Implementation and Testing of EQUISOLV II in the CMAQ Modeling System

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Presentation Outline

- Background and Objectives
- Box Model Comparison
- 3-D Testing and Evaluation
  - Episode, Model Configuration, Available Measurements
  - Preliminary Results
- Summary and Future Work

Background and Objectives

- **Background**
  - Thermodynamic equilibrium affects gas-particle partitioning and PM formation (e.g., nitrate, ammonium, chloride);
  - Uncertainties in experimental data (e.g., activity coefficients, DRH);
  - Numerical difficulties in simulating a mixed-phase system;
  - Existing modules are computationally efficient but numerically less accurate and vice versa.
- **Objectives**
  - Improve EQUISOLV II in terms of numerical accuracy and computational speed;
  - Incorporate EQUISOLV II into CMAQ and CMAQ-MADRID as an alternative thermodynamic module to ISORRPIA;
  - Apply and evaluate CMAQ-EQUISOLV II's performance for the 12-28 June 1999 episode.

Main Features of ISORROPIA and EQUISOLV II

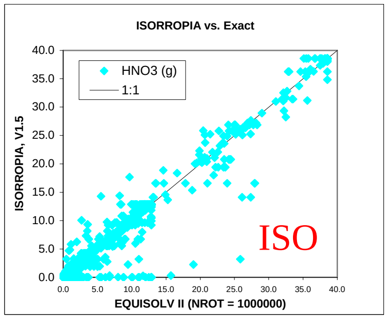
	ISORROPIA	EQUISOLV II
System solved	NH_4-Na-NO_3-SO_4-Cl	NH_4-Na-Ca-Mg-K-NO_3-SO_4-Cl-CO_3
Equilibrium reaction/ chemical species	15 reactions 21 species (3 gases, 9 liquids, 9 solids)	18 reactions 26 species (4 gases, 13 liquids, 9 solids)
Solution method	Iterative bisection Iterative bisection-Newton for H^+	Mass Flux Iteration (MFI) and Analytical Equilibrium Iteration (AEI)
Chemical regime	Subdomains (sulfate very rich/rich/poor)	Full domain
Activity coefficient	Binary - Kusik and Meissner, 1978 Multi-component – Bromley, 1973 Precalculated lookup table	Binary - Hamer and Wu, 1972; Goldberg, 1981; Bassett and Seinfeld, 1984; Filippov et al., 1985; and Pitzer, 1991 Multi-component - Bromley method, 1973 Precalculated lookup tables
Temperature-dependence	Equilibrium constants, DRHs	Equilibrium constants, DRHs, activity coefficients, solute and water activity coefficients down to 190 K for several species
Solid treatment	(1) Solid formed when RH < MDRH (meta-stable) (2) No solid formation for all RHs (liquid only)	(1) Solid formed when RH < CRH (meta-stable) (2) Solid formed when RH < DRH (stable) (3) No solid formation for all RHs (liquid only)
Size-resolved equilibrium	No	Yes
3-D implementation	Single-cell only	(1)Single-cell (2)Multiple-cell (vectorization)
Reference	Nenes et al., 1998, 1999	Jacobson et al., 1996; Jacobson, 1999 a & b

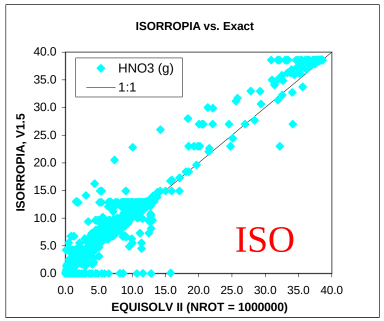
Box Model Test Conditions

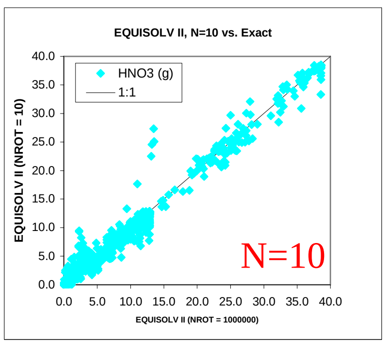
$[H_2SO_4]$, μg m^{-3}	5	20
TNH4/TSO4	2 -16	0.5 - 4
TNO3/TSO4	1.32 - 12	0.33 -3
TNaCl/TSO4	0, 2-8	0, 0.5-2
Temperature, K	278, 288, 298, 308	278, 288, 298, 308
RH, %	1-100	1-100
Solid treatment	Solid formed when RH < CRH; No solid for all RHs	Solid formed when RH < CRH; No solid for all RHs
Iteration number used in EQUISOLV II, N	10, 100, 10000, 1000000 Benchmark: 1000000	10, 100, 10000, 1000000 Benchmark: 1000000
Total number of cases	1120	1120
Total number of simulations	(1120 + 1120 × 4 N) × 2 solid treatments = 11,200	(1120 + 1120 × 4 N) × 2 solid treatments = 11,200

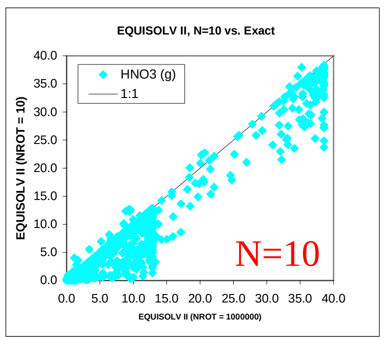
Box Model Results: $HNO_3(g)$

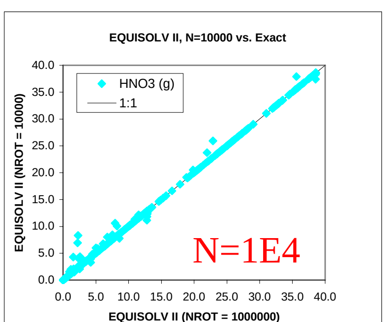
TSO4 = 5 TSO4 = 20

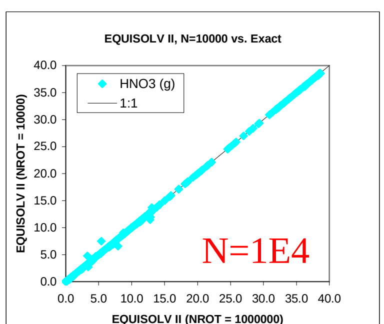


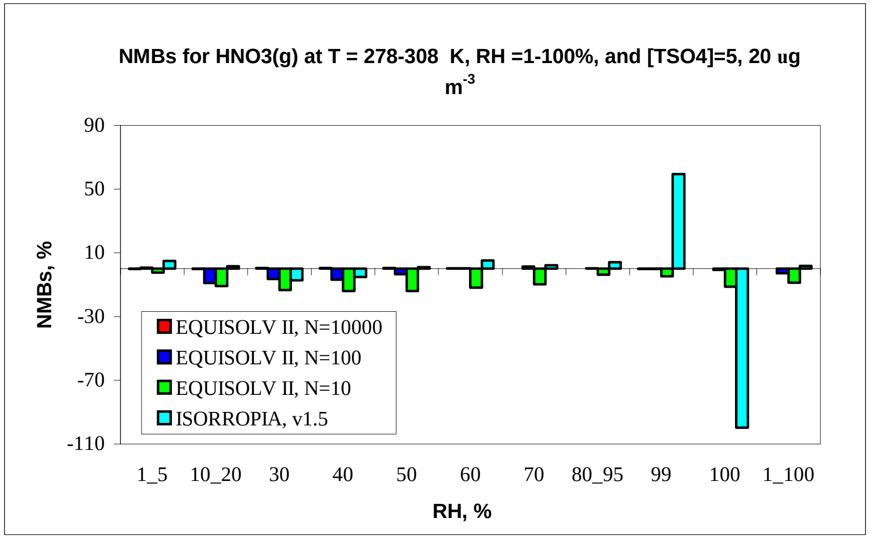


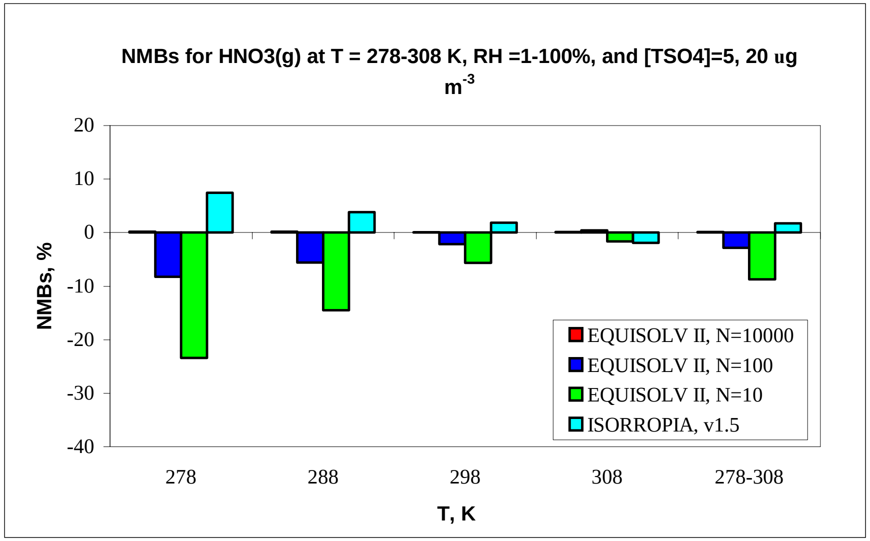






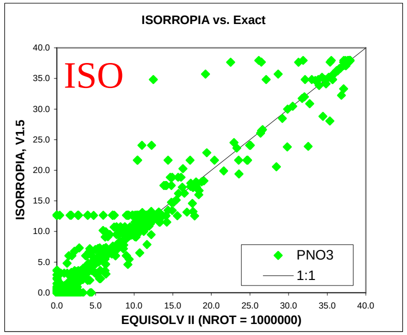


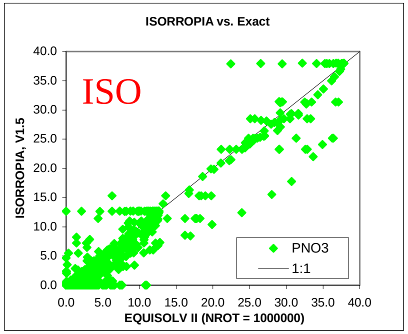


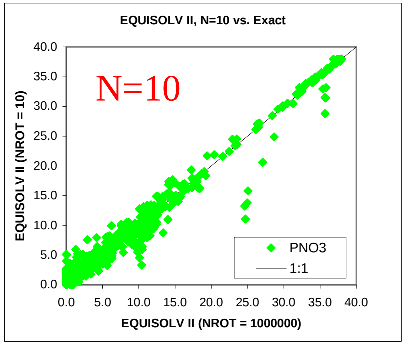


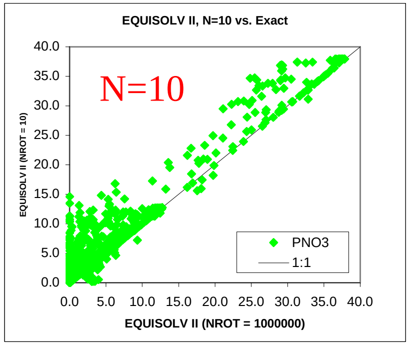
Box Model Results: NO_3^-

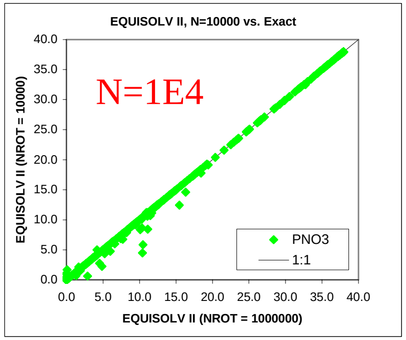
TSO4 = 5 TSO4 = 20

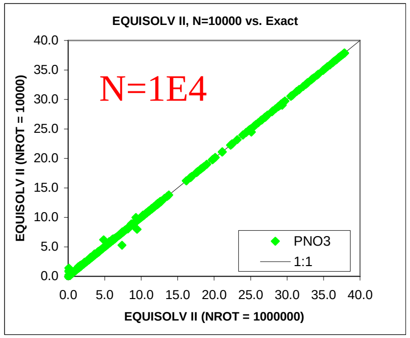


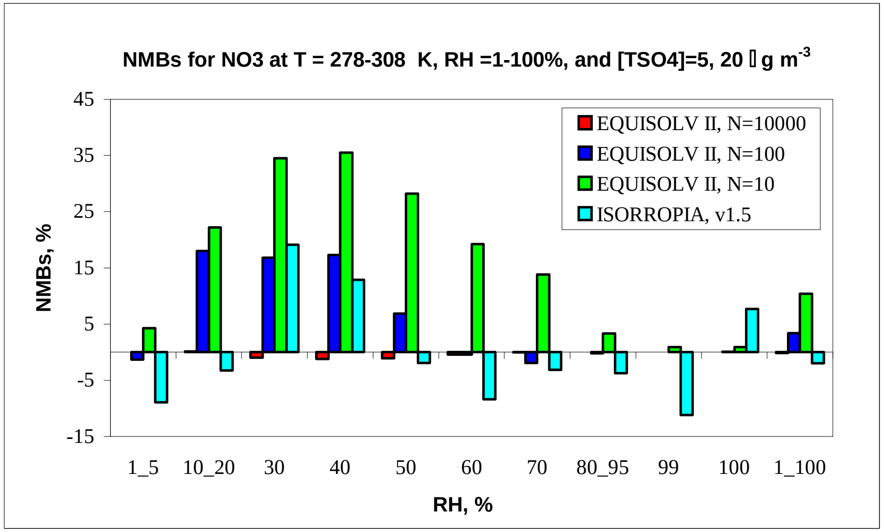


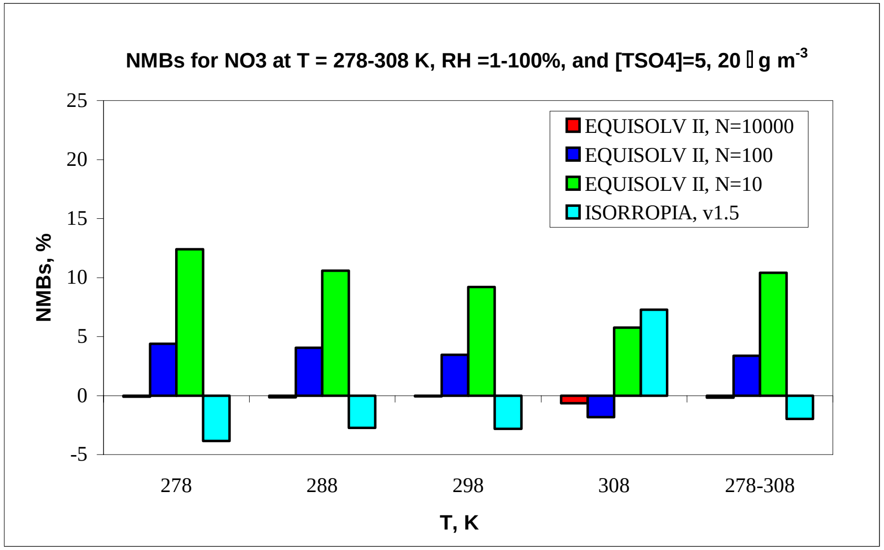






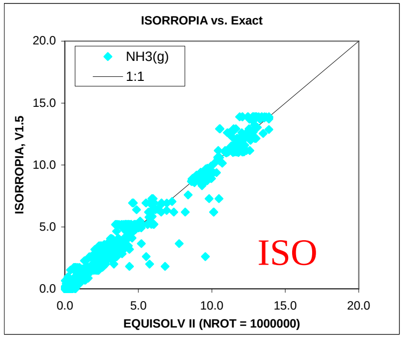


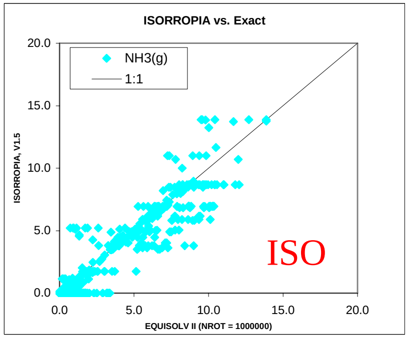


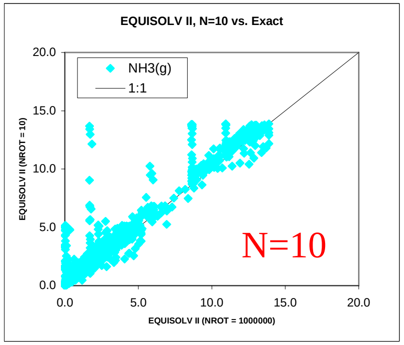


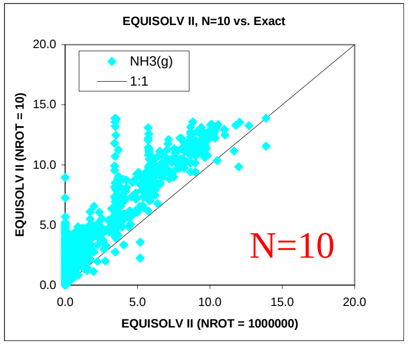
Box Model Results: $NH_3(g)$

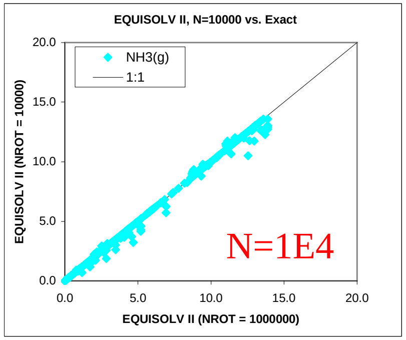
TSO4 = 5 TSO4 = 20

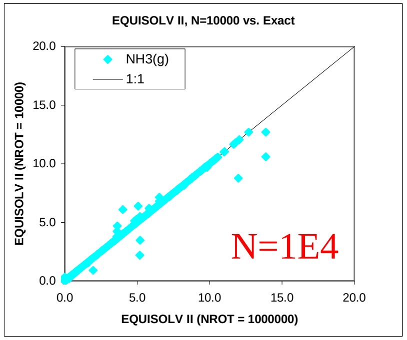


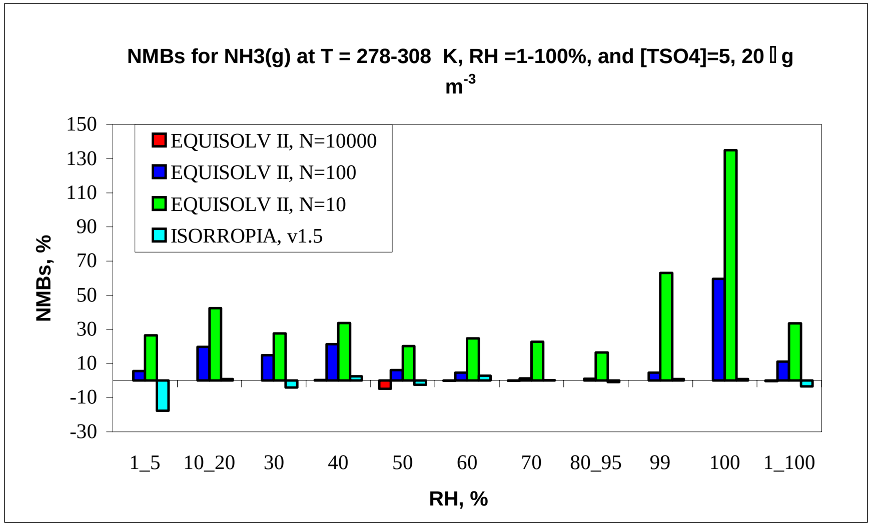


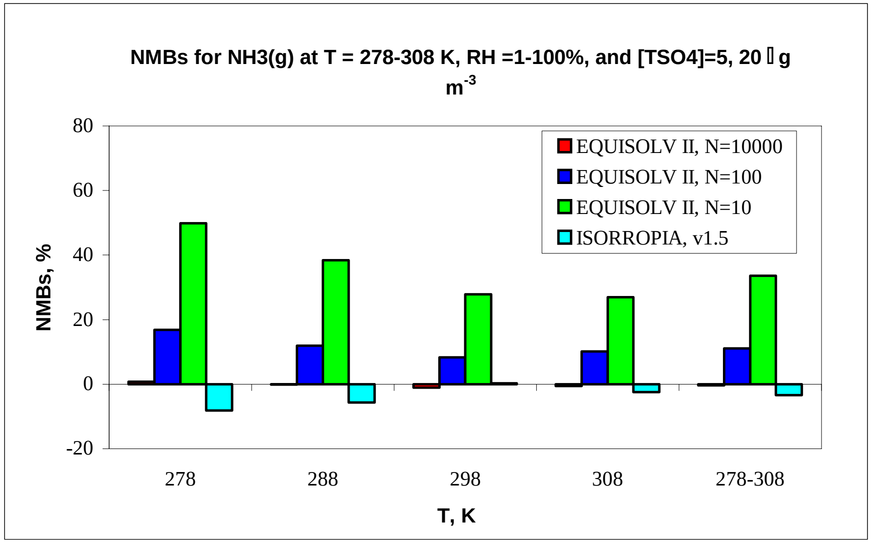






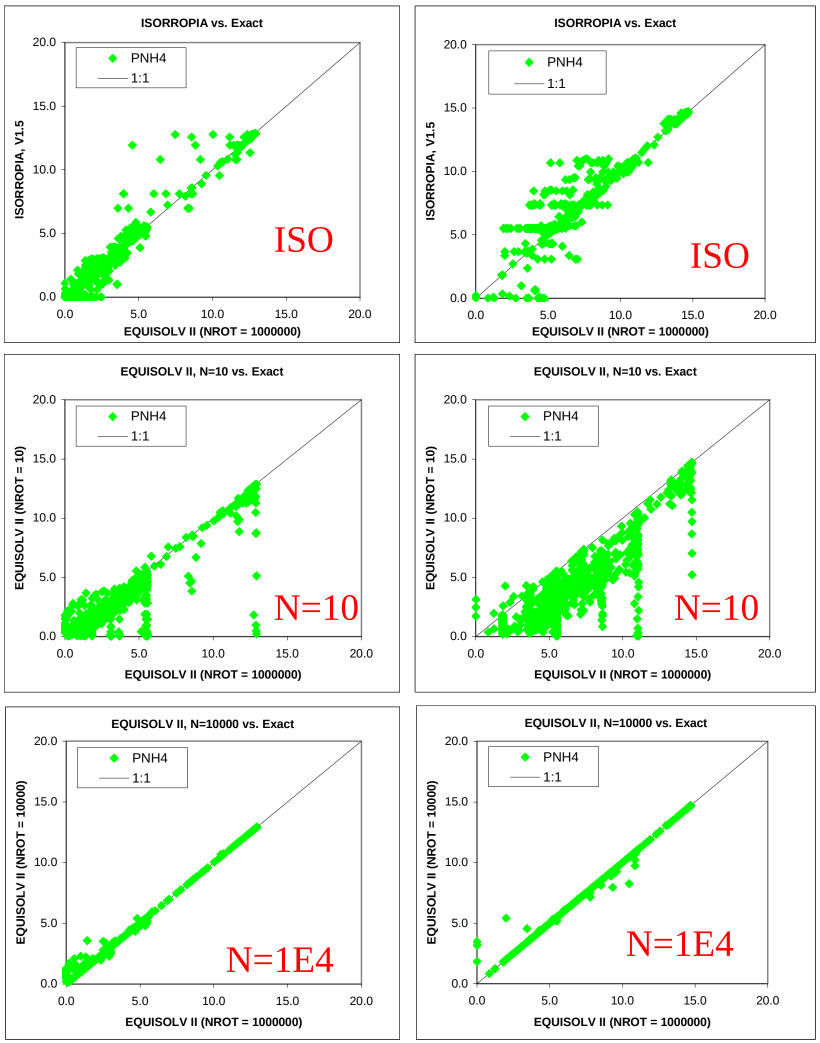


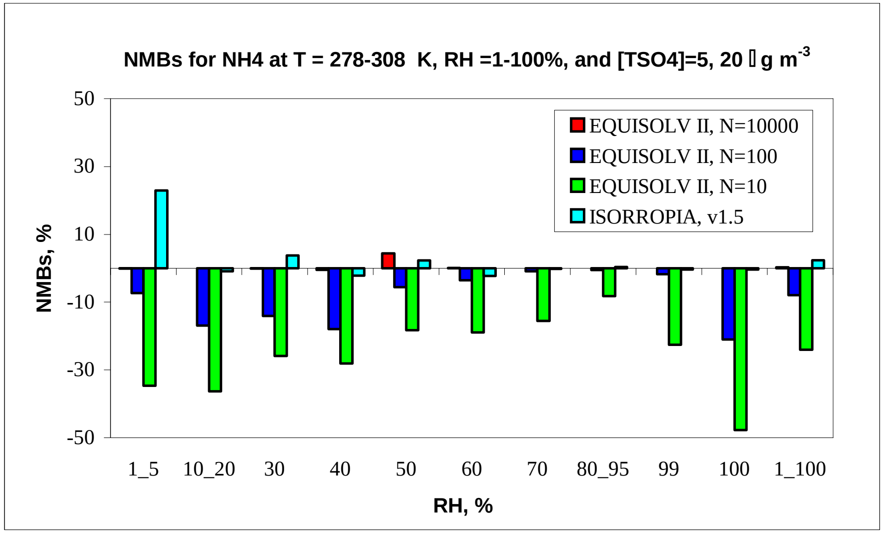


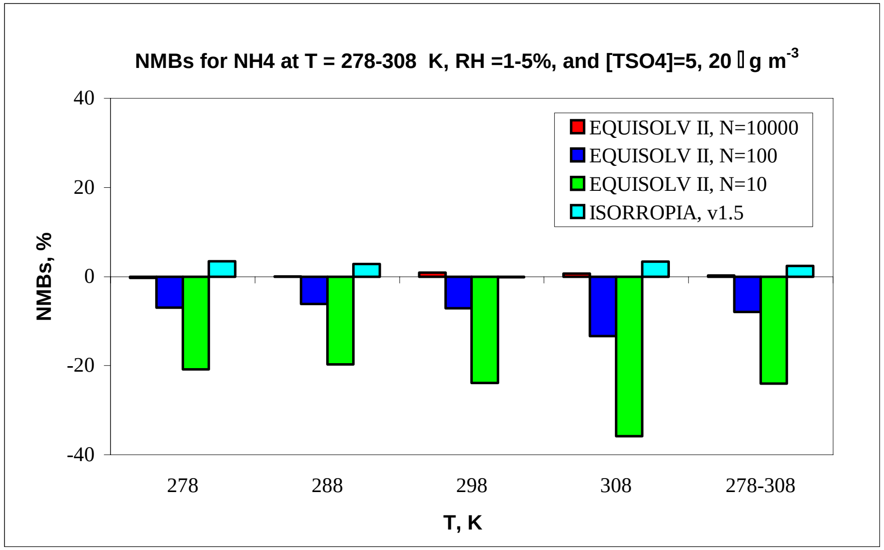


Box Model Results: NH_4^+

TSO4 = 5 TSO4 = 20

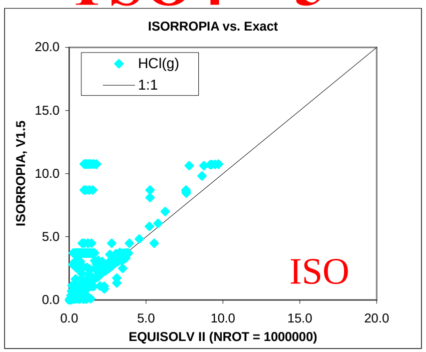


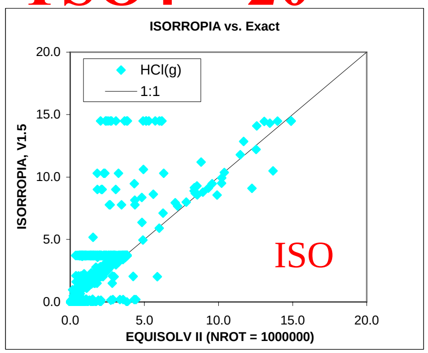


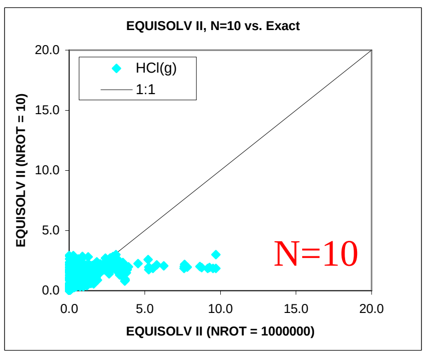


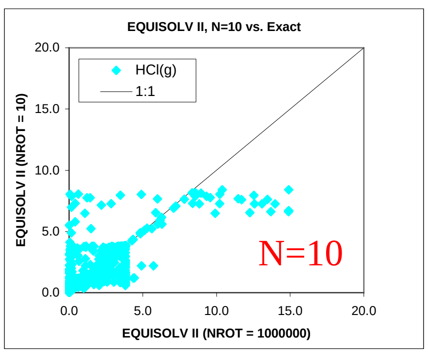
Box Model Results: HCl(g)

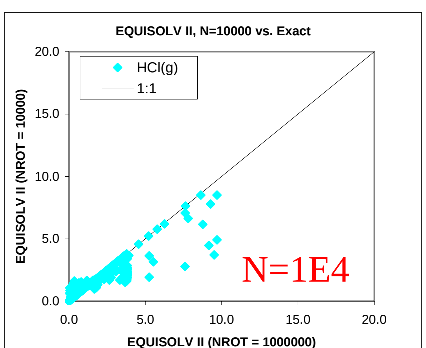
TSO4 = 5   TSO4 = 20

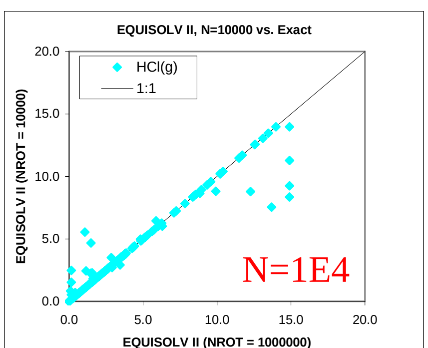


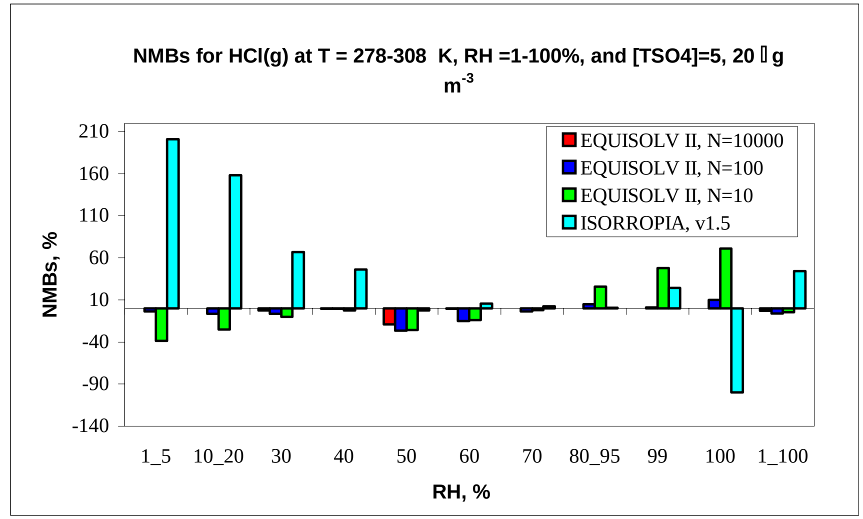


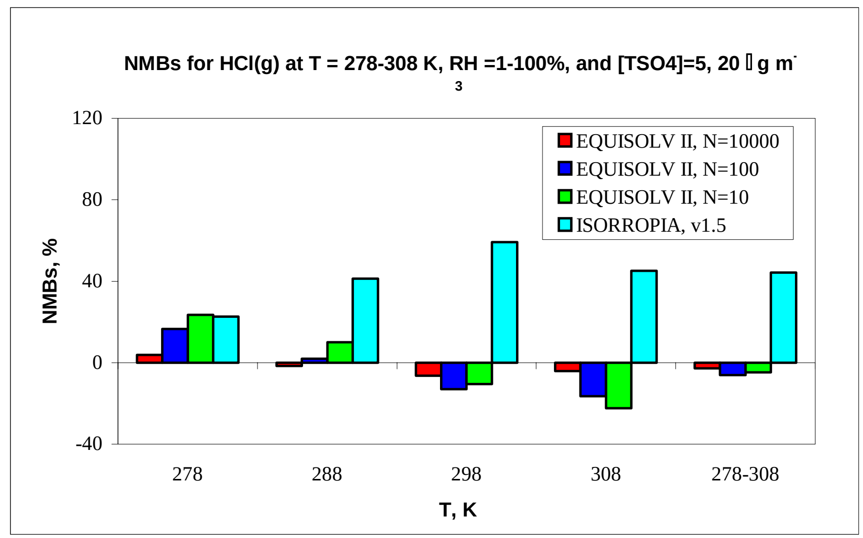






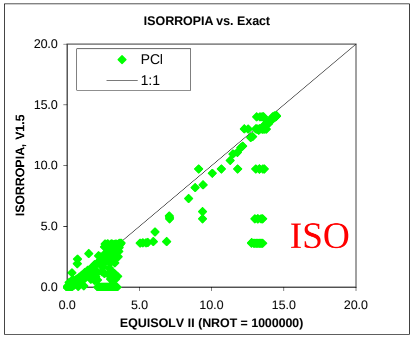


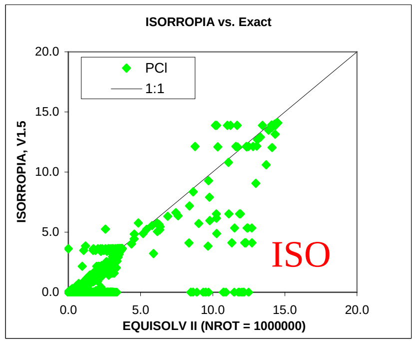


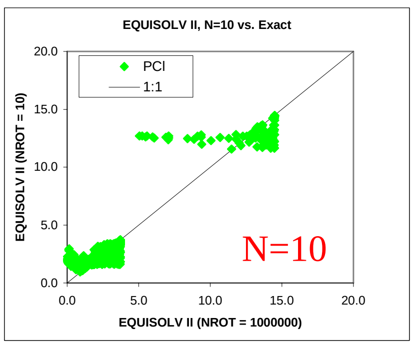


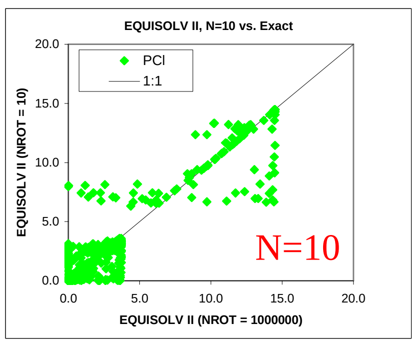
Box Model Results: Cl^-

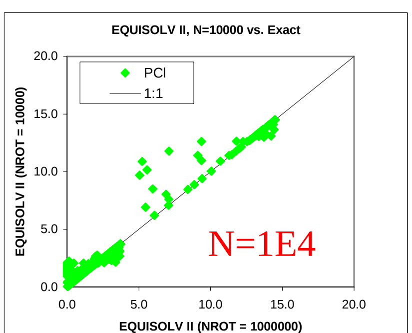
TSO4 = 5   TSO4 = 20

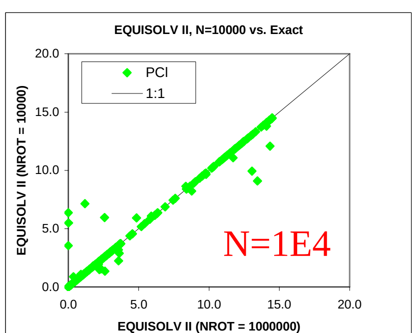


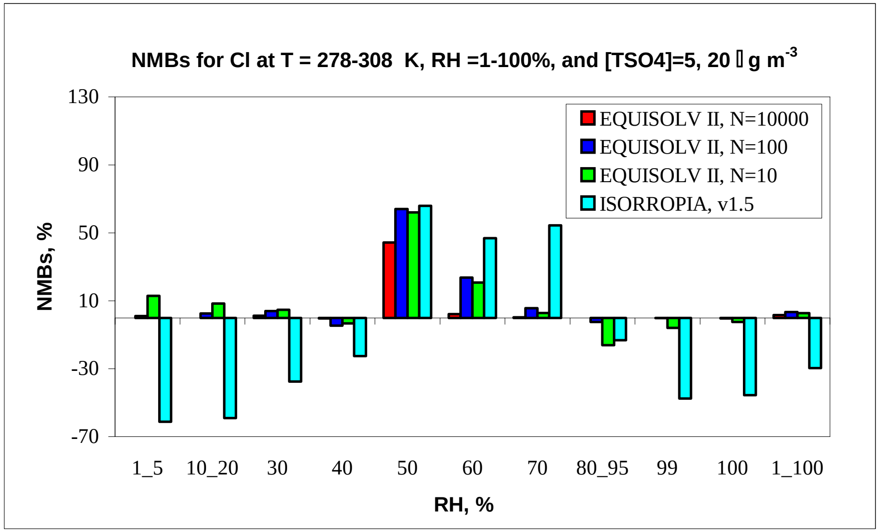


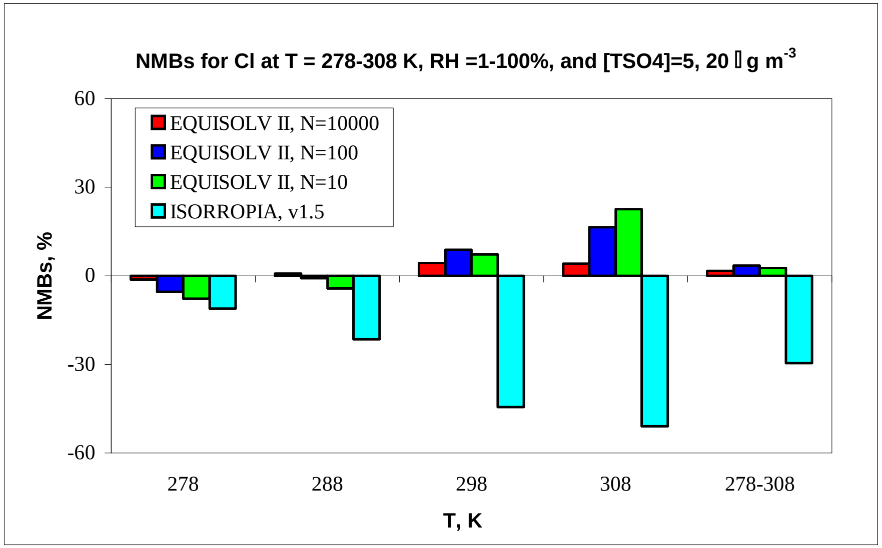












Differences in Equilibrium Reactions

EQUISOLV II

1. $NH_3(g) + H^+ \Leftrightarrow NH_4^+$
2. $NH_3(g) + HNO_3(g) \Leftrightarrow NH_4^+ + NO_3^-$
3. $NH_4Cl(s) \Leftrightarrow NH_4^+ + Cl^-$
4. $NH_4NO_3(s) \Leftrightarrow NH_4^+ + NO_3^-$
5. $HNO_3(g) \Leftrightarrow HNO_3(l)$
6. $H_2SO_4(l) \Leftrightarrow H^+ + HSO_4^-$

→ **Gives lower HNO_3(g) /NH_4^+; higher NO_3^-/NH_3(g)/Cl^-**

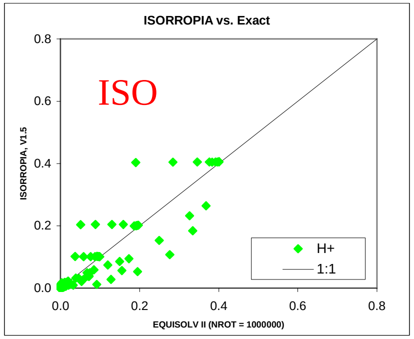
ISORROPIA

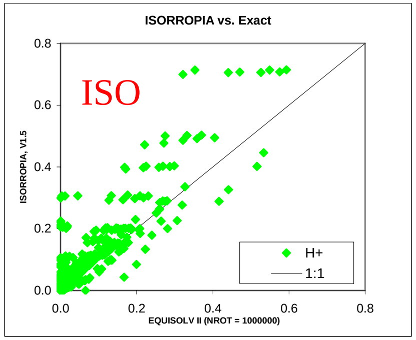
7. $NH_3(g) + H_2O \Leftrightarrow NH_4^+ + OH^-$
8. $NH_4Cl(s) \Leftrightarrow NH_3(g) + HCl(g)$
9. $NH_4NO_3(s) \Leftrightarrow NH_3(g) + HNO_3(g)$

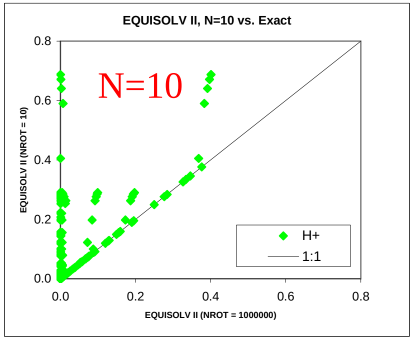
→ **Gives higher HNO_3(g)/NH_4^+/ HCl(g); lower NO_3^-/NH_3(g)**

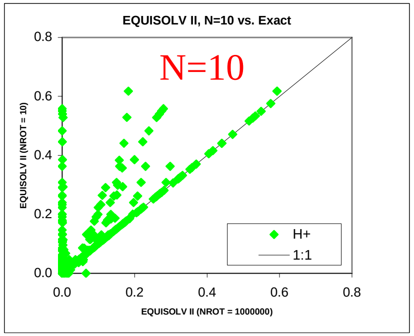
Box Model Results: H^+

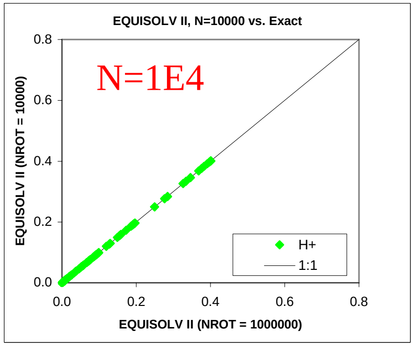
TSO4 = 5 TSO4 = 20

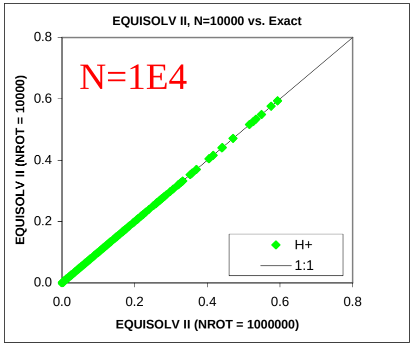


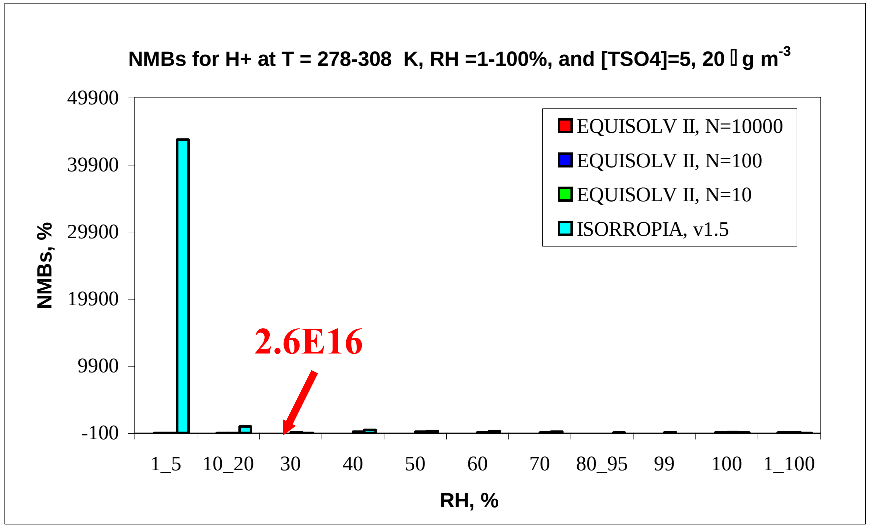


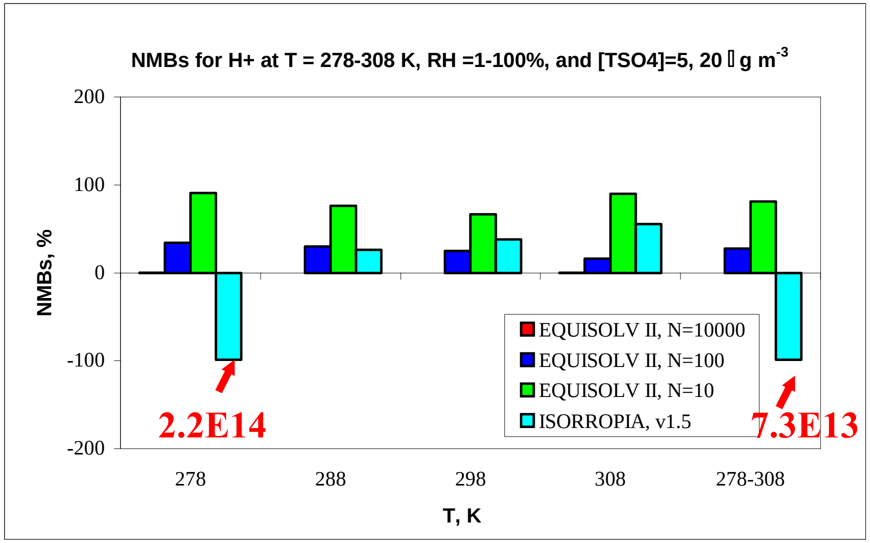




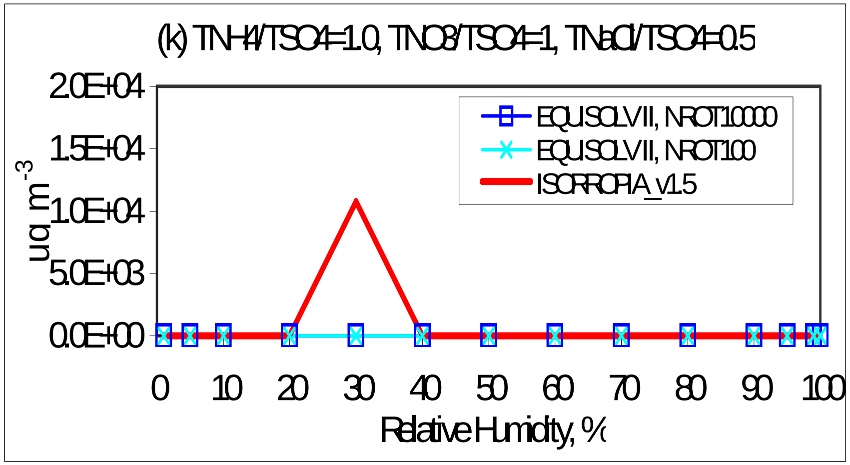


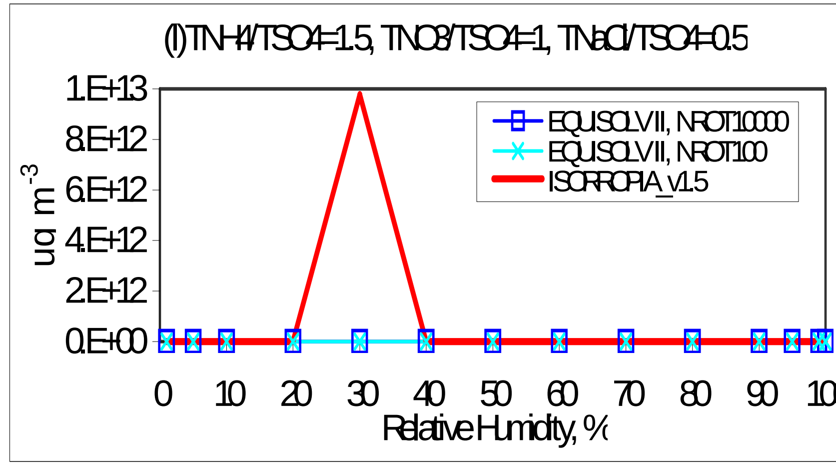


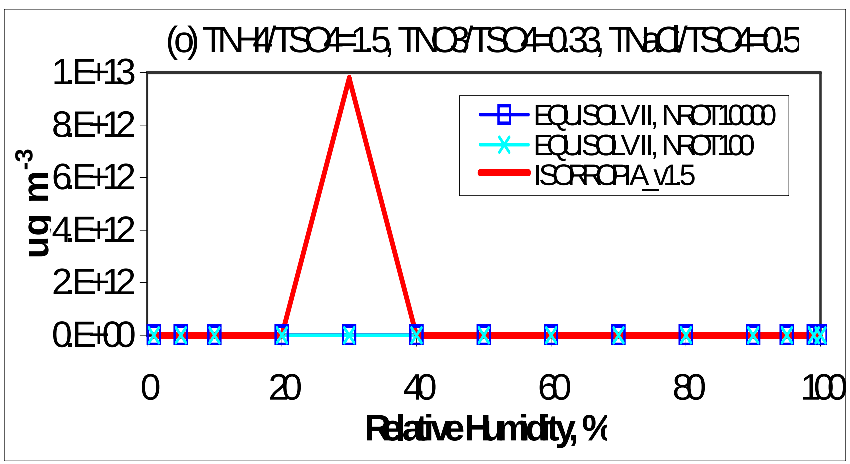


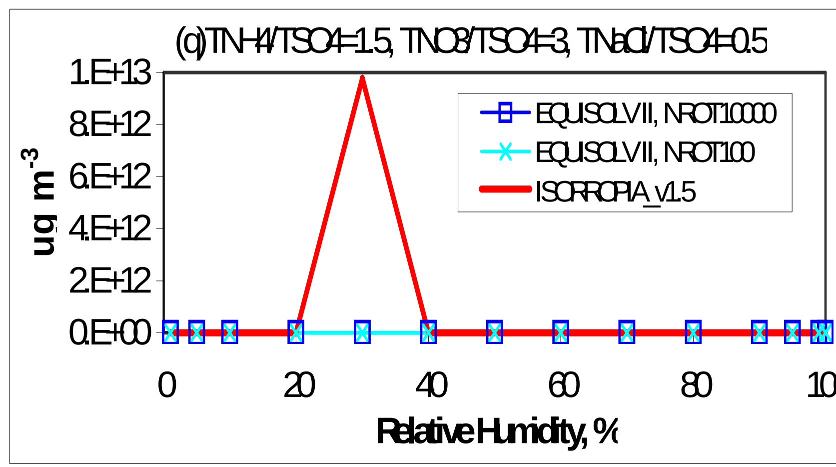


Predicted $[H^+]$ at T = 278 K, TSO4 = 20 $\mu g\ m^{-3}$



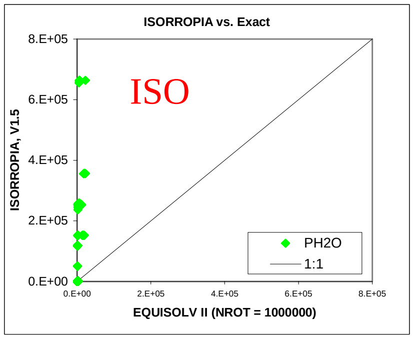


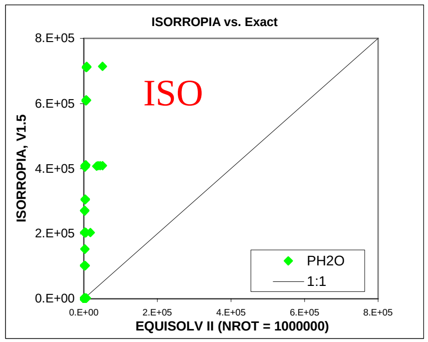


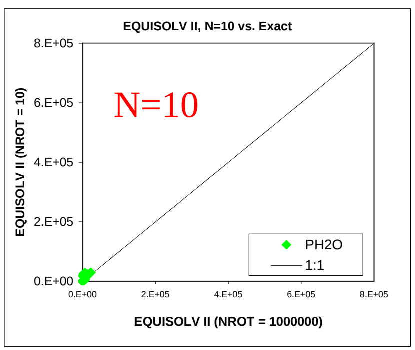


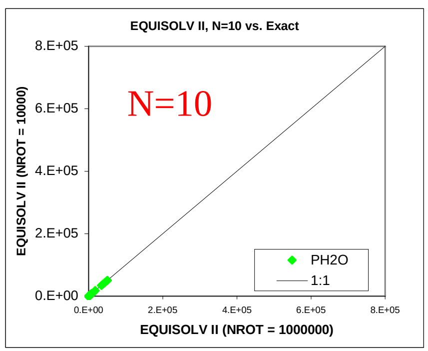
Box Model Results: H_2O

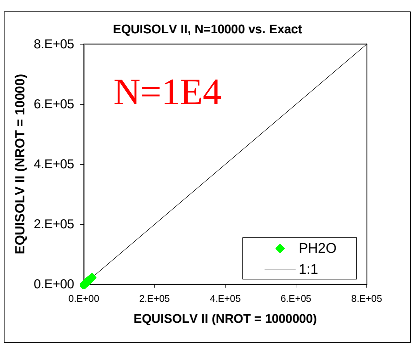
TSO4 = 5 **TSO4 = 20**

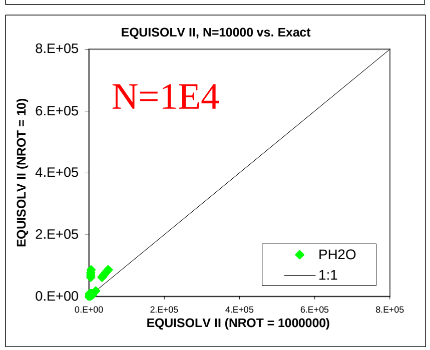


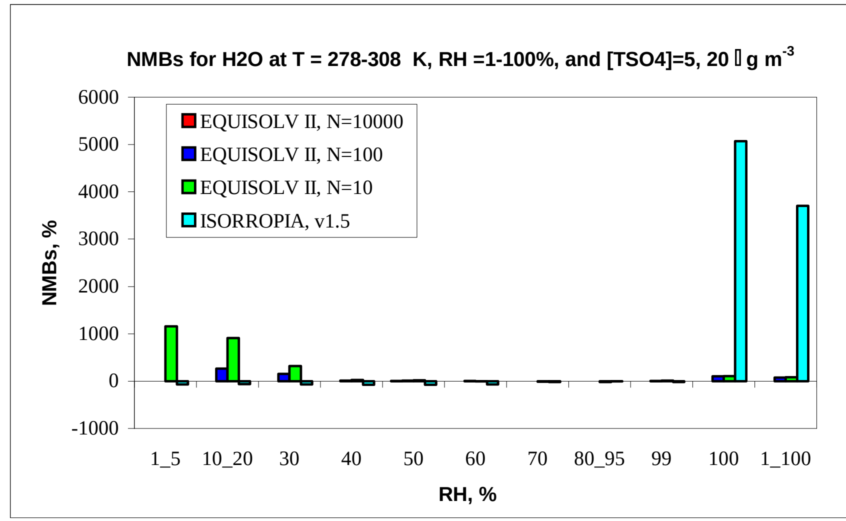


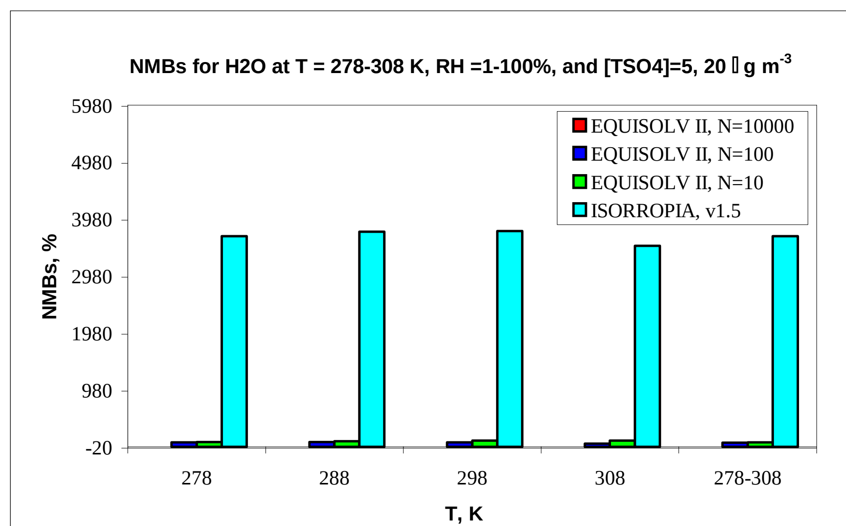








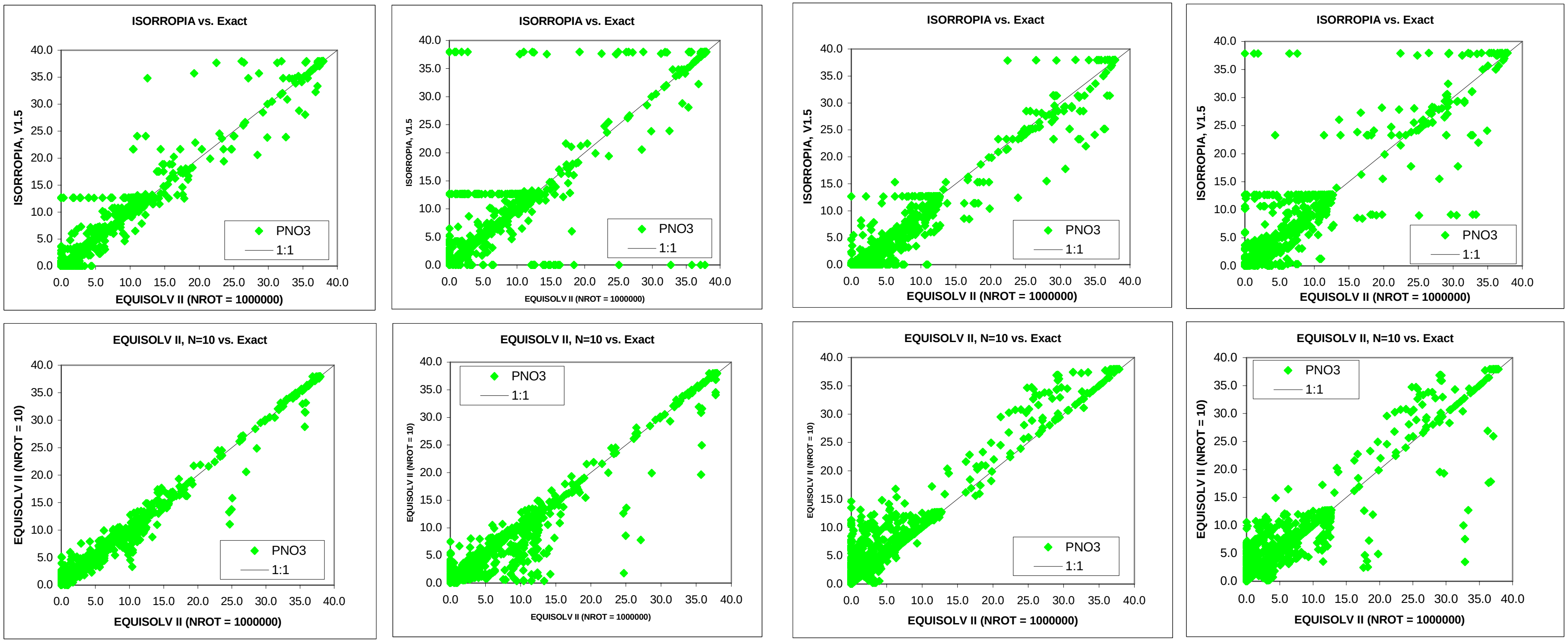




Box Model Results: Predictions of NO_3^- Solid + Liquid vs. Liquid only

TSO4 = 5 TSO4 = 20

Solid+Liquid Liquid Solid+Liquid Liquid



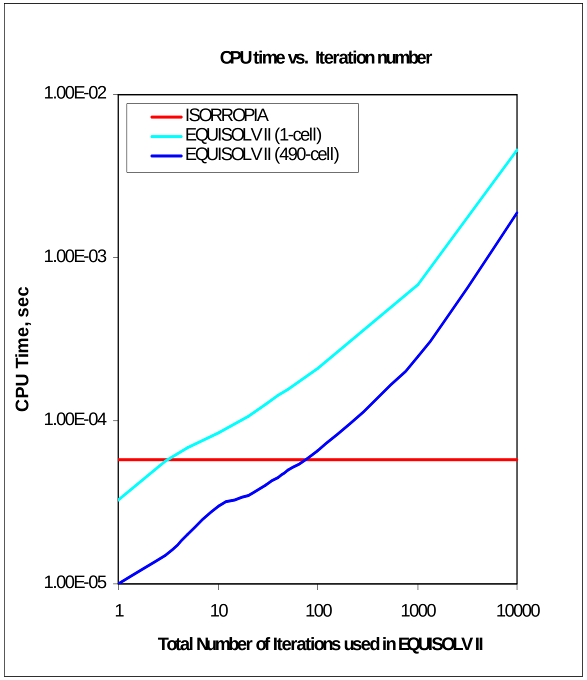
Top: ISORROPIA vs. Exact

Bottom: EQUISOLV II, NROT = 10 vs. Exact

Box Model: Timing Test

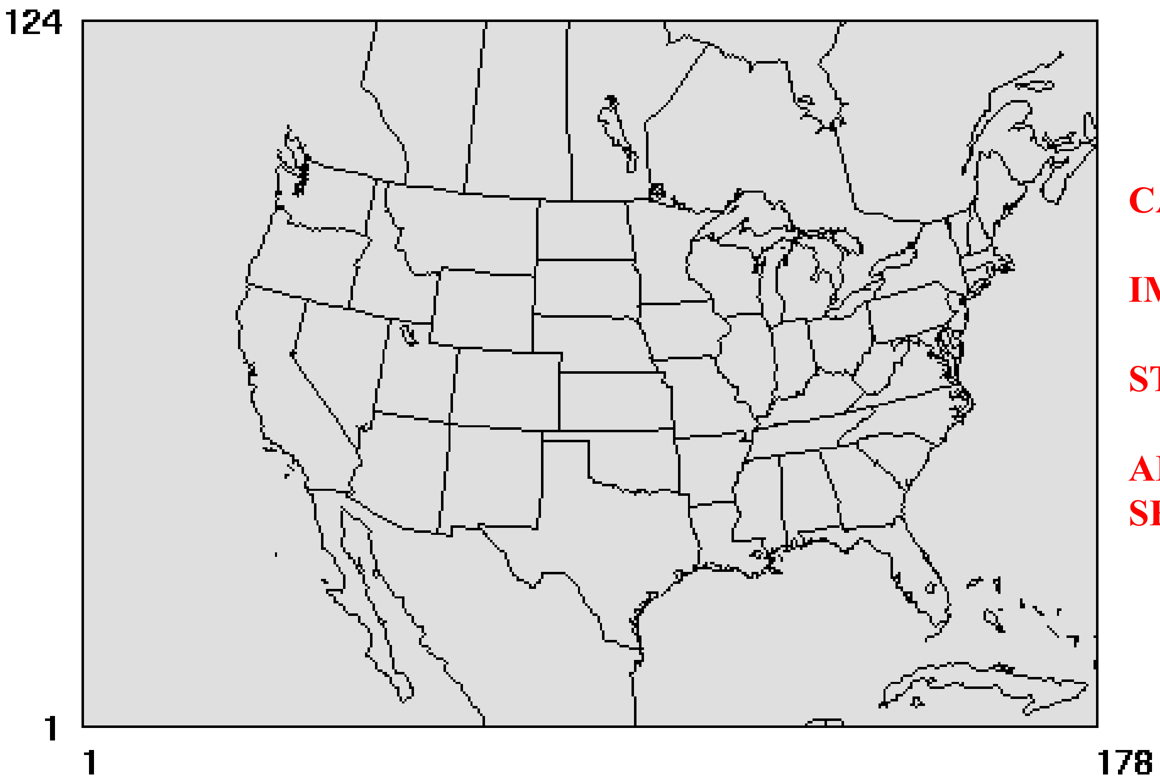
280 Cases with T=298 K, RH=1-100%, TSO4= 20 µg m^{-3}

ISORROPIA		EQUISOLV II		
Iteration Numbers	CPU Time, s	NROT	CPU Time, s (Single-cell)	CPU Time, s (490-cell)
MAXIT=100 NSWEEPI=4	5.77×10^{-5}	1	2.97×10^{-5}	1.00×10^{-5}
		3	5.36×10^{-5}	1.50×10^{-5}
		5	6.49×10^{-5}	2.00×10^{-5}
		10	8.06×10^{-5}	3.00×10^{-5}
		20	1.03×10^{-4}	3.51×10^{-5}
		30	1.21×10^{-4}	4.01×10^{-5}
		40	1.35×10^{-4}	4.49×10^{-5}
		50	1.51×10^{-4}	5.03×10^{-5}
		100	2.02×10^{-4}	6.49×10^{-5}
		1000	6.74×10^{-4}	2.50×10^{-4}
		10000	4.34×10^{-3}	1.89×10^{-3}



3-D Test with CMAQ for the June 1999 SOS Episode

• Simulation Period	12-28 June 1999
• Grid Resolution	32 km, 178 × 124 grid cells, 19 layers
• Meteorology	MM5/FDDA
• Emissions	EPA's NEI'99 inventory
• Initial/Boundary cond.	2-day spinup, CMAQ default ICs/BCs
• CMAQ	V 4.4, SAPRC99/EBI or ROS3, modified to include ternary nucleation



Datasets for Evaluation

CASTNet: hourly O_3, weekly SO_4^{2-}, NO_3^-, NH_4^+ at 83 sites

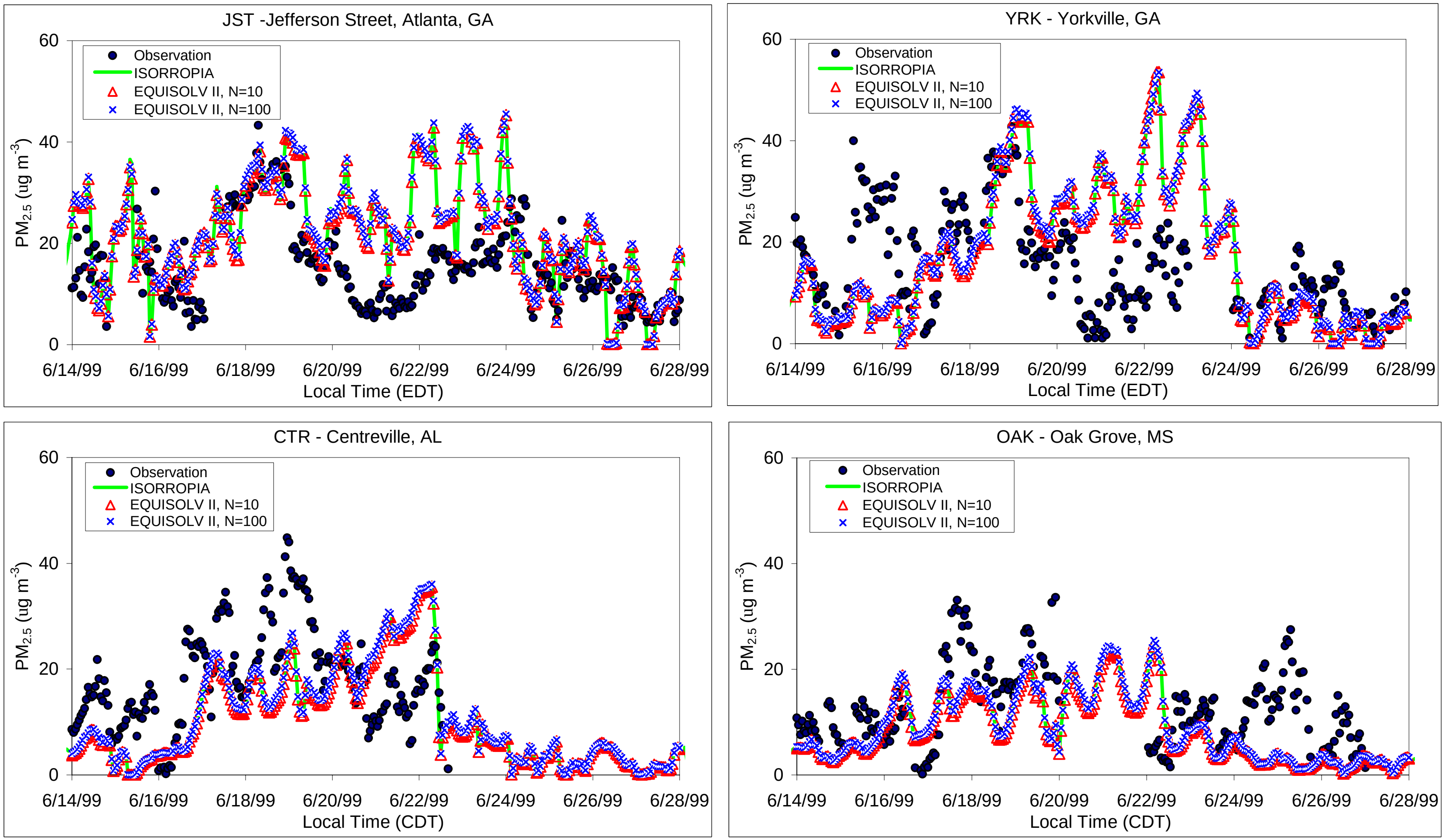
IMPROVE: 3-day SO_4^{2-}, NO_3^-, NH_4^+, EC, OC; 24-hr $PM_{2.5}$ at 145 sites

STN: 3-day SO_4^{2-}, NO_3^-, NH_4^+, EC, OC, $PM_{2.5}$ at 139 sites

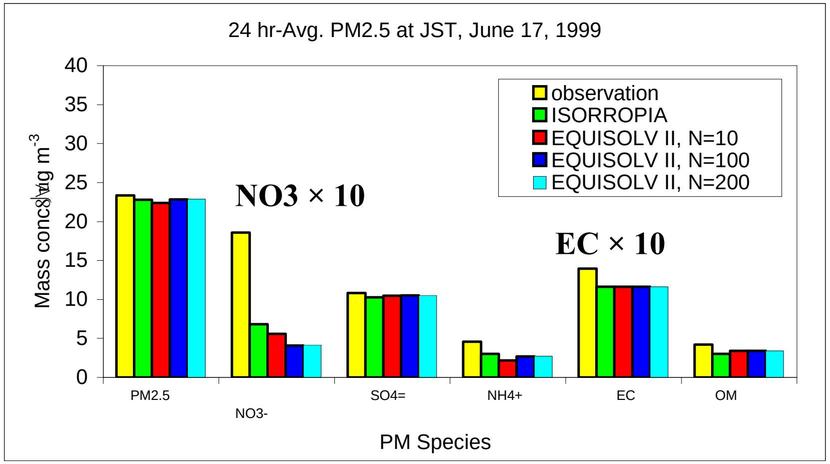
AIRS: hourly O_3 at 1161 sites

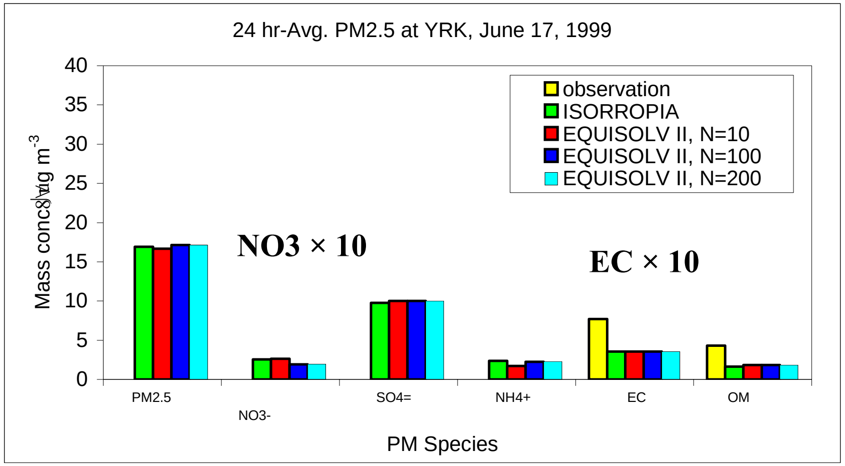
SEARCH: Hourly O_3; 24-hr $PM_{2.5}$ at JST, YRK, BHM, CTR, OLF, PNS, OAK, GFP

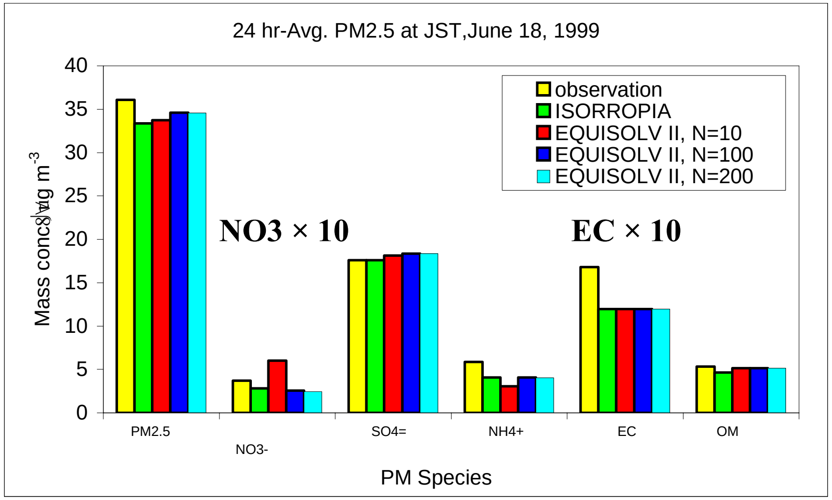
Observed vs. Predicted $PM_{2.5}$ at SEARCH Sites

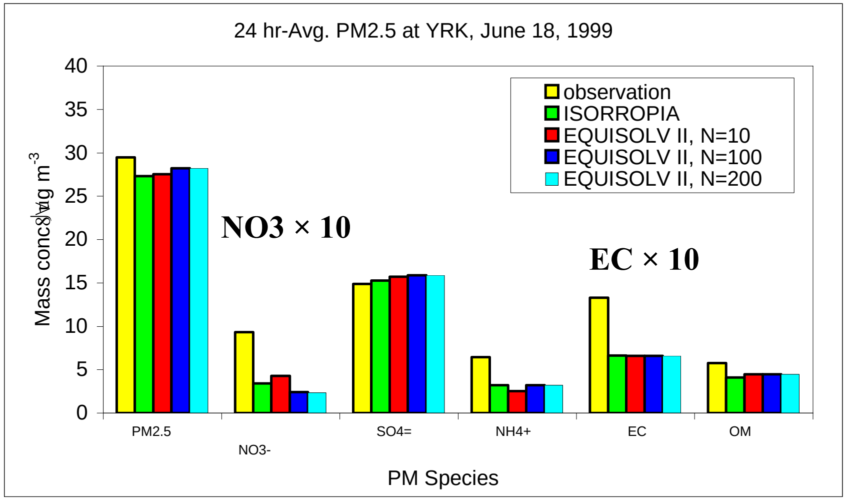


Observed vs. Predicted $PM_{2.5}$ and Its Composition at JST and YRK, GA

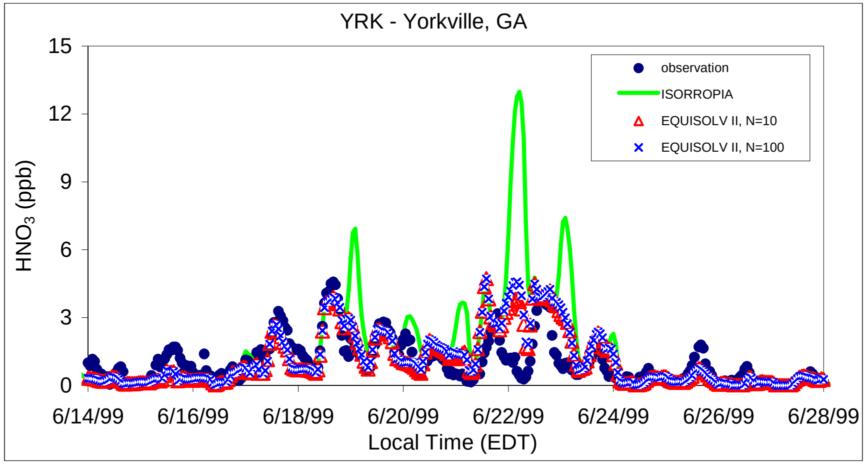


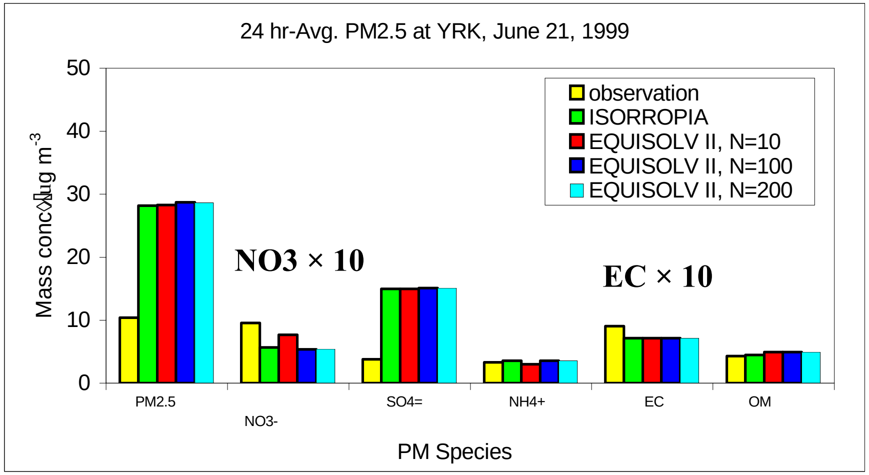


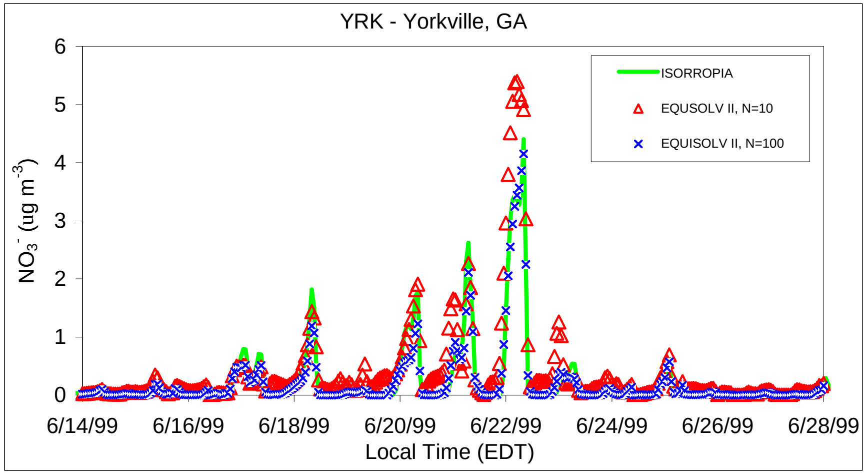


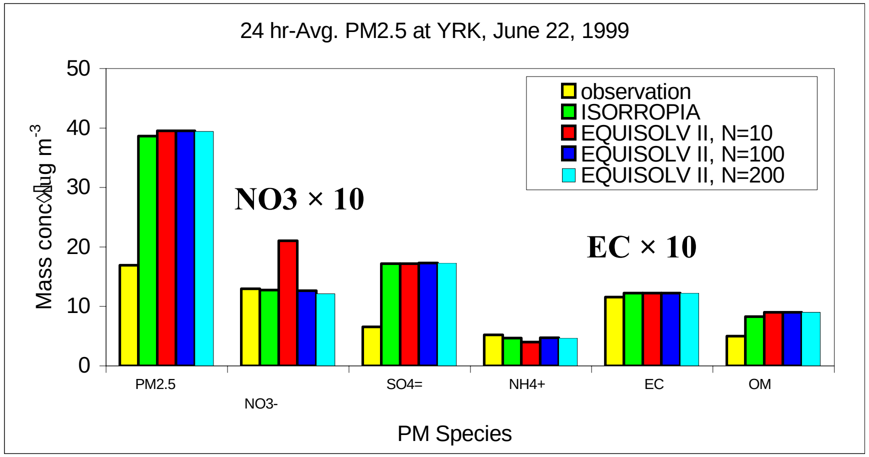


Observed vs. Predicted HNO_3, NO_3^- and $PM_{2.5}$ Composition at YRK, GA









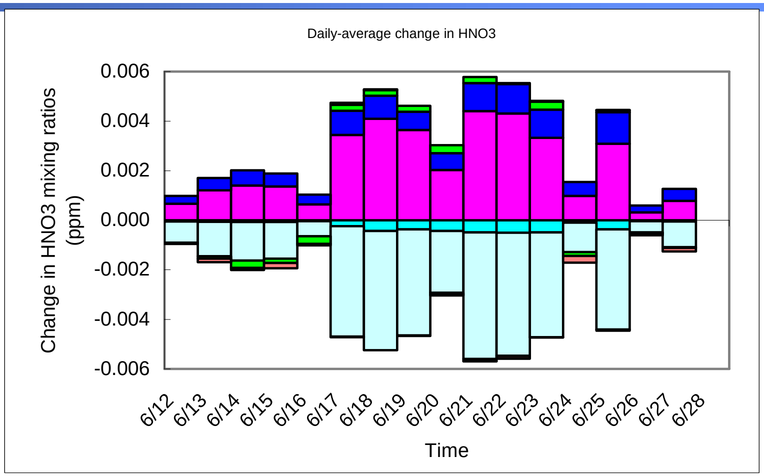
ISORROPIA vs. EQUISOLV: Performance Statistics

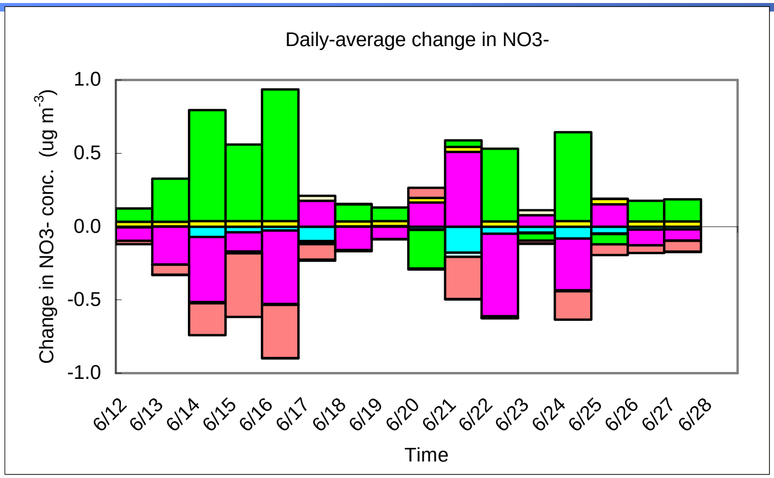
Normalized Mean Error and Bias (Fraction)

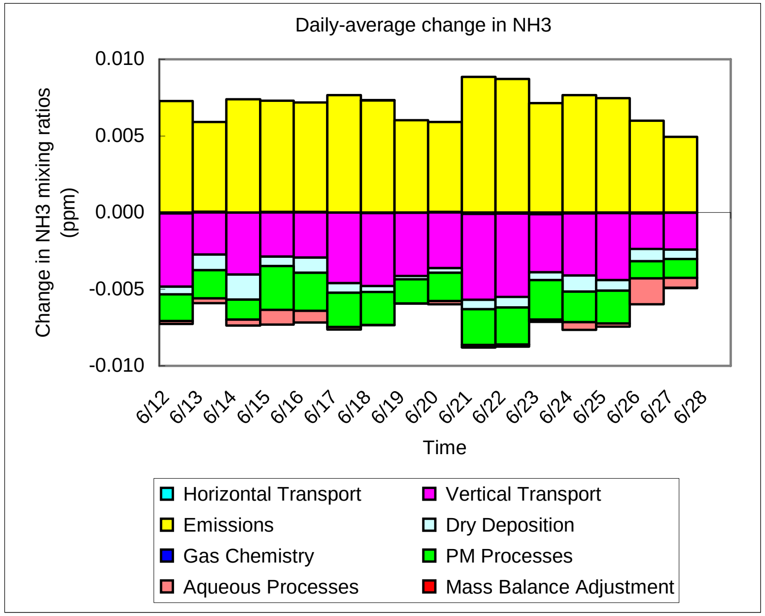
Normalized Mean Error Factor and Bias Factor (Fraction)

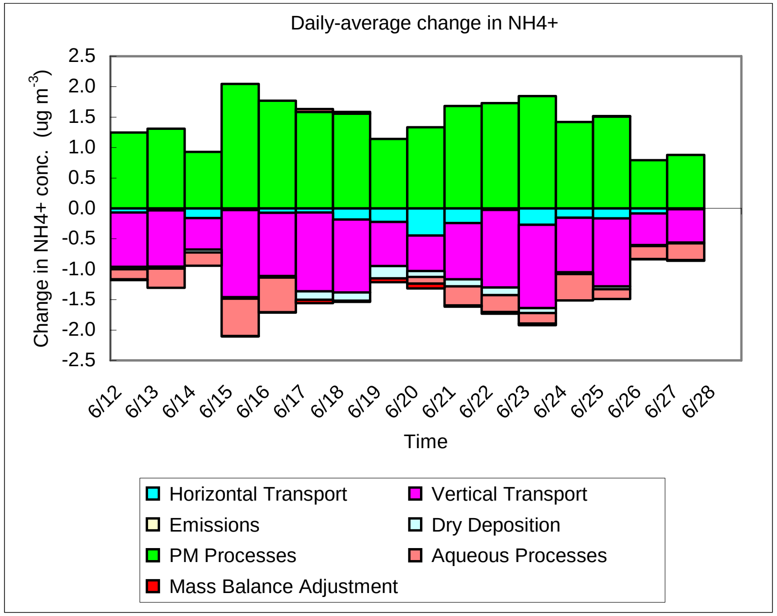
	Module	CASTNet		IMPROVE		SEARCH	
		NME %	NMB %	NME %	NMB %	NME%	NMB %
$PM_{2.5}$	ISO EQUI			38 39	-26 -29	42 42	-3 -5
$Sulfate_{2.5}$	ISO EQUI	29 30	14 15	49 49	18 19	53 53	22 23
$Nitrate_{2.5}$	ISO EQUI	89 75	-16 -24	96 89	-42 -49	76 67	-71 -51
$Ammonium_{2.5}$	ISO EQUI	28 41	5 -37	36 30	23 -22	47 63	-32 -60
$BC_{2.5}$	ISO EQUI			47 47	-34 -35	55 54	-53 -51
$OC_{2.5}$	ISO EQUI			43 43	-25 -25	41 41	-34 -34

Daily Average Changes in HNO_3/NO_3^- and NH_3/NH_4^+ Due to Major Processes









Summary

- EQUISOLV II ($N \leq 10$) gives lower biases (< 10%) for HNO_3, NO_3^-, HCl, Cl^-, SO_4^{2-}, H_2O, H+, and NH_3 (except for RH $\geq$ 99) and moderate biases (~27%) for NH_4^+. ISORROPIA gives lower biases for HNO_3, NO_3^-, SO_4^{2-}, H_2O (except RH = 100) , H^+ (except RH $\leq$ 5), NH_3 and NH_4^+; moderate biases (~30-60%) for HCl, Cl^- and abnormally high H_2O and H^+ biases (> 4E3-2.6E14%) under some conditions. Larger biases occur for RH $\leq$ 40 or $\geq$ 99 for most species.
  - A thermodynamically metastable system (solid + liquid)
  - ➢ High sulfate conditions: ISORROPIA overestimates HNO_3(g) and underestimates NO_3^-; EQUISOLV II (N=10) gives opposite trends.
  - A supersaturated system (no solid)
  - ➢ ISORROPIA gives some abnormally high or low HNO_3(g) and NO_3^-; EQUISOLV II with $N \leq 100$ gives slightly worse results than the metastable system (solid+liquid).
- CMAQ with EQUISOLV II and ISORROPIA performs similarly except for NO_3^- and NH_4^+. EQUISOLV II (solid and liquid) gives better NO_3^- at SEARCH sites, ISORROPIA (no solid) gives slightly better NO_3^- for IMPROVE and CASTnet sites, but it gives [HNO_3] much higher than the observed one at some sites. Differences in NO_3^- and NH_4^+ predictions can be explained by different reactions and the high NO_3^- predicted by ISORROPIA with liquid only. Thermodynamics only may not explain the observed gas/particle partitioning.
- Future work include multiple-cell implementation, size-resolved equilibrium, and application of CMAQ-EQUISOLV II for regions with crustal species and sea-salt.