Updates to Secondary Organic Aerosol (SOA) Module

Bonyoung Koo, *ENVIRON* and Alex Guenther, *NCAR*
with Ralph Morris and Greg Yarwood, *ENVIRON*

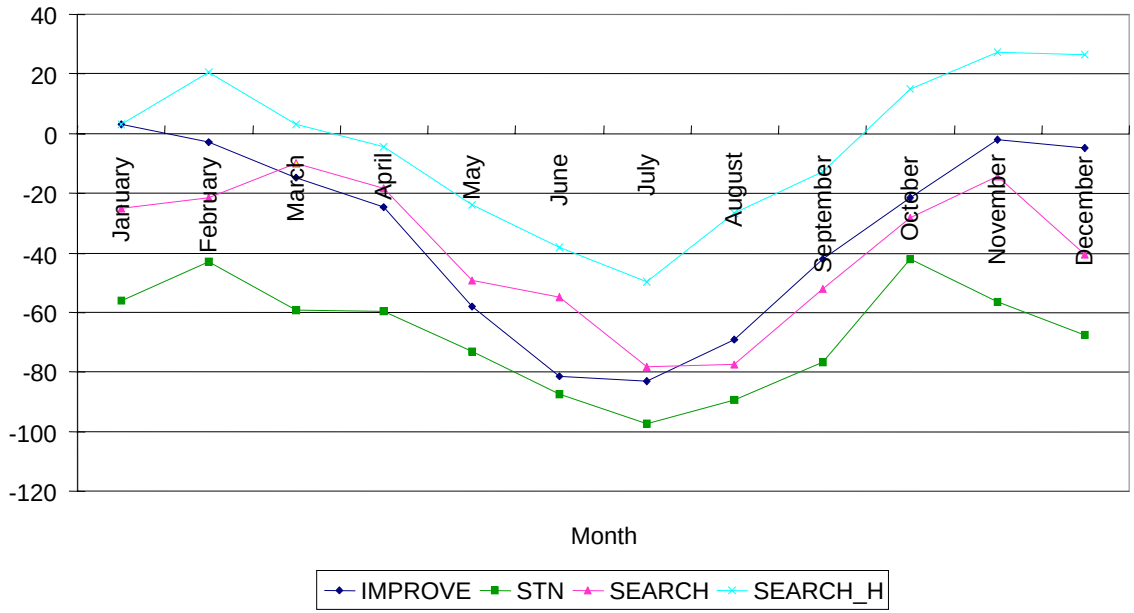
RPO National Technical Meeting
Adams Mark Hotel
Denver, Colorado
June 10, 2005

Background

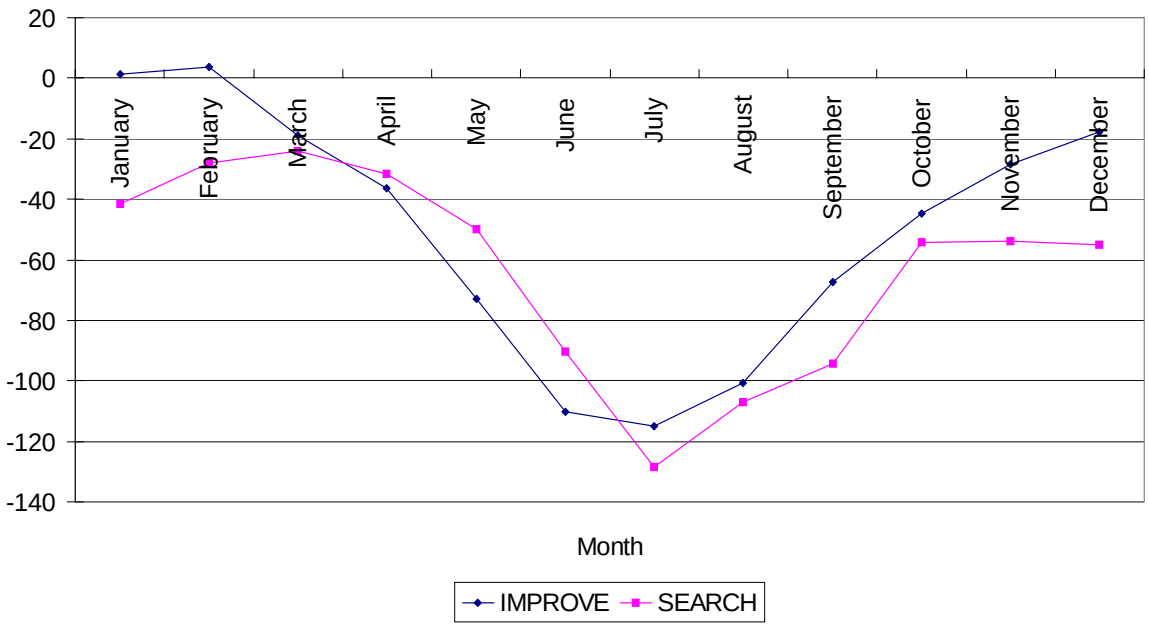
- VISTAS initial 2002 CMAQ V4.3 base case (Base A) exhibited large (-80%) Summer Organic Matter Carbon (OMC) underestimation bias
  - Revised CMAQ simulation (2002 Base C) using CMAQ V4.4 (October 2004 release) degraded OMC performance (-100% Summer OMC) compared to CMAQv4.3 (Base A)
    - Believe due to correction of CMAQ vertical transport mass conservation error
- Resulted in intense effort at the end of 2004 to identify cause and potential corrective action for the CMAQ OMC summer underestimation bias

VISTAS

Organic Carbon (OMC) CMAQ 36 km Fractional Bias



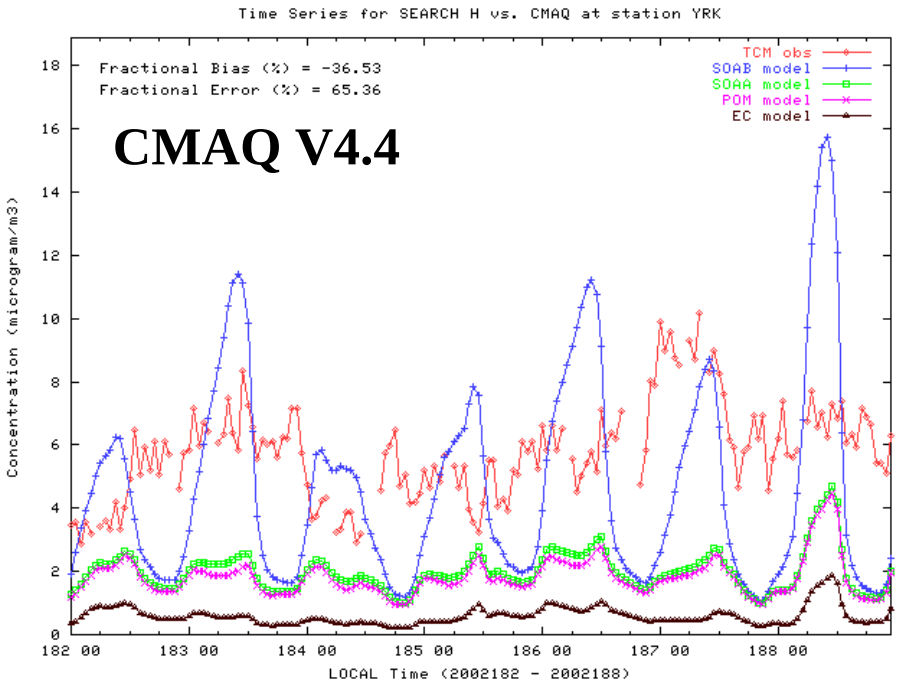
←Base A
IMPROVE/SEARCH

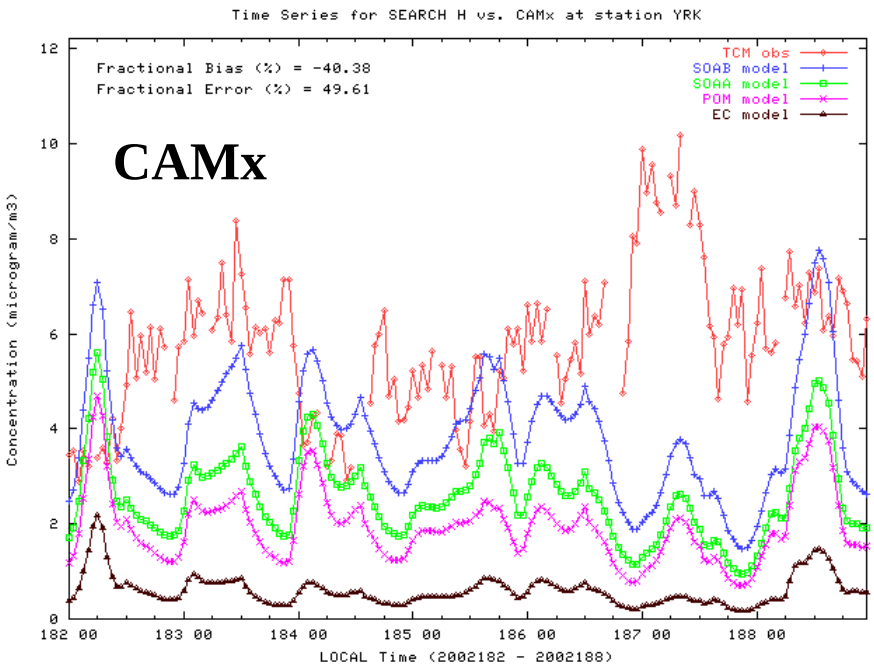


←Base C
IMPROVE/SEARCH

Mainly degradation in OMC performance toward larger underestimation

Hourly TCM Comparisons at SEARCH Yorktown, Georgia Site July 1-7, 2002





Elemental Carbon (EC)

Primary Organic Carbon (POC)

Anthro Secondary OA (SOA_A)

Biogenic Secondary OA (SOA_B)

- CMAQ SOA_A lower than CAMx
- CMAQ SOA_B goes to zero
- CMAQ too little TCM and too much diurnal variation driven primarily by SOA_B

→ Found CMAQ better OMC performance for July 2002 using CMU/CAMx SOA parameters

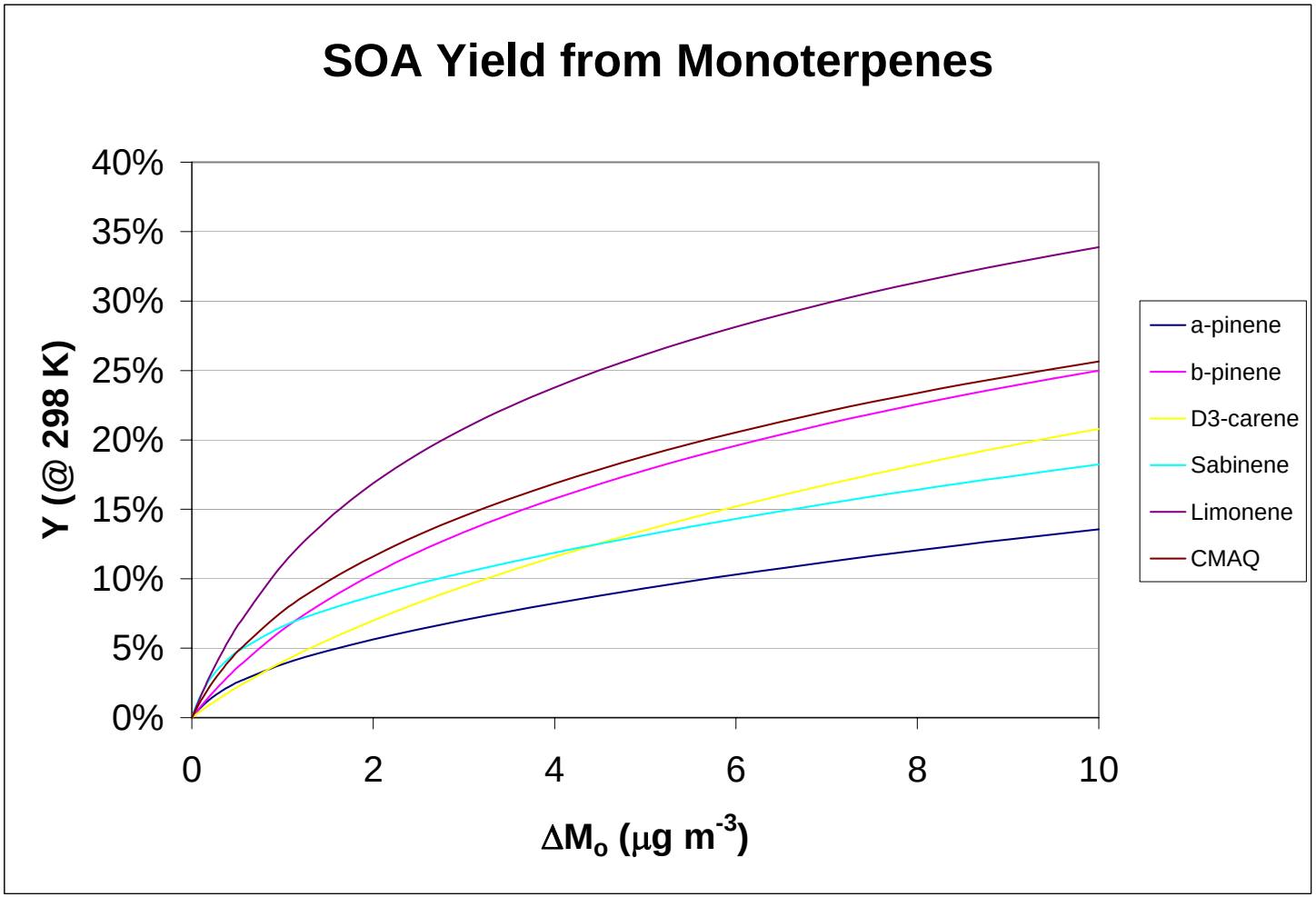
CMAQ SOA Module

- VOC SOA Precursors: Aromatics & Terpenes
  - Yields = amount of Condensable Gas (CG) obtained from VOC oxidation
  - Cstar = saturation concentration of condensable gas
  - Hvap = heat of vaporization (thermodynamics)
- Oxidation: VOC + OH ➔ CG (Yields)
- Equilibrium: CG ⇔ SOA (Cstar and Hvap)
- CMAQ transports SGTOT = CG + SOA
  - Split into CG and SOA in aerosol module and save for output

CMAQ V4.4 SOA Module

- VOC SOA Precursors: Aromatics & Terpenes
  - Anthropogenic SOA from CB-IV ARO and XYL aromatic species
  - Biogenic SOA from BEIS3 TERPB species
- TERPB Biogenic Terpenes
  - Based on measured lower yield/lower reactivity monoterpene species (MT1) that are believed to be overstated
  - Does not include higher yield/high reactivity monoterpenes (MT2) or sesquiterpenes (SQT)
- CMAQ TERPB SOA parameters (yields, Cstar and Hvap) based on fit to MT1 monoterpene data from CalTech smog chambers
  - Two product representation

CMAQ 2-Product SOA Module fit to Chamber Data



CMAQ SOA Module Parameters fit to lower yield/lower reactive (MT1) monoterpenes

α-pinene

β-pinene

D3-carene

Sabinene

Limonene

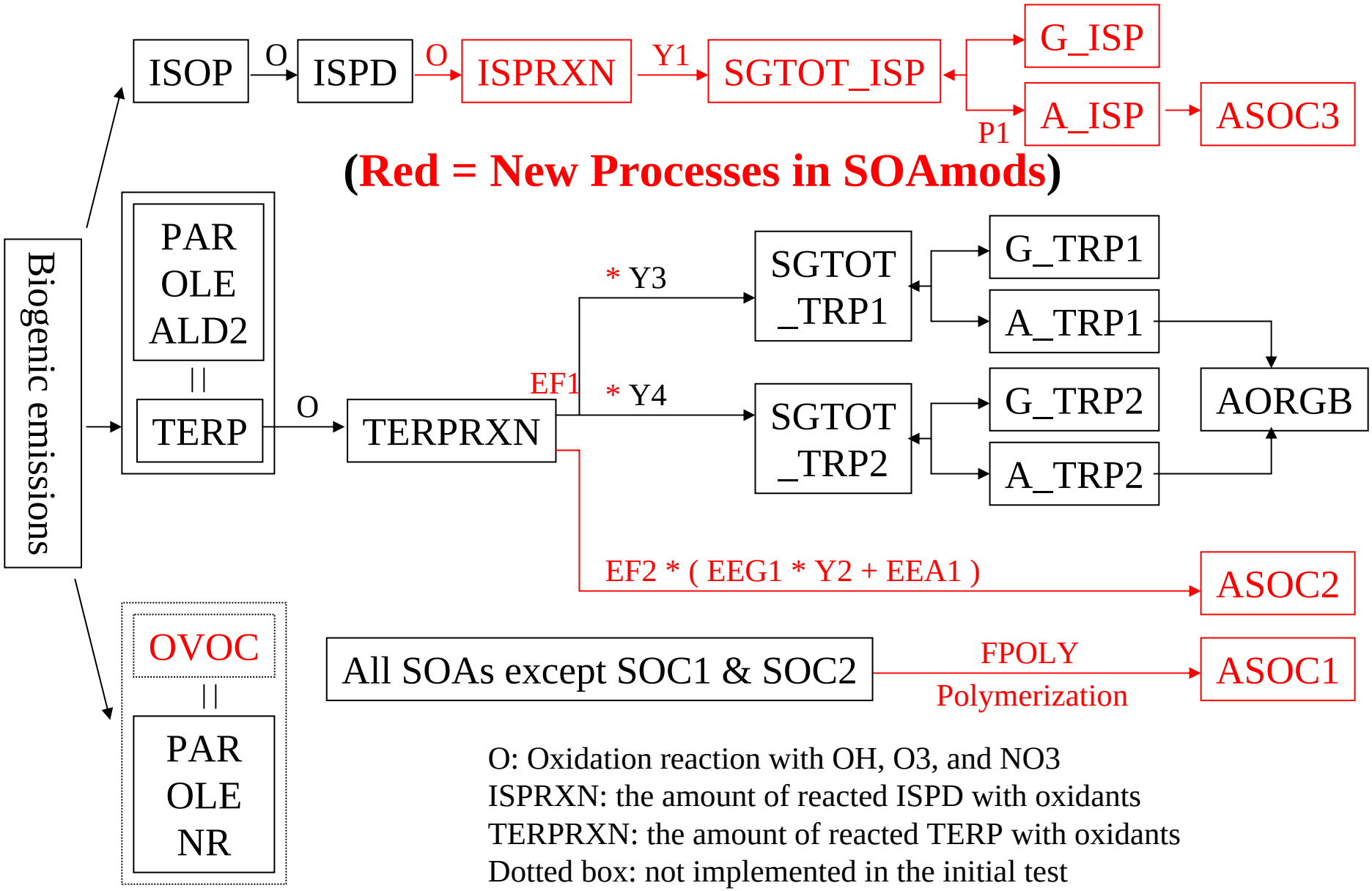
Uncertain and Missing Processes in Current SOA Modules

- Uncertain SOA Parameters: CalTech chamber data used to fit CMAQ SOA parameters have artifacts (Keywood et. al. 2003)
- Polymerization: SOA becomes nonvolatile
  - e.g. after 20 hours 50% of SOA no longer volatile (Kalberer et al., Science 2004 303 1659; Jang et al., 2002)
- Sesquiterpenes: Not included, known important SOA
- Higher Yield Monoterpenes (MT2): Not included
- Isoprene: Not included, high in southeastern US
  - New evidence that isoprene may be SOA precursor (Claeys et al., Science 2004 303 1173) that appears to be sensitive to SO2/SO4
- Biogenic OVOC: Also SOA precursor (e.g., Nonanal)
- Acid Catalyzed Formation: Some biogenic SOA formation higher under more acidic conditions (e.g., isoprene)

SOAmods Updates

- Constraint: Keep same CMAQ inputs so that SOAmods is plug&play with CMAQ V4.4
- Keep CMAQ 2-product SOA parameters that are fit to CalTech smog chamber for lower yield monoterpenes (MT1)
- Update CMAQ SOA module to include:
  - Polymerization of SOA into non-volatile particles
  - SOA from sesquiterpenes and higher yield/higher reactive monoterpenes (MT2)
  - SOA from isoprene
- Still missing from SOAmods module
  - Reactivity (decay) of Condensable Gases (CG)
  - SOA from biogenic OVOC emissions
  - Acid catalyzed reaction rates
  - Better linkage between gas-phase chemistry and SOA modules

Enhanced CMAQ SOA Module



O: Oxidation reaction with OH, O3, and NO3
ISPRXN: the amount of reacted ISPD with oxidants
TERPRXN: the amount of reacted TERP with oxidants
Dotted box: not implemented in the initial test

New SOAmods Parameters

EF1	= 0.7	(mean value of 0.4 ~ 1)
EF2	= 0.4	(mean value of 0.2 ~ 0.6)
EEG1	= 0.325	(mean value of 0.2 ~ 0.45)
EEA1	= 0.2	(mean value of 0.05 ~ 0.35)
Y2	= 0.875	(mean value of 0.75 ~ 1)
Y1	= 0.11	(mean value of 0.06 ~ 0.16)
P1	= 0.45	(mean value of 0.15 ~ 0.75)

Emission Factors (EF) and canopy Escape Efficiencies (EE) based mainly on field studies at Duke Forest, North Carolina

P1 (partitioning ratio = ratio of aerosol to total (gas+aerosol))

$$= \frac{c_1(aer)}{c_1(gas) + c_1(aer)} = \frac{x_1 M_0 (MW_1 / MW_0)}{x_1 c_1^* + x_1 M_0 (MW_1 / MW_0)}$$

M_0 is total organic mass ~ 10 μg/m^3 (used to calculate c^* for CMAQ's biogenic SOAs)
Assuming $(MW_1/MW_0) = (100/150)$,

$$c_1^* = \frac{1 - P_1}{P_1} M_0 \frac{MW_1}{MW_0} = 8.148$$

FPOLY = 0.025 / hr (50% polymerization for 20 hours)

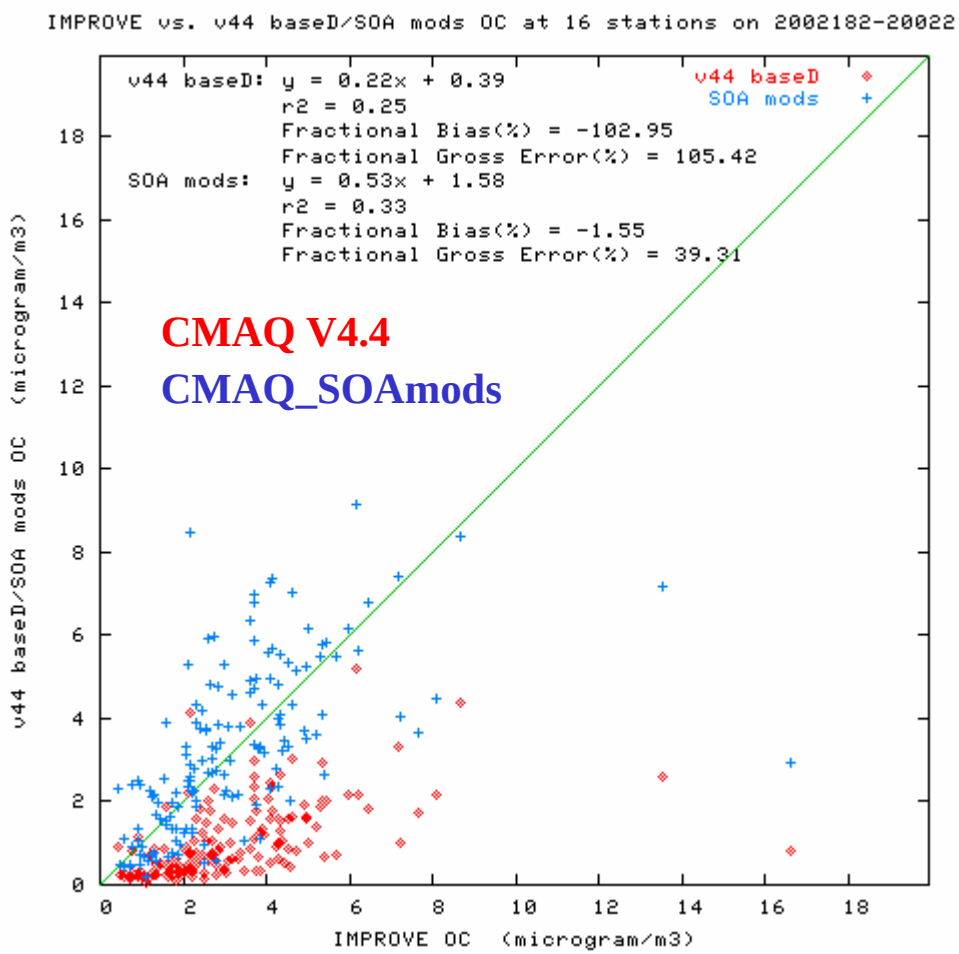
CMAQ SOAmods Testing

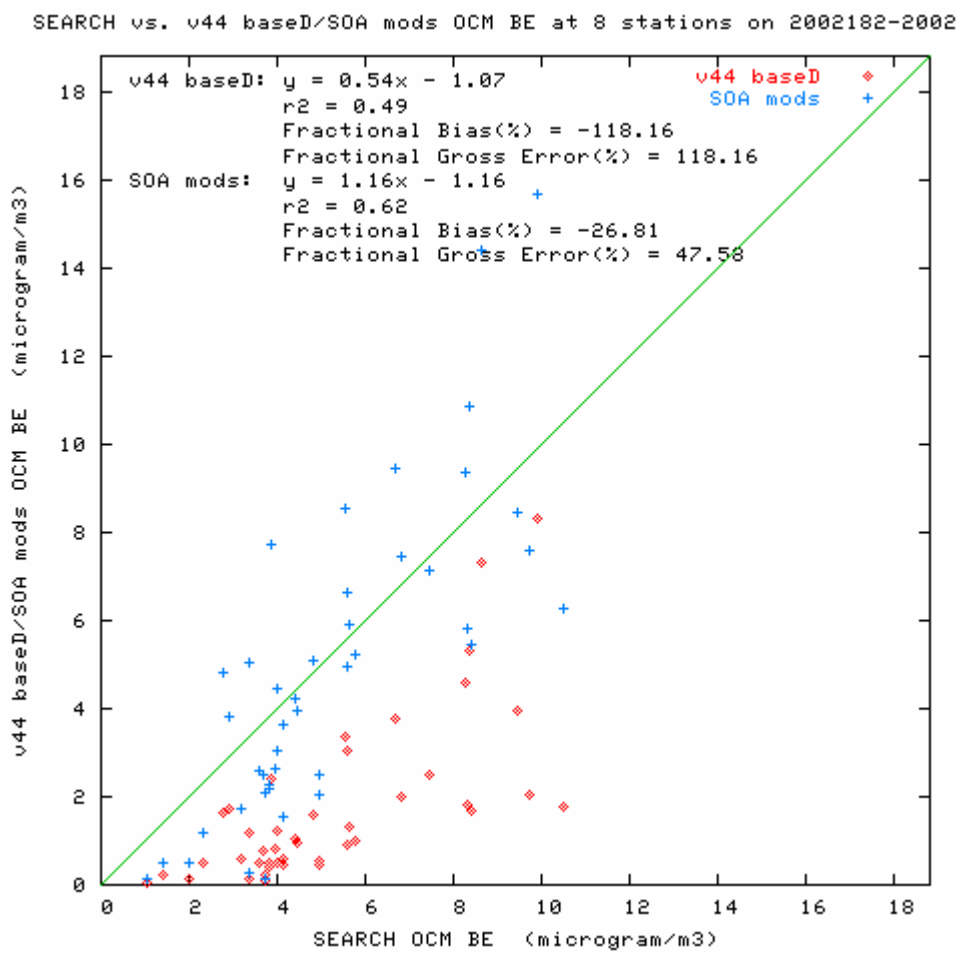
- Applied to January 2002 and July 2002
  - Standard CMAQv4.4
  - CMAQv4.4 with SOAmods
  - Continental US Inter-RPO 36 km domain
- Examined Organic Matter Carbon (OMC=1.4 x OC) at IMPROVE and SEARCH and Total Carbon Mass (TCM) at STN and SEARCH_H
- Examined various U.S. sub-domains
  - VISTAS, MRPO, MANE-VU, CENRAP, WRAP
- Annual 2002 Base Case run

OMC at VISTAS (July 2002) IMPROVE & SEARCH

FB: -103% → -2%

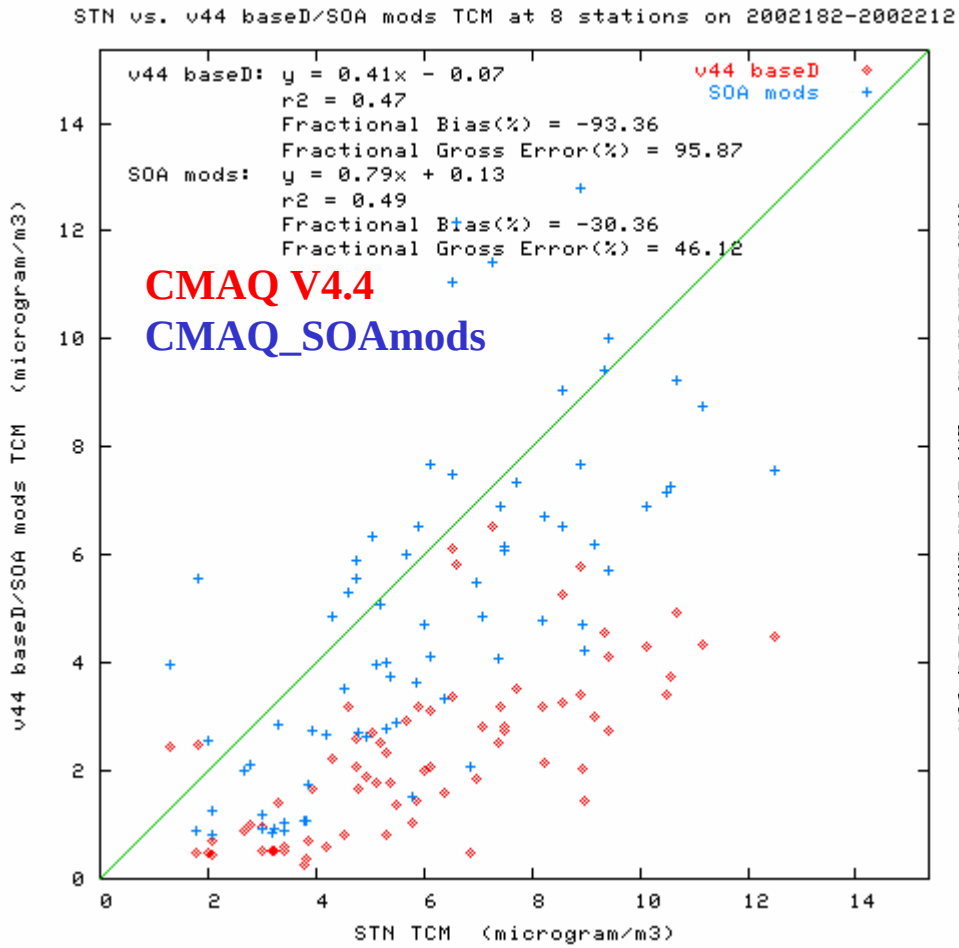
FB: -118% → -27%



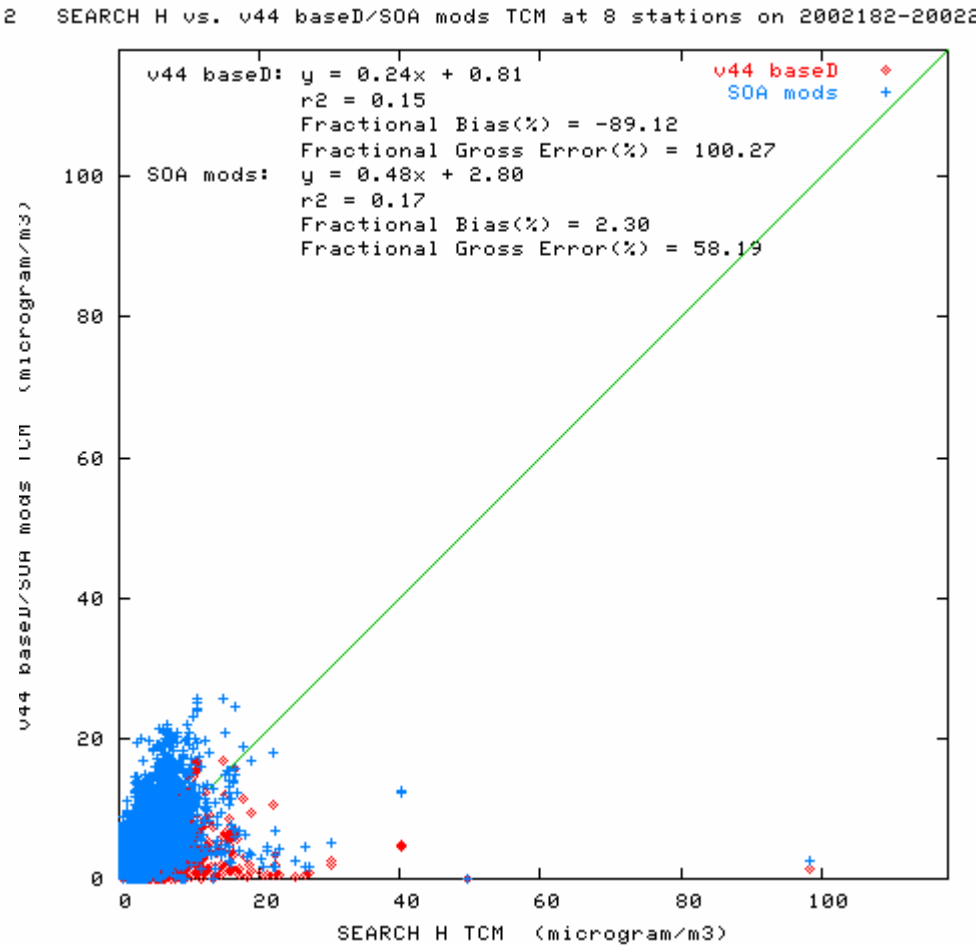


TCM at VISTAS (July 2002) STN & SEARCH_H

FB: -93% → -31%

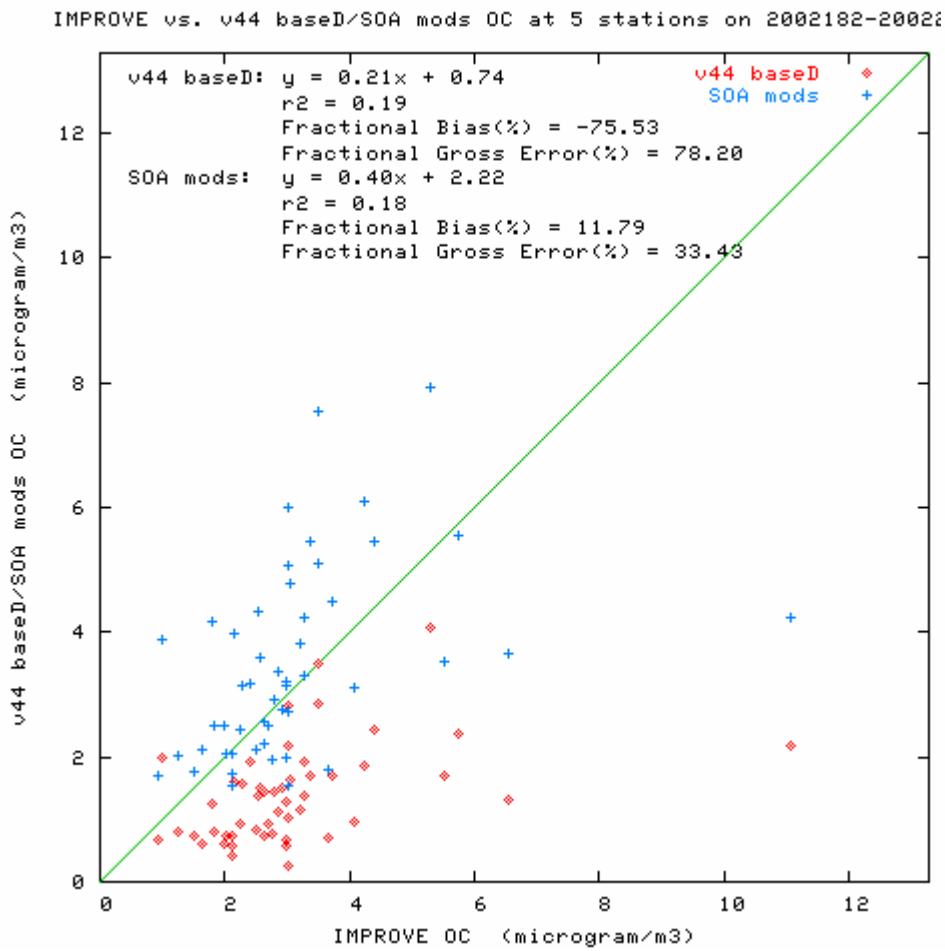


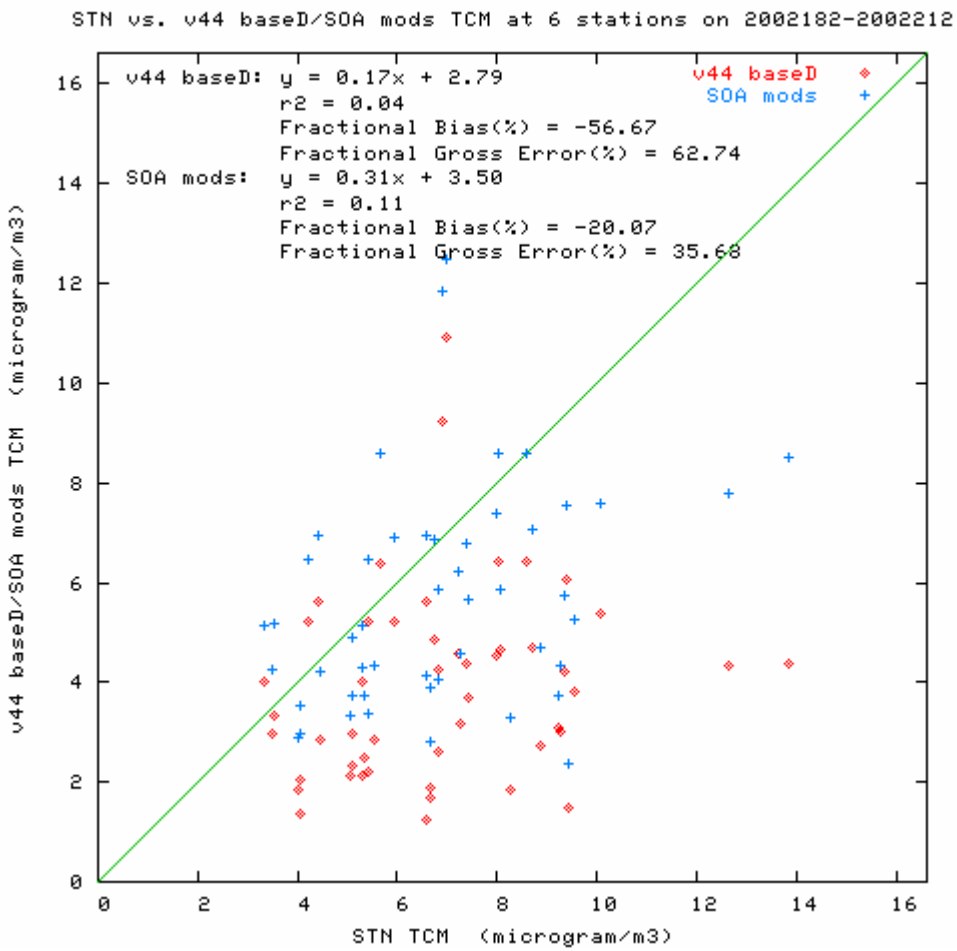
FB: -89% → +2%



OMC/TCM at MRPO (July 2002) IMPROVE & STN

OMC FB: -76% → TCM FB: -57% → -20%

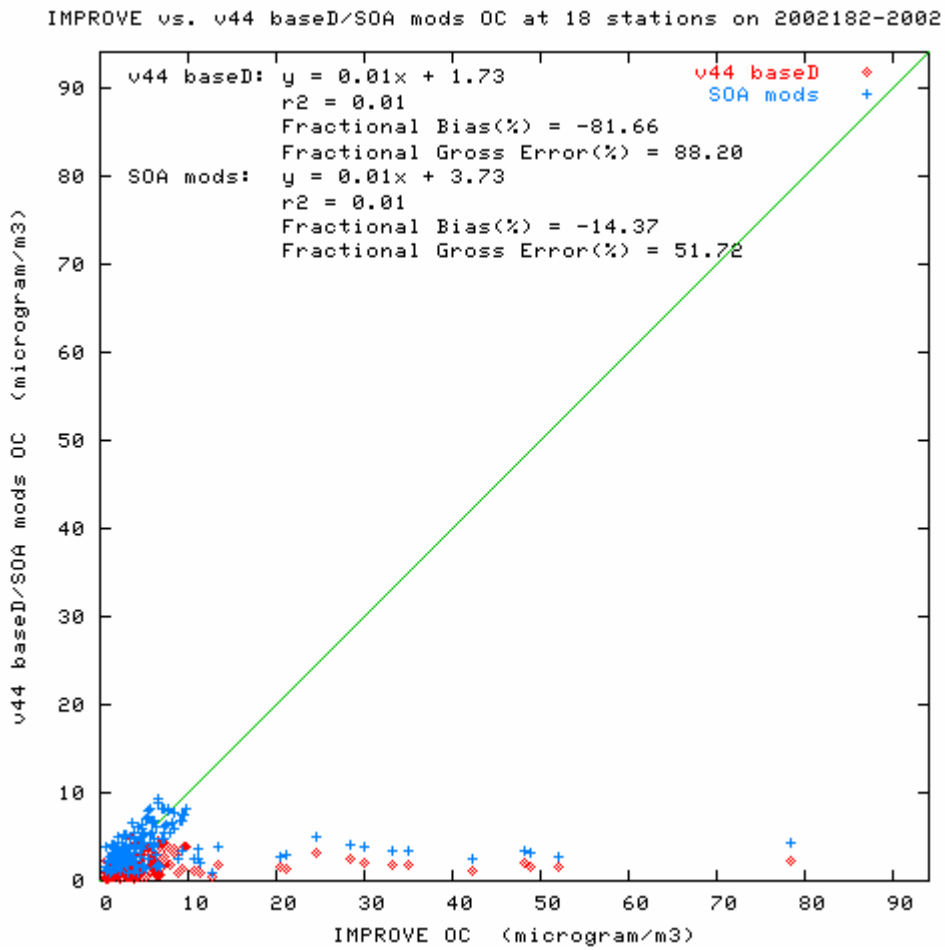


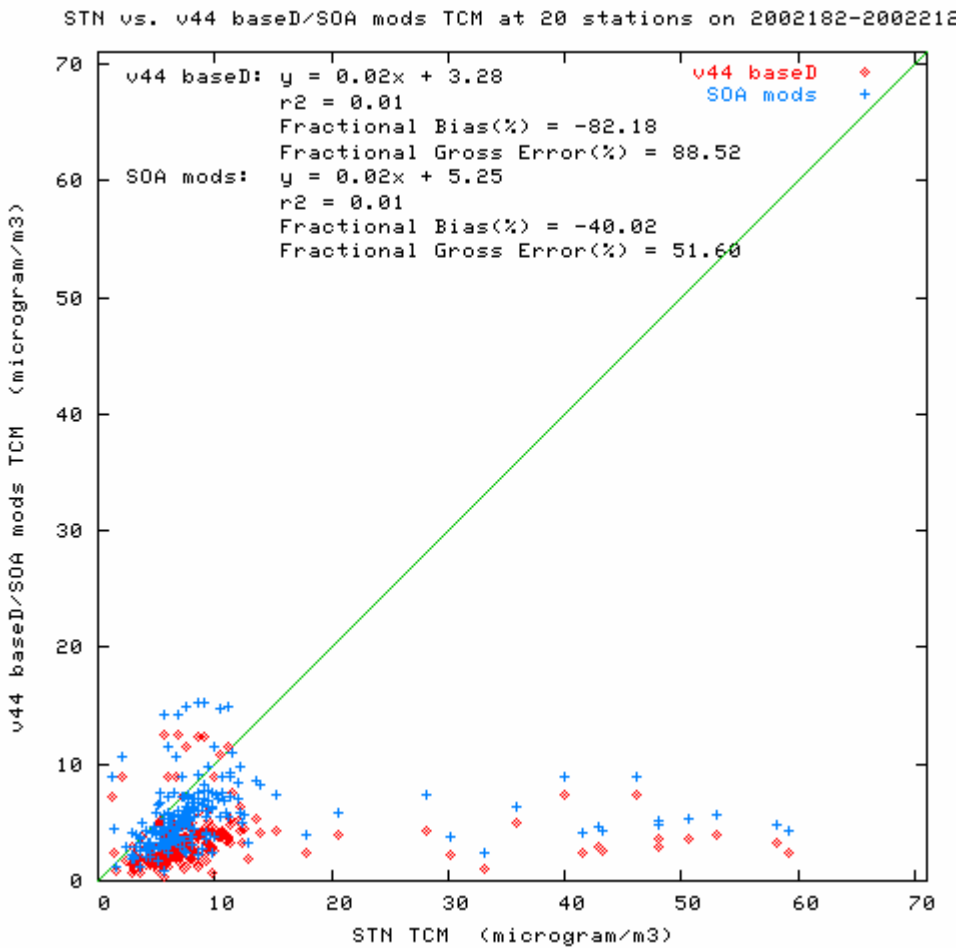


OMC/TCM at MANE-VU (July 2002) IMPROVE & STN

OMC FB: -82% → -

TCM FB: -82% → -40%

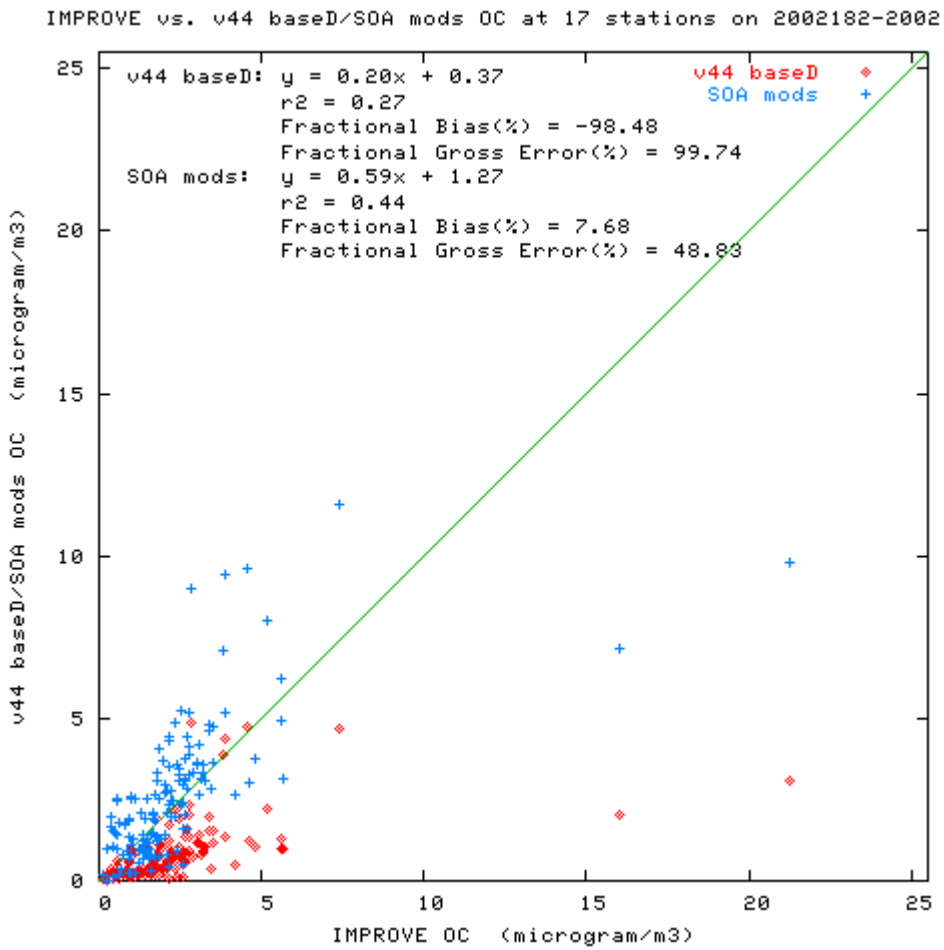


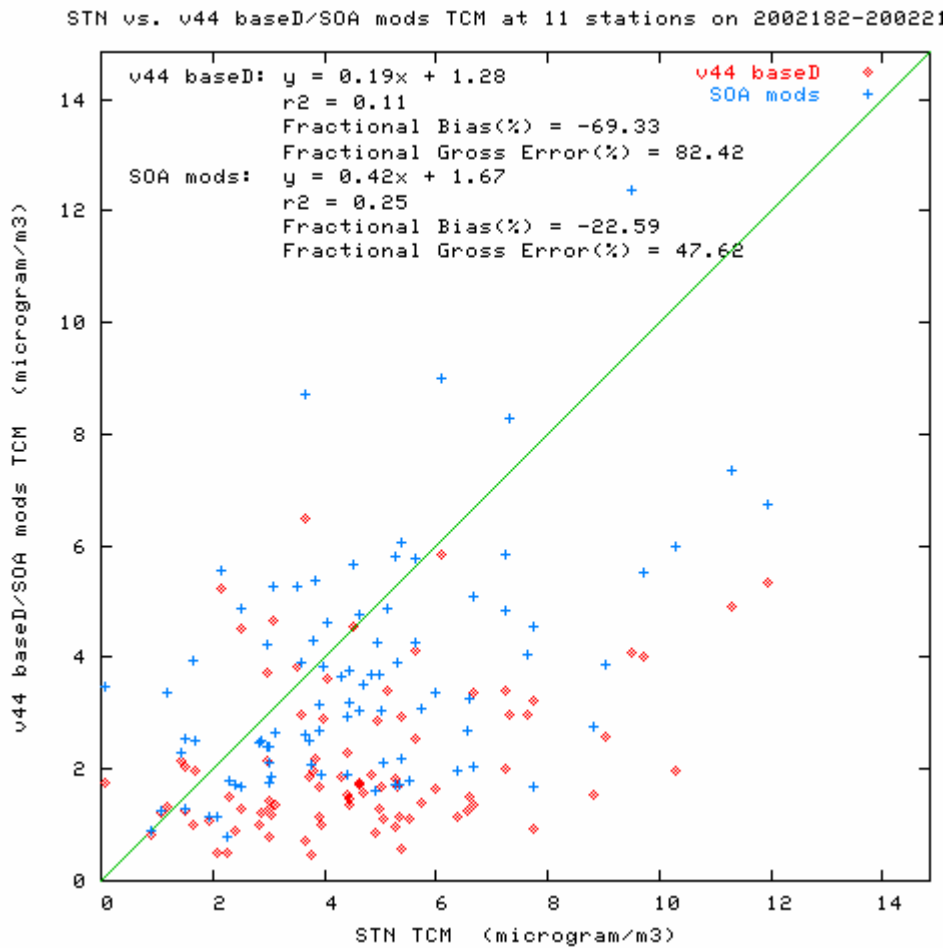


OMC/TCM at CENRAP (July 2002) IMPROVE & STN

OMC FB: -98% → 8%

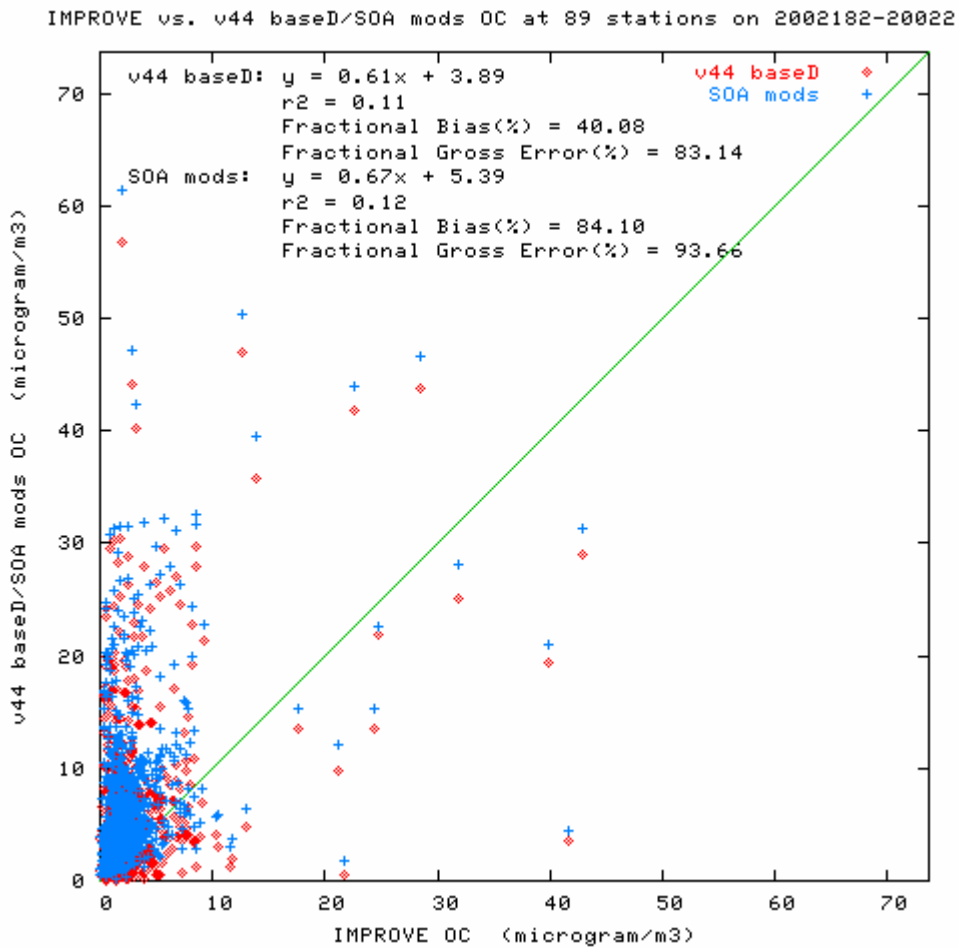
TCM FB: -69% → -23%

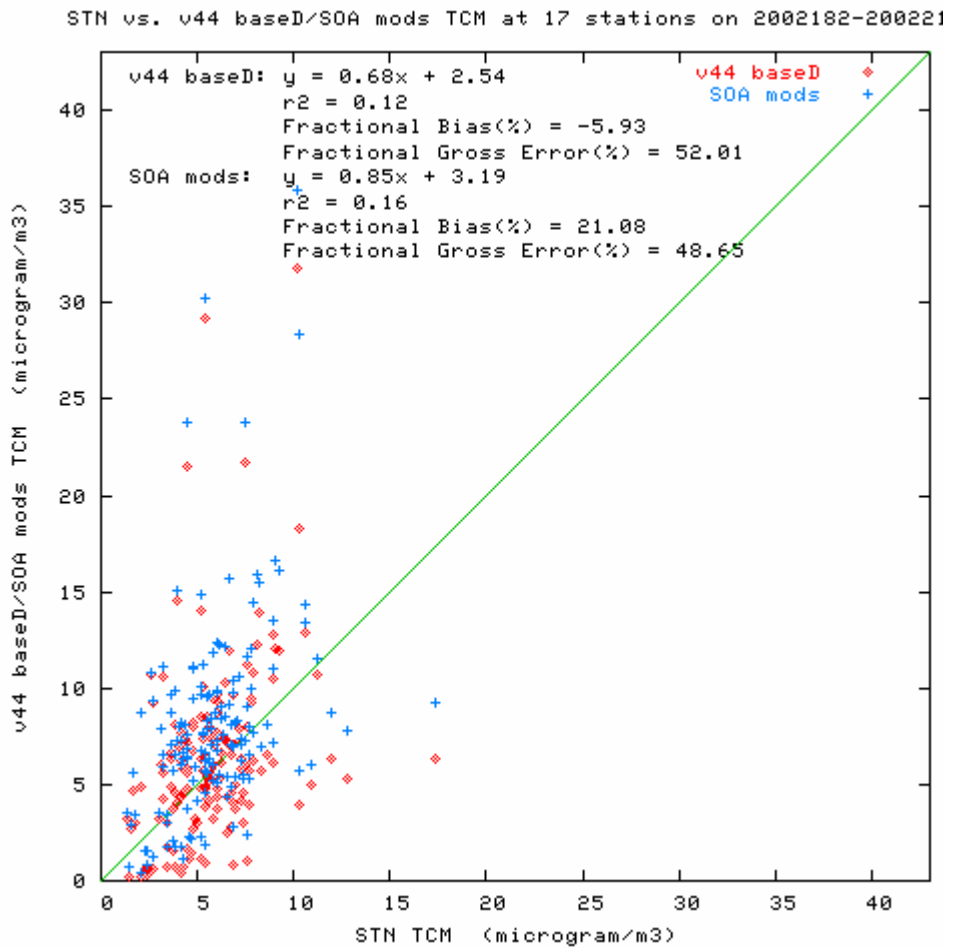




OMC/TCM at WRAP (July 2002) IMPROVE & STN

OMC FB: +40% → TCM FB: -6% → +21%



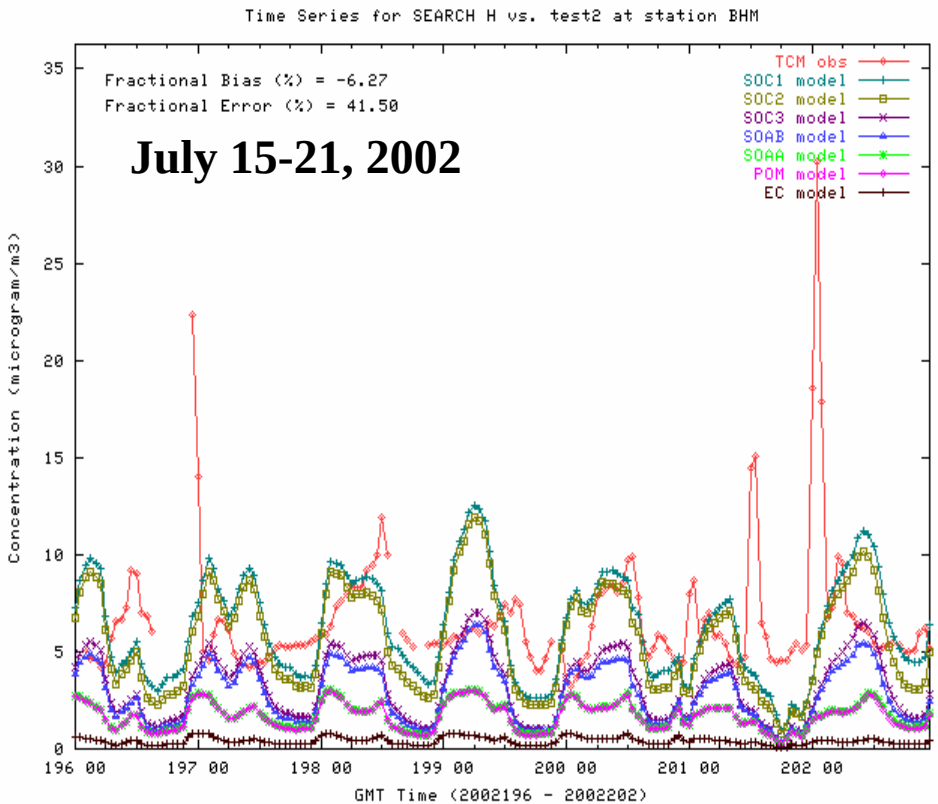


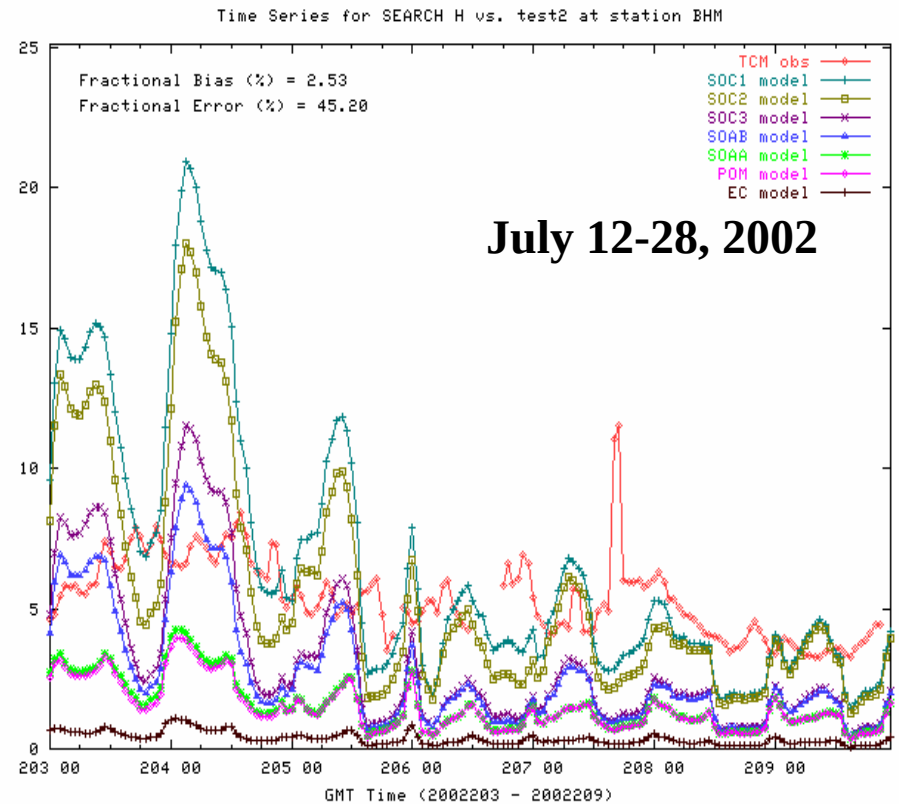
Summary of Results (July 2002)

	IMPROVE (OMC)		STN (TCM)	
F. BIAS	CMAQv4.4	SOA_mods	CMAQv4.4	SOA_mods
VISTAS	-103%	-2%	-93%	-30%
MRPO	-76%	+12%	-57%	-20%
MANE-VU	-82%	-14%	-82%	-40%
CENRAP	-98%	+8%	-69%	-23%
WRAP	+40%	+84%	-6%	+22%

F. ERROR	CMAQv4.4	SOA_mods	CMAQv4.4	SOA_mods
VISTAS	105%	39%	96%	46%
MRPO	78%	33%	63%	36%
MANE-VU	88%	52%	89%	52%
CENRAP	100%	49%	82%	48%
WRAP	83%	94%	52%	49%

Hourly TCM (SEARCH) at Birmingham CMAQ SOAmods

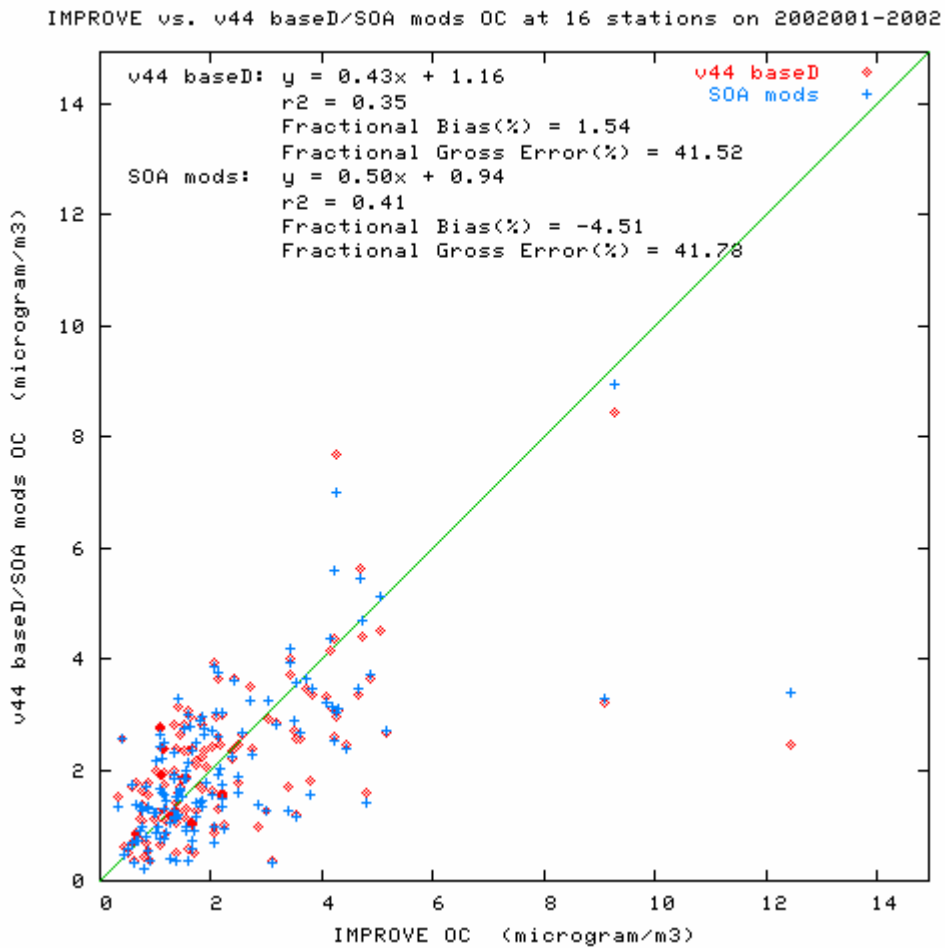




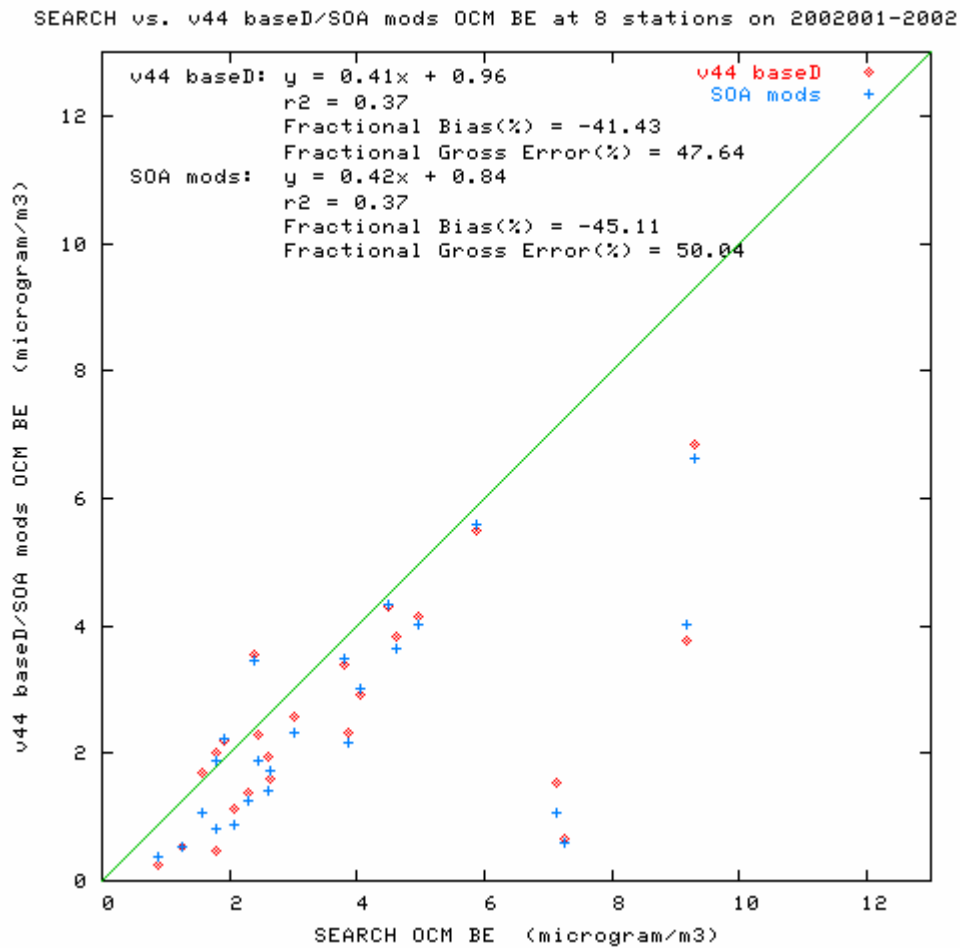
- **SOC1 (Polymerized), SOC2 (SQT+MT2), SOC3 (Isoprene)**
- Largest TCM components are SOC2 (sesquiterpenes), SOAB (MT1), and POM (primary)
- Diurnal variation still greater than observed

OMC at VISTAS (January 2002) IMPROVE & SEARCH

FB: 2% → -5%

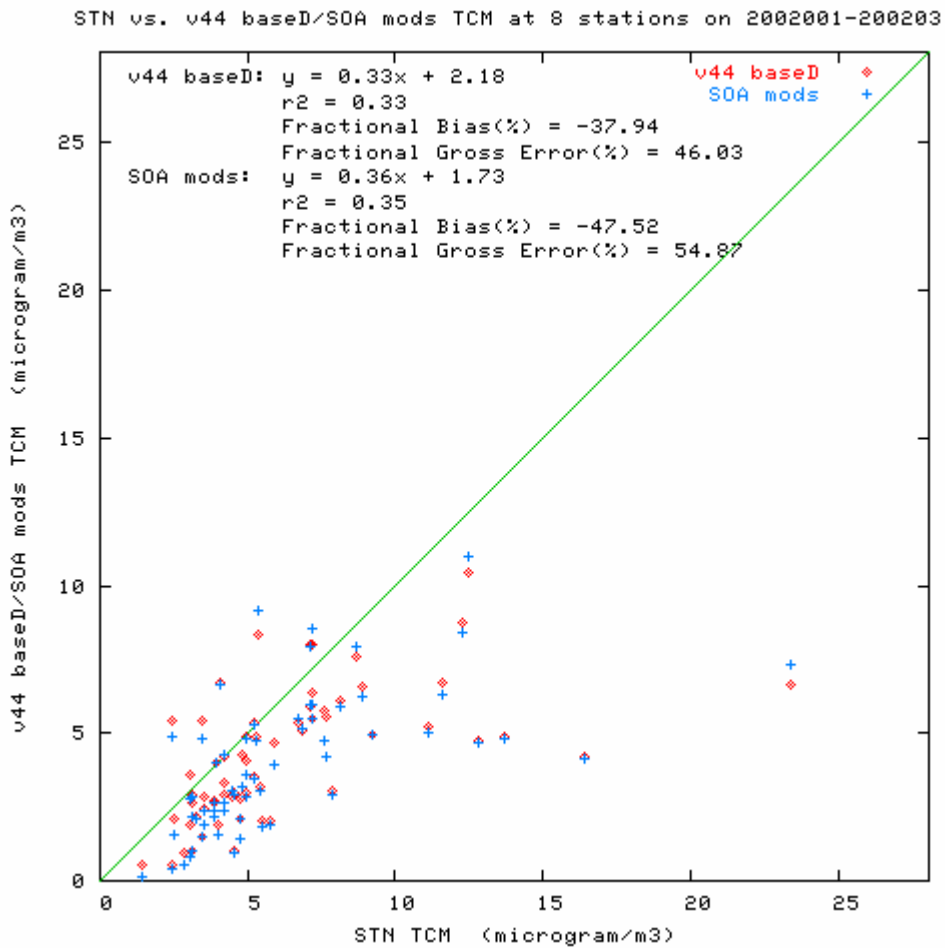


FB: -42% → -45%

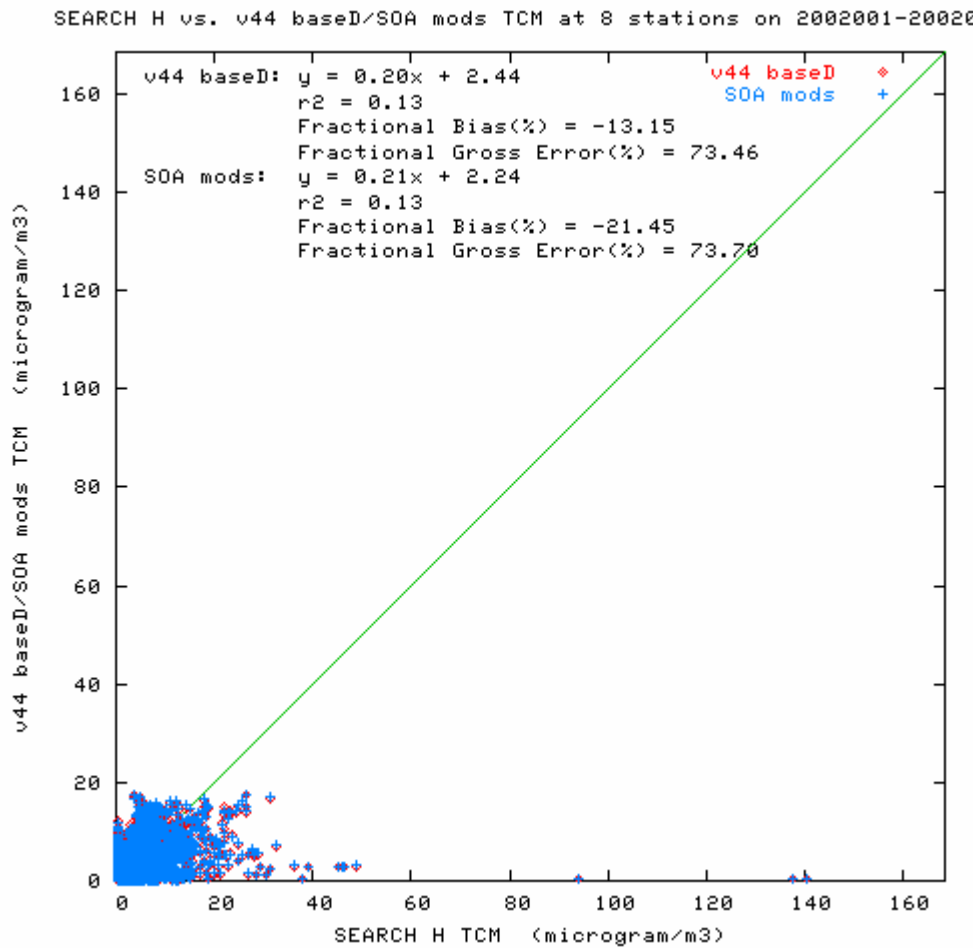


TCM at VISTAS (January 2002) STN and SEARCH_H

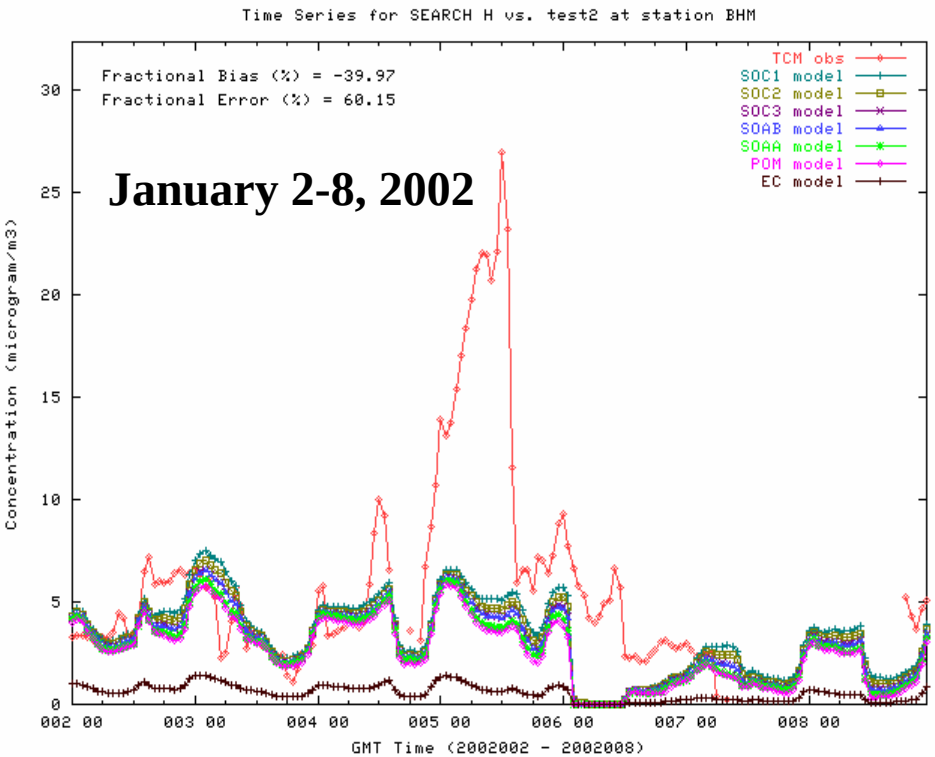
FB: -38% → -48%

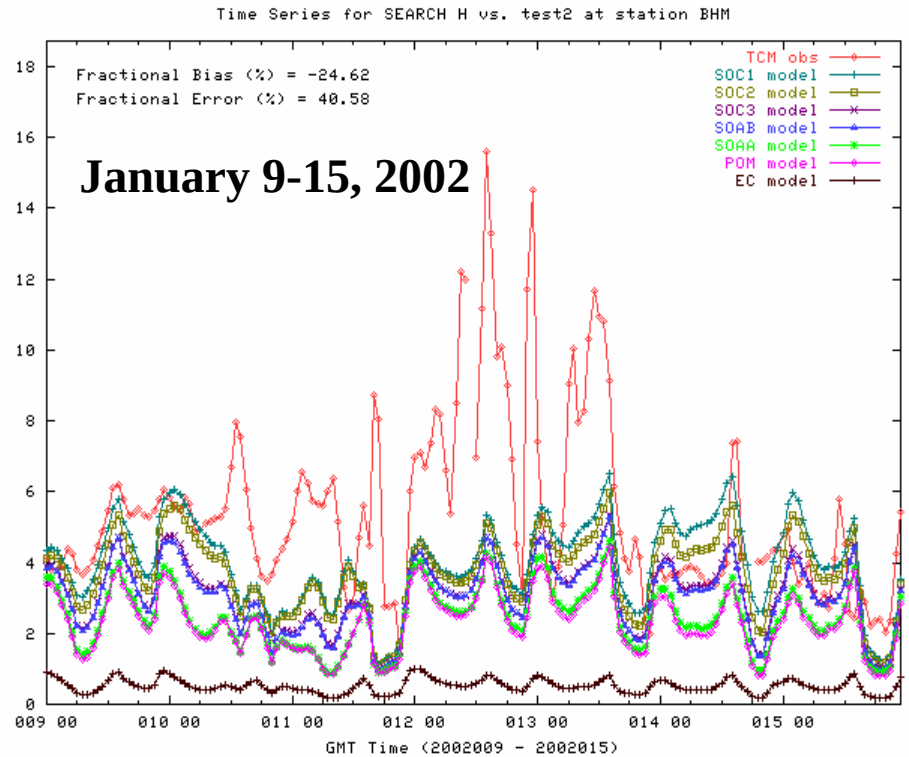


FB: -13% → -21%



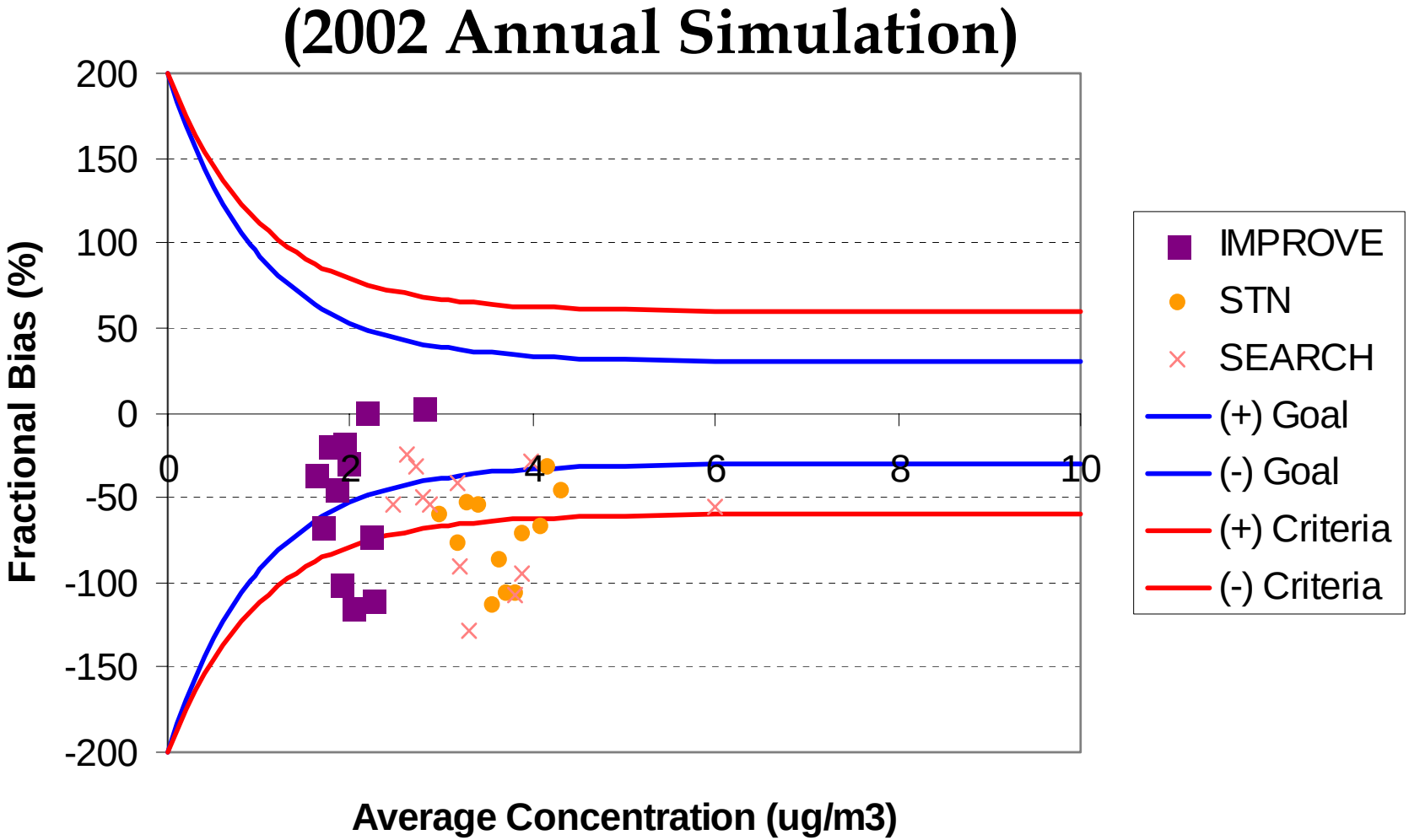
TCM (SEARCH) at Birmingham



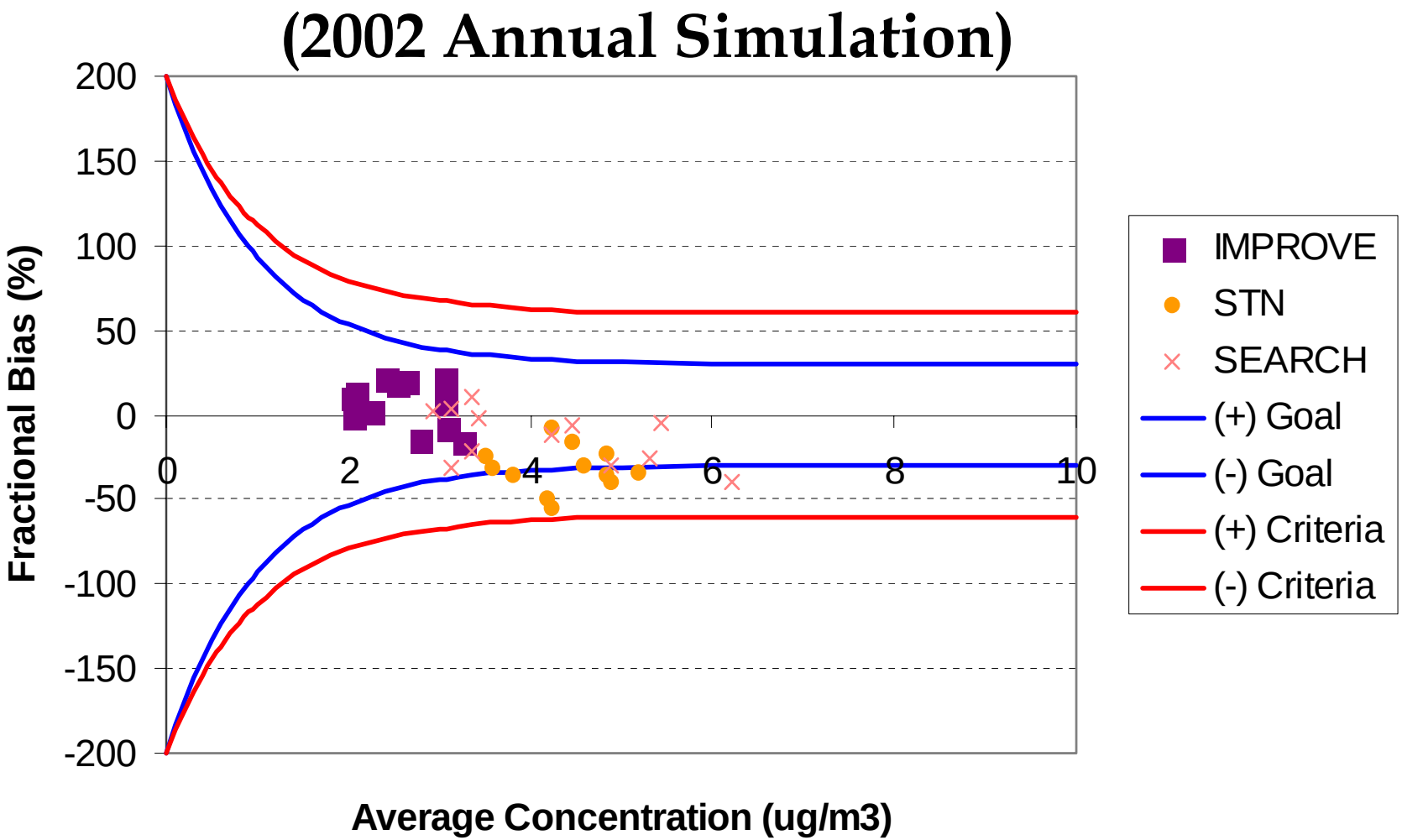


- **SOC1 (Polymerized), SOC2 (Sesquiterpenes), SOC3 (Isoprene)**
- POM largest component of TCM. SOA generally small.
- Large day-to-day variations not captured by model.
- Missing urban POM emissions in Birmingham???

2002 Annual Performance (OMC) CMAQ V4.4



2002 Annual Performance (OMC) CMAQ SOAmods



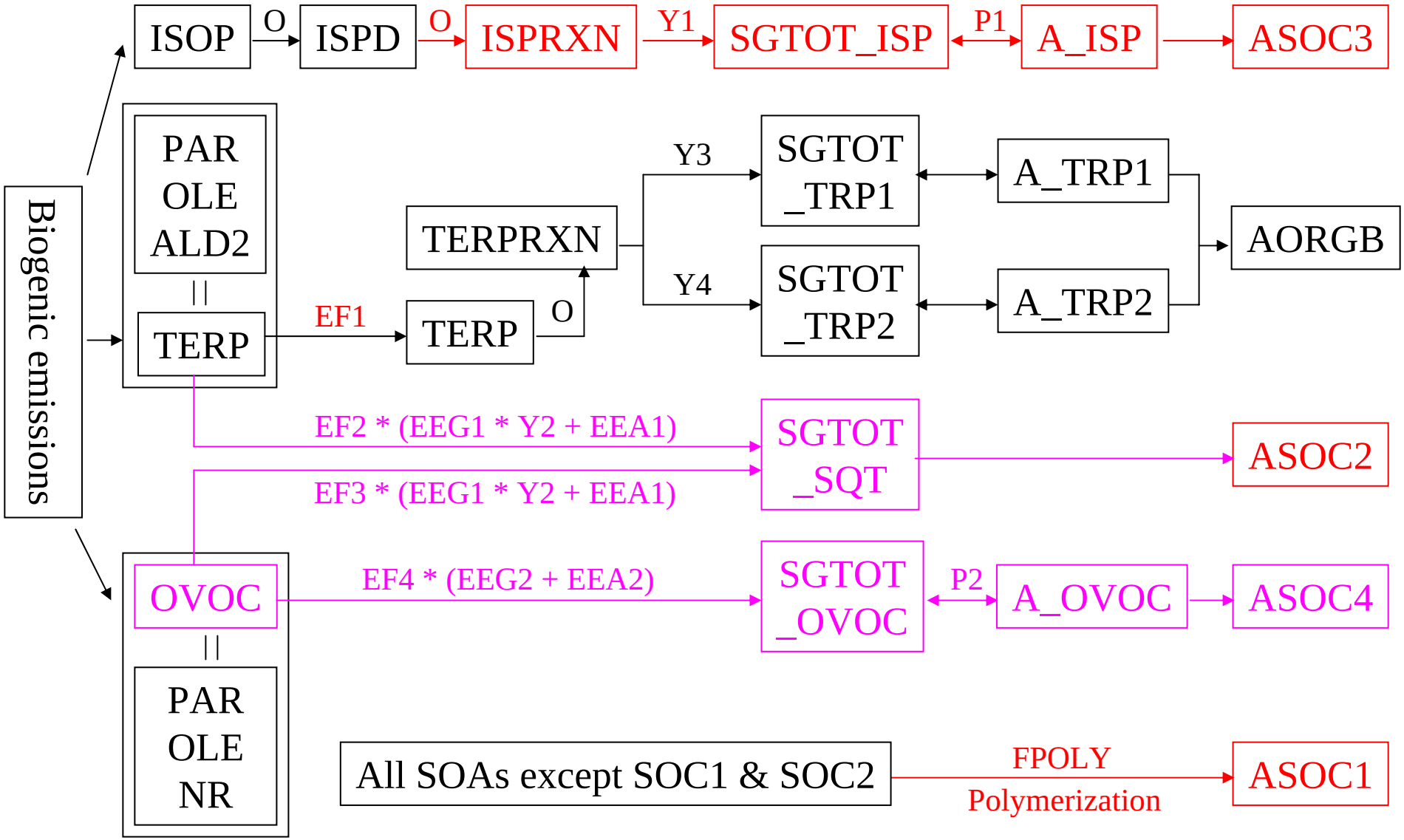
SOAmods Summary

- In summer, the SOAmods improves OMC and TCM performance in most RPOs, degraded in WRAP region
  - SOC2 (sesquiterpenes+MT2) largest contributor
  - Afternoon OMC/TCM peaks still too high
  - SOAmods parameterization based mainly on eastern US field study data, may not be representative of western US
- In winter, the SOAmods does not significantly change the OMC and TCM model performance over standard CMAQv4.4
  - POM largest contributor
  - CMAQ SOAmods OMC and TCM < CMAQv4.4
    - Needs further investigation
- Still OMC/TCM under-prediction bias in urban areas (e.g., STN)
  - Suspect missing primary OMC (POM) emissions (SMAT?)

Next Steps (VISTAS)

- Further refinement of SOAmods (SOAmods2)
  - Add OVOC to emissions
  - Add SOA products from OVOC
  - Base sesquiterpene and MT2 emissions on TERPB and OVOC emissions
  - Decided not to include CG decay
- Investigate primary OMC and EC emission inventories
  - Emissions might be too low – explain urban OMC underestimation
- Compare model results to OMC measurements that have been analyzed to separate old/new and primary/secondary carbon (e.g., SEARCH analysis)
  - For more rural OMC events not affected by fires new Carbon will be primarily biogenic SOA

Updated SOAmods2 module (June 2005) – original CMAQ SOA module, first SOAmods update, and latest additions (SOAmods2)



Updated SOAmods module (June 2005) Parameters

EF1	= 0.7	(mean value of 0.4 ~ 1)
EF2	= 0.2	(mean value of 0.1 ~ 0.3)
EF3	= 0.15	(mean value of 0.05 ~ 0.25)
EF4	= 0.07	(mean value of 0.02 ~ 0.12)
EEG1	= 0.33	(mean value of 0.2 ~ 0.45)
EEG2	= 0.38	(mean value of 0.25 ~ 0.5)
EEA1	= 0.2	(mean value of 0.05 ~ 0.35)
EEA2	= 0.2	(mean value of 0.1 ~ 0.3)
Y1	= 0.11	(mean value of 0.06 ~ 0.16)
Y2	= 0.88	(mean value of 0.75 ~ 1)
P1	= 0.45	(mean value of 0.15 ~ 0.75)
P2	= 0.5	(mean value of 0.2 ~ 0.8)

P1 (partitioning ratio = ratio of aerosol to total (gas+aerosol)) $= \dfrac{c_1(aer)}{c_1(gas)+c_1(aer)} = \dfrac{x_1 M_0 (MW_1/MW_0)}{x_1 c_1^* + x_1 M_0 (MW_1/MW_0)}$

$$c_1^* = \frac{1-P_1}{P_1} M_0 \frac{MW_1}{MW_0} = \frac{1-0.45}{0.45} \times 10 \times \frac{100}{150} = 8.2\ \mu g/m^3$$

$$c_2^* = \frac{1-P_2}{P_2} M_0 \frac{MW_2}{MW_0} = \frac{1-0.5}{0.5} \times 10 \times \frac{100}{150} = 6.7\ \mu g/m^3$$

M_0 is total organic mass (assumed ~10 μg/m^3)

FPOLY = 0.025 / hr (50% polymerization for 20 hours)

Next Steps (MRPO)

- Linked Emissions and AQ model updates in a consistent fashion to incorporate SOAmods concepts
- CONCEPT biogenic emissions model update to include new (MEGAN) emission factors, additional species and other factors important to biogenic SOA formation
  - Mark Jansen, Jim Wilkinson and Alex Guenther
- CAMx air quality model updated to interface with new CONCEPT biogenics model and SOA improvements
  - Kirk Baker, Bonyoung Koo, Alex Guenther, Greg Yarwood
- Implementation and evaluation of new linked COCEPT/CAMx modeling system (2005-2006)

CMAQ SOAmods Conclusions

- EPRI very good review of SOAmods, agreement with some processes (e.g., inclusion of sesquiterpenes) and some disagreement with processes and implementation
  - Recognize uncertainties in representations, but our belief is it is better to include uncertain representation of known processes than exclude completely
- EPA performing laboratory tests of SOA processes and expects to formulate new module for CMAQ ~2006
- SOAmods evaluation (June-July, 2005)
- SOAmods2 testing and evaluation (July-August 2005)
- Implementation of SOAmods concepts in emissions model (CONCEPT) and CAMx 2005-2006 (MRPO)