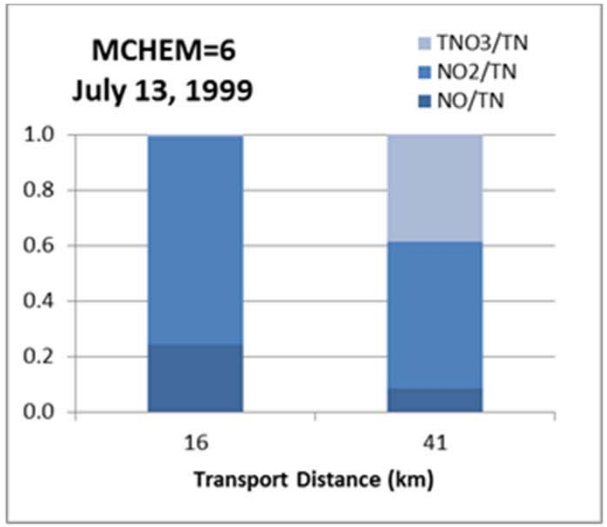


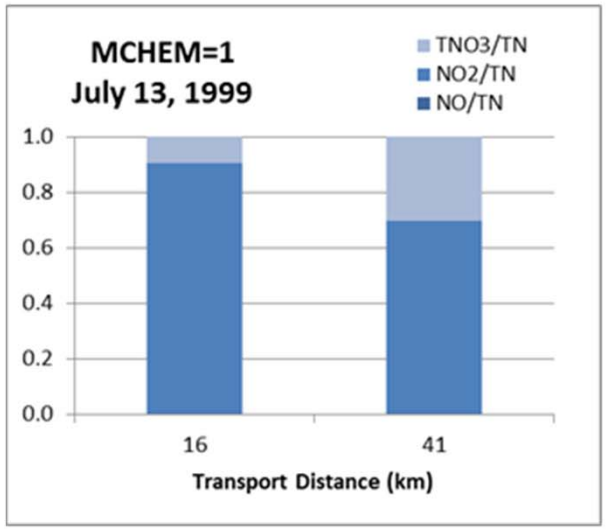


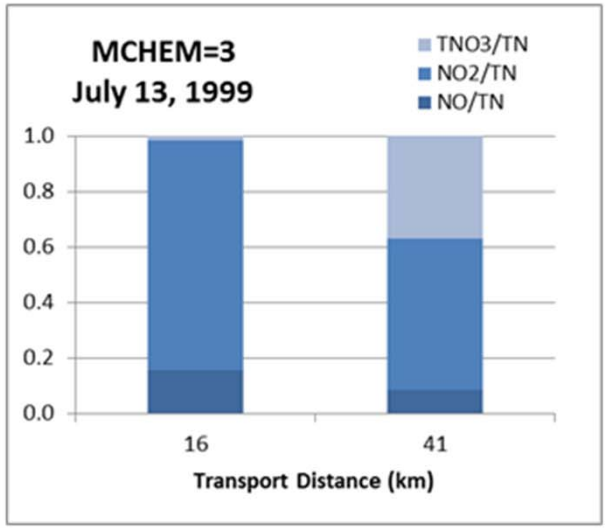


July, 1999 Cumberland Plume Study

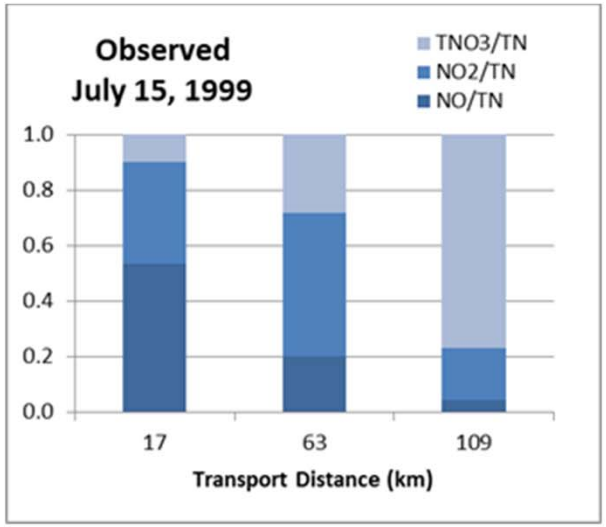


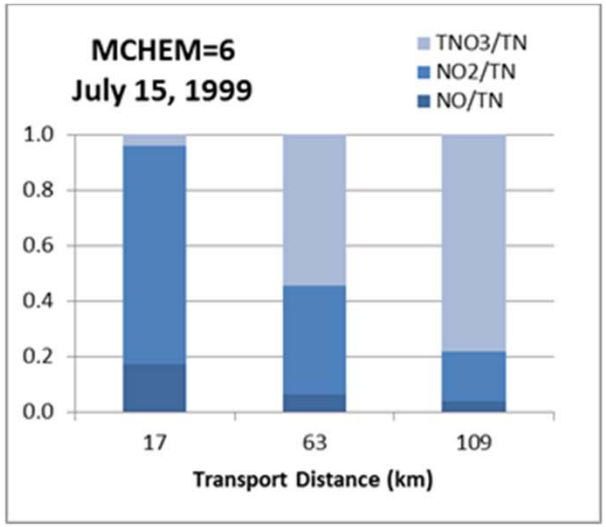


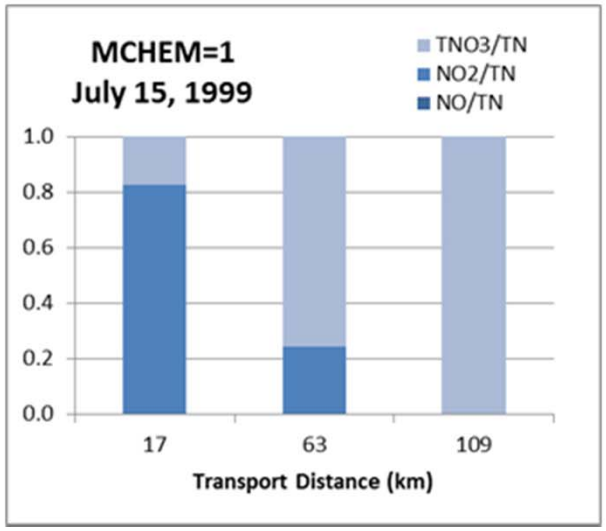


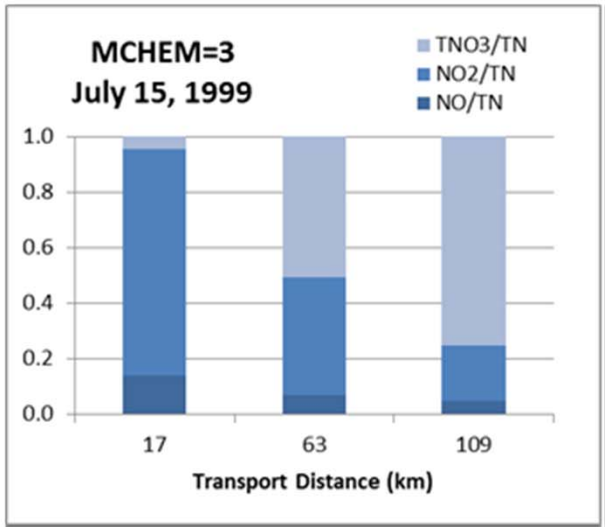


July, 1999 Cumberland Plume Study









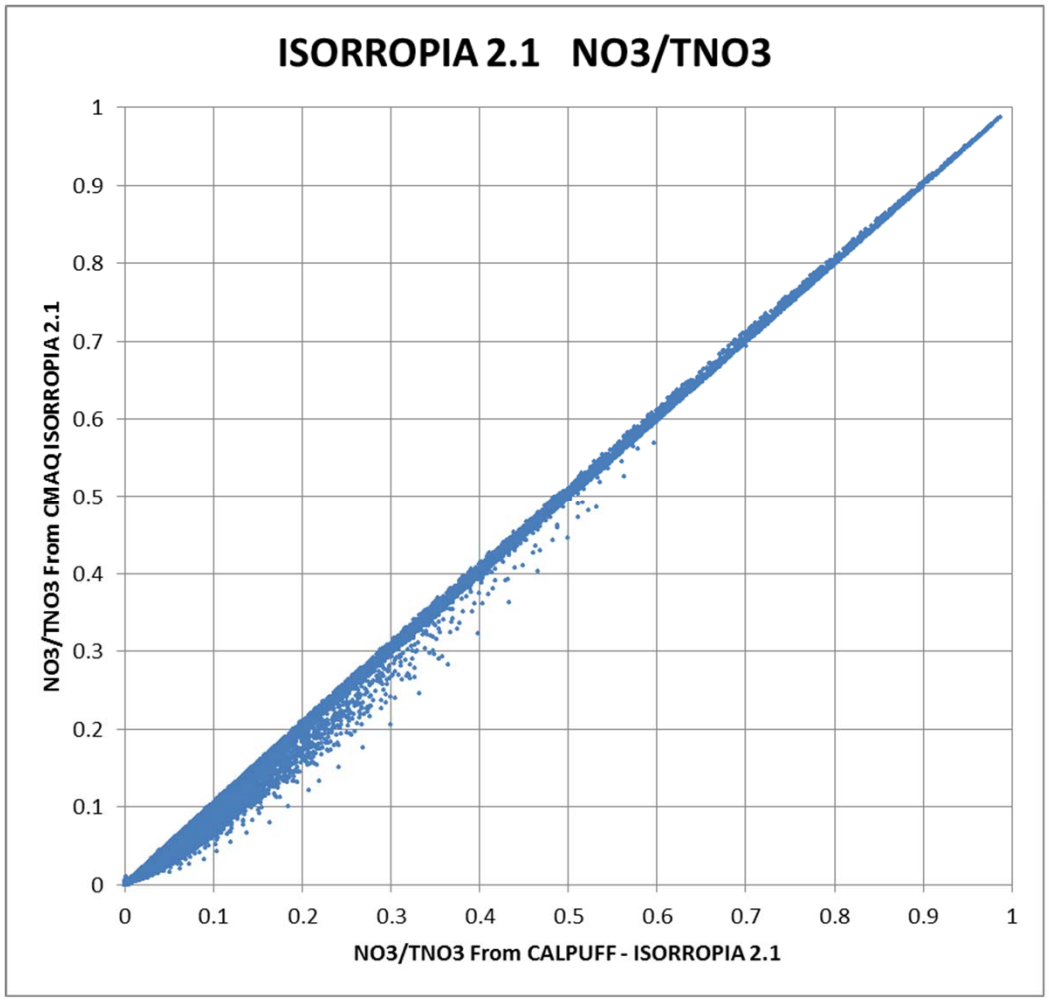
Cumberland Plume Summary

- **Revised and original RIVAD implementations are nearly equivalent in modeling the NO_x transformation data for this plume, and improve model performance relative to MESOPUFF II**
- **Updated RIVAD implementation improves modeled SO_4 Conversion Rate**
  - Upper-bound rate on July 15 at 63 km and 109 km = 3.4%/hr (+/-1.2)
  - RIVAD(updated) = 2.7 to 2.9 %/hr (MCHEM=6)
  - RIVAD = 4.2 to 4.4 %/hr (MCHEM=3)
  - MESOPUFF II = 1.8 to 2.1 %/hr (MCHEM=1)
- **Modeled plume nitrate is nearly all HNO_3, with little particulate NO_3, consistent with the partition expected for the indicated meteorological conditions**

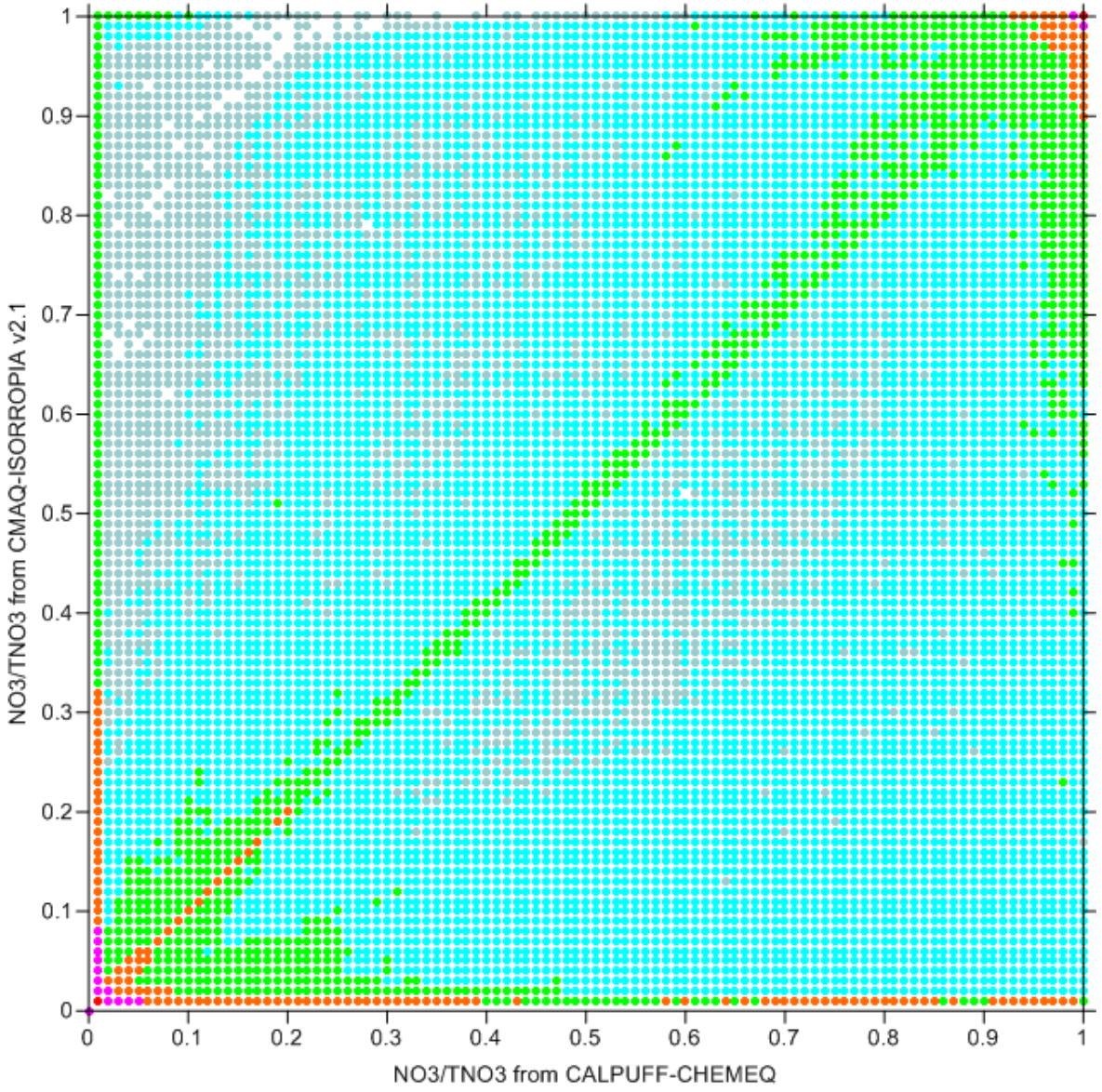
ISORROPIA II in CMAQ v5.0

- **CMAQ v5.0 released February 2012**
- **Subroutines in CALPUFF and CMAQ compared**
  - Bug in array assignment fixed in CMAQ version, and several lines are re-activated
  - New version of ISORROPIA is expected soon
- **Evaluation**
  - Monte Carlo driver compares equilibrium ratio of particulate NO_3 to total nitrate (TNO_3 = NO_3 + HNO_3) for range of temperature, relative humidity, and total concentrations of sulfate, nitrate, NH_3
  - Differences in NO_3 / TNO_3 ratios are less than 0.01 in over 99% of the simulations made, and less than 0.1 in all 3 million simulations
  - Compared to CHEMEQ, differences between the two schemes can range up to 100% of the total nitrate, although over 63% of the simulations result in a difference in the NO_3/TNO_3 ratio less than 0.01 and over 84% result in a difference less than 0.10

ISORROPIA II in CMAQ and CALPUFF



OLD CALPUFF (CHEMEQ) vs CMAQ



Summary - 1

- **CALPUFF v6.42b includes significant improvements in the treatment of chemical reactions**
  - ISORROPIA II model for inorganic gas-particle equilibrium as in CMAQ
  - Revised gas phase chemical transformation module for SO_2 conversion to sulfate and NO_x conversion to nitric acid and nitrate
  - Aqueous phase oxidation and wet scavenging module adapted from the RADM cloud implementation in CMAQ/SCICHEM, with access to 3D cloud water fields from MM5/WRF
  - New option for anthropogenic secondary organic aerosol (SOA) formation based on the CalTech SOA routines implemented in CMAQ-MADRID

Summary – 2

- **SWWYTAF evaluations with enhanced resolution MM5 meteorological data demonstrates significant improvement in performance over the default FLAG (2010) chemistry options**
- **Large overprediction of average observed nitrate concentrations with the older chemistry mechanism is reduced or eliminated with new chemistry**
- **Cumberland plume simulations indicate O_3 depletion improves the modeled sulfate transformation rate, and both RIVAD module options improve modeled NO_x transformation at large distances**

Conclusions

- **New chemistry modules in v6.42b use well-established algorithms referenced in the referred literature and almost universally accepted in the modeling community as better science**
- **CALPUFF v6.42b is backwardly compatible with v5.8 (after bug fixes are introduced into v5.8). CALPUFF should be adopted as a replacement for v5.8 to allow access to 7 years of optional model improvements, including the new chemistry. Because v6.42b is equivalent to v5.8 when run in the same mode, v6.42b is an equivalent model.**
- **New chemistry can and should be accepted under Section 3.2 of Appendix W**
  - Section 3.2 is designed to allow use of important model enhancements in a timely way on a case-by-case basis, without the 3-5 year wait for formal rulemaking
  - BART rule indicates CALPUFF is acceptable but also allows for alternative models
- **EPA should approve v6.42b on case-by-case basis for use in BART applications**