Updates to CMAQ SOA Module and Kz_min Values

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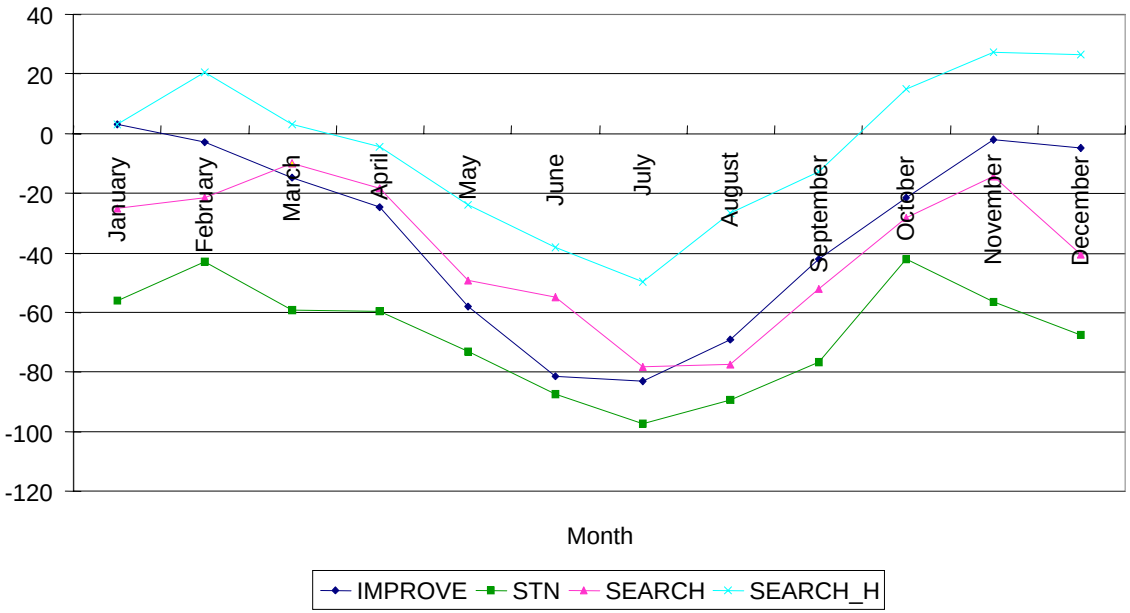
CMAQ SOA Module

Background

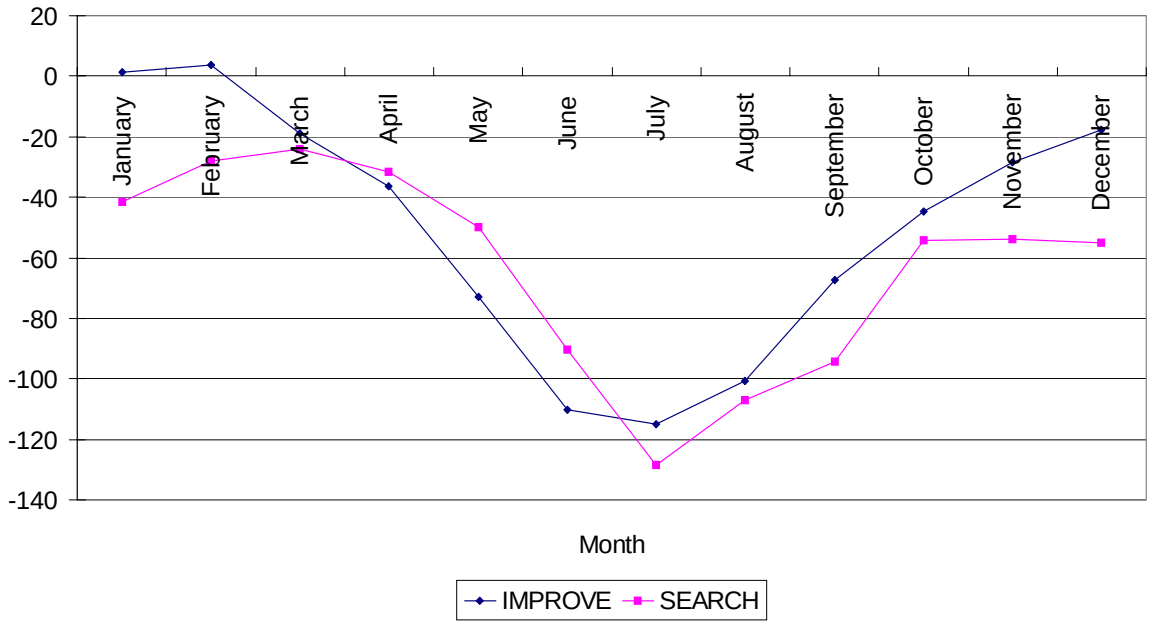
- SOA work was performed by ENVIRON, Alpine Geophysics, UC Riverside, and Alex Guenther (NCAR) with funding from VISTAS
- Large Summer OC Underestimation Bias
  - Revised CMAQ simulation using CMAQv4.4 (Base C) degraded OC performance compared to CMAQv4.3 (Base A)
    - January (2002) and July (2002) at 36 km
    - Believe due to correction of CMAQ vertical transport mass conservation error
  - CMAQ SOA module neglects several important processes



Organic Carbon (OC) CMAQ 36 km Fractional Bias

←Base A

IMPROVE/SEARCH

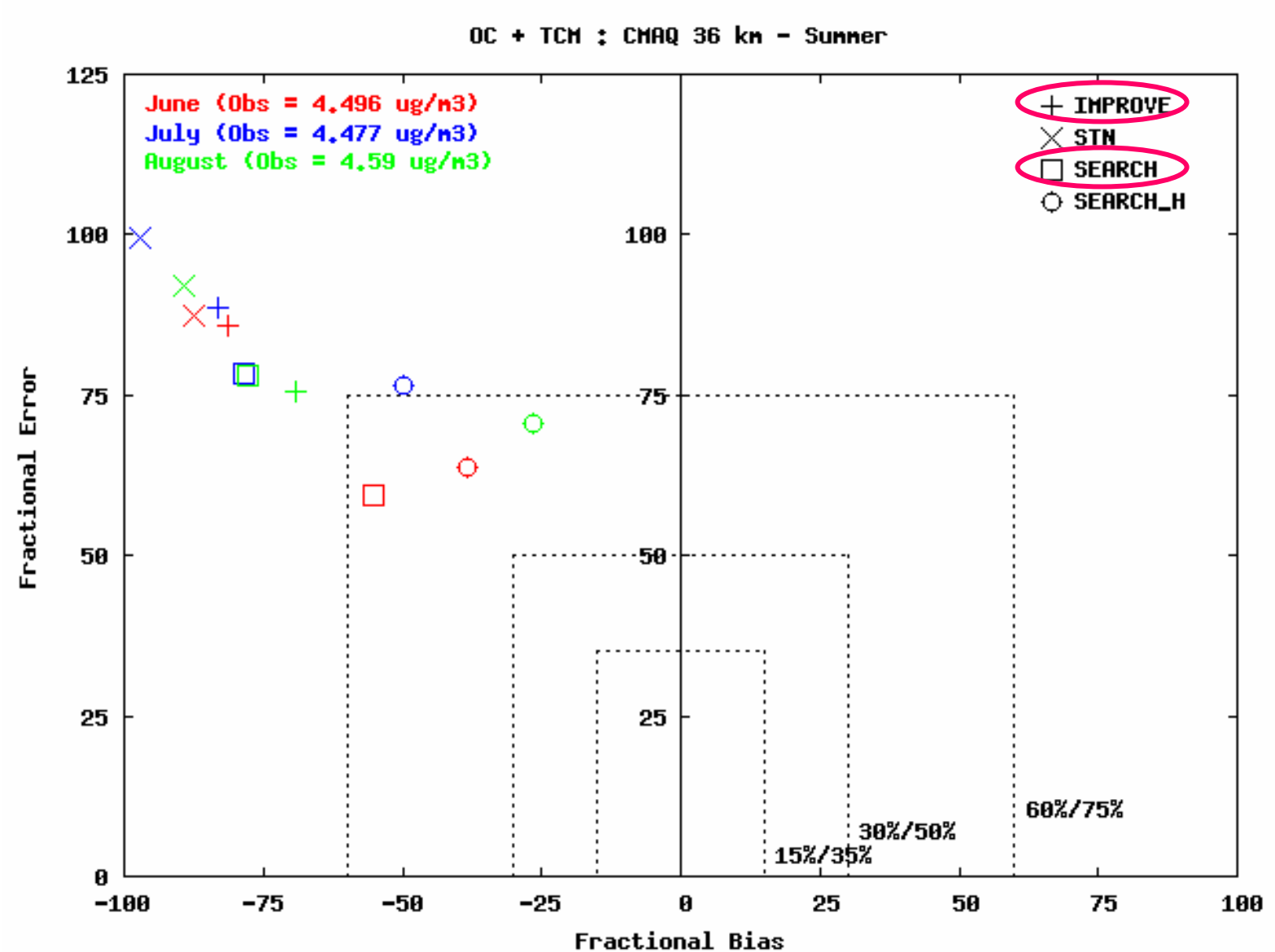


←Base C

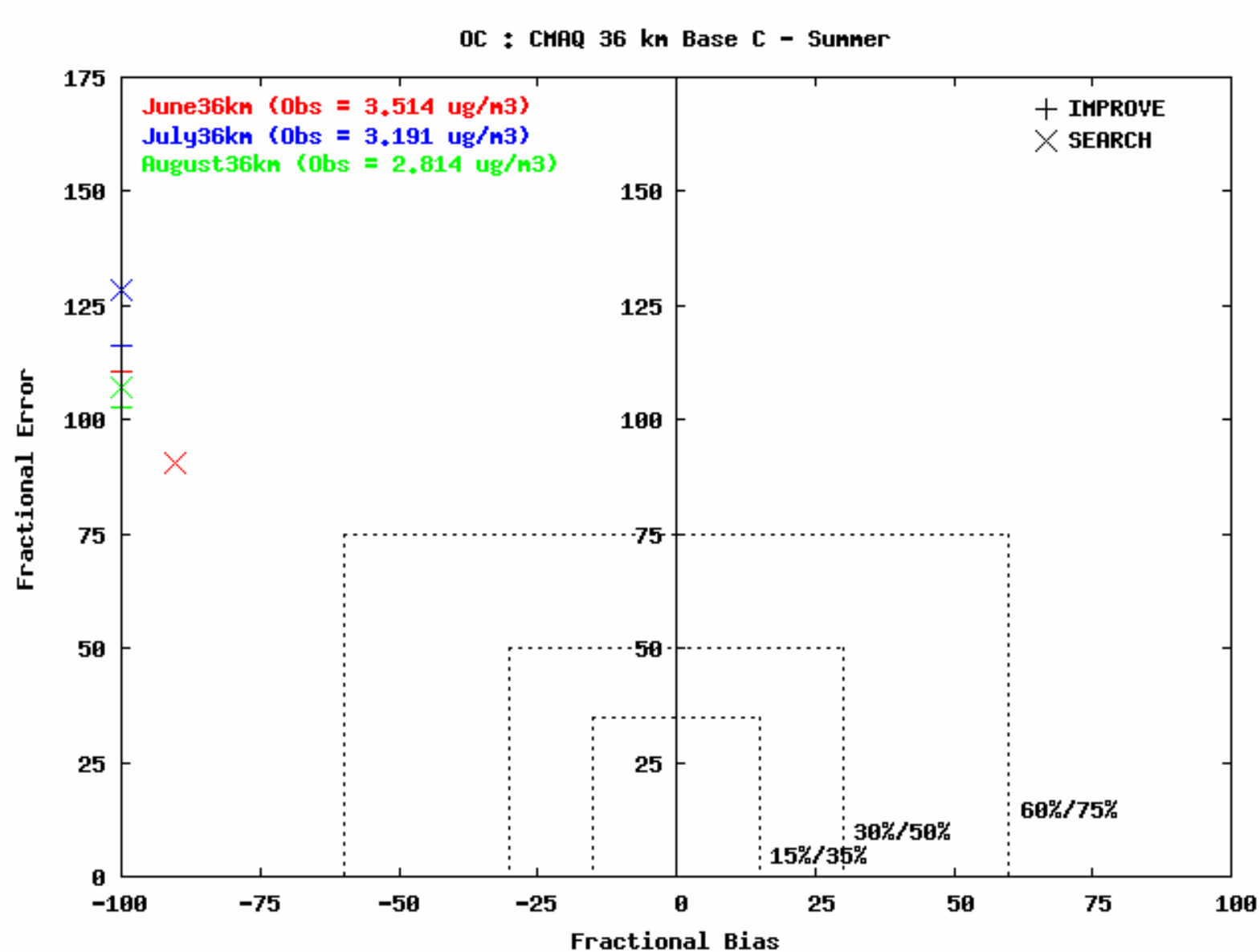
IMPROVE/SEARCH

Mainly degradation in OC performance toward larger underestimation

OC for Summer 2002 (Base A)



OC for Summer 2002 (Base C)



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

Uncertain and Missing Processes

- Uncertain SOA Parameters: CalTech chamber data used to fit CMAQ SOA parameters found to 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
- Isoprene: Not included, high in southeastern US
  - New evidence that isoprene may be SOA precursor (Claeys et al., Science 2004 303 1173)
- Reactivity: CGs are reactive VOCs that should oxidize and participate in photochemistry
- Biogenic OVOC: Also SOA precursor

Enhancement SOA Module

- Challenges:
  - BEIS TERB monoterpene emissions includes higher yield monoterpenes (MT2) and sesquiterpene emissions but treat them all as lower yield monoterpenes (MT1)
  - Additional biogenic terpene species beyond those in BEIS TERPB
  - No Biogenic OVOC emissions in CMAQ inputs
  - CMAQ SOA Module decoupled from photochemistry so CG decay difficult to implement
- Solutions:
  - MT1, MT2, and Sesquiterpene emissions ratio of TERPB
  - Neglect OVOC SOA formation for now
  - Neglect CG reactivity for now

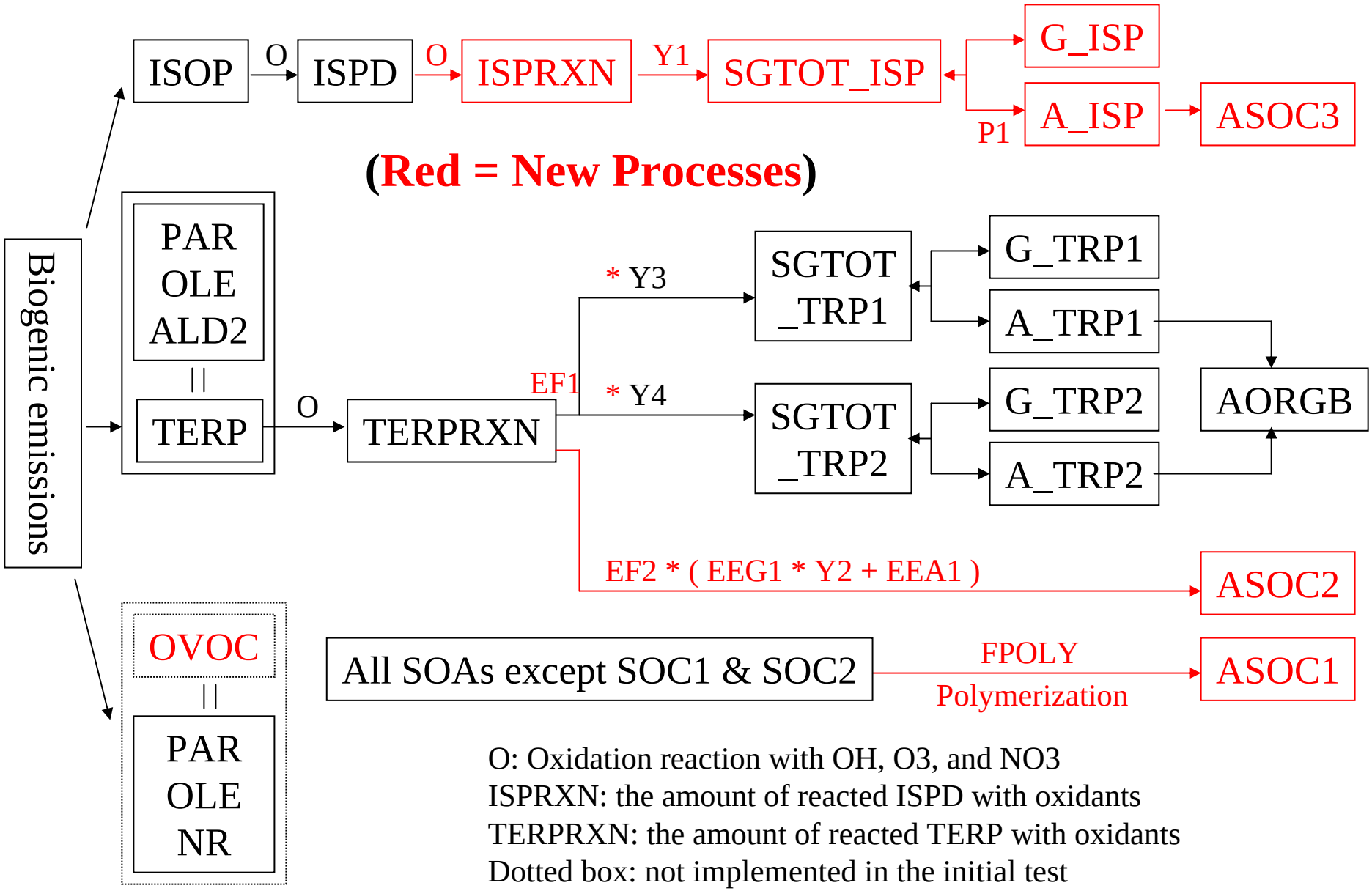
"SOA mods" Updates

- Keep CMAQ SOA parameters that are fit to CalTech smog chamber for lower yield monoterpenes (MT1)
- Keep same CMAQ inputs and existing CMAQ 2-product MT1 SOA module
- Update CMAQ SOA module to include:
  - Polymerization of SOA into non-volatile particles
  - SOA from sesquiterpenes, isoprene, and other monoterpenes
- Still missing from SOA module
  - Reactivity (decay) of Condensable Gases (CG)
  - SOA from biogenic OVOC emissions

"SOA mods" Definitions

- Add three new SOA species
  - ASOC1 ➔ Polymerized SOA (all SOA species except SOC1 and SOC2)
  - ASOC2 ➔ SOA from Sesquiterpenes and higher yield monoterpenes (MT2) (non-volatile)
  - ASOC3 ➔ SOA from Isoprene (volatile)
  - Still have AORGB = SOA from lower yield monoterpenes (MT1) (volatile)
- Types of Factors
  - EF ➔ Emissions Factors to adjust reacted CMAQ TERPB species to Monoterpenes 1 and 2 (MT1 & MT2) and Sesquiterpenes
  - EEG and EEA ➔ Canopy Escape Efficiencies
  - Y ➔ Yields

Revised 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 "SOA mods" 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 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)

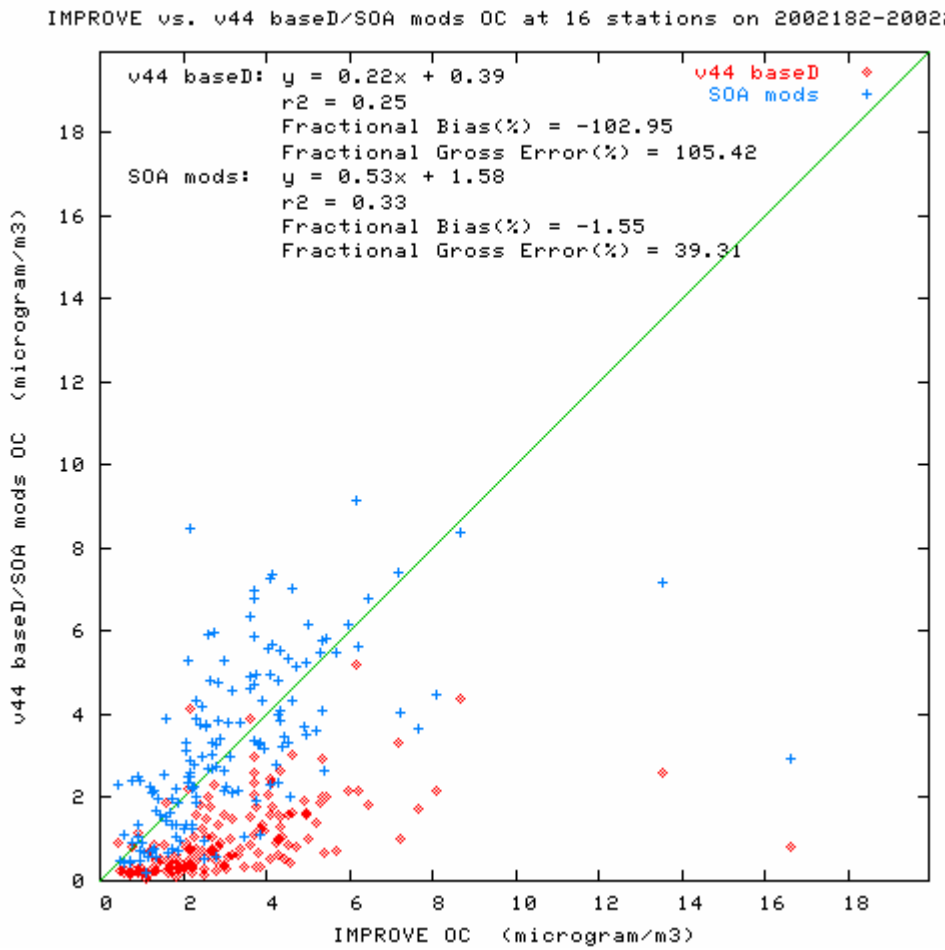
"SOA mods" Testing

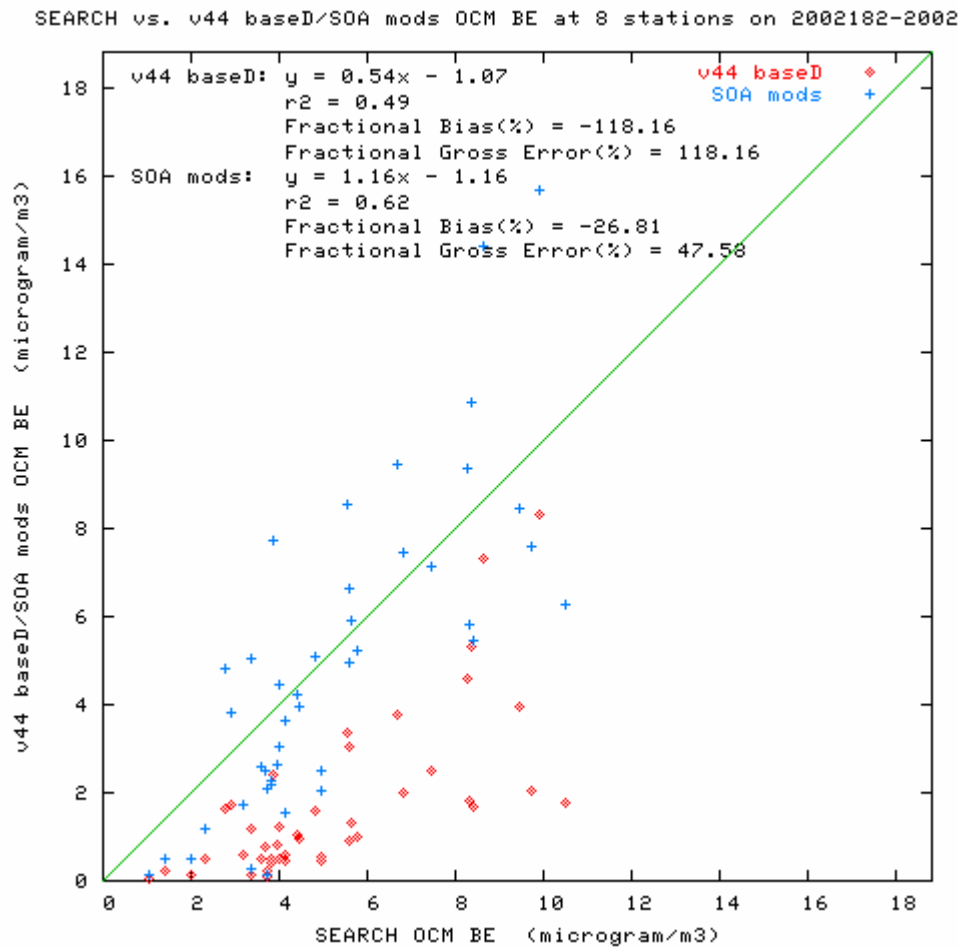
- Applied to January 2002 and July 2002
  - Standard CMAQv4.4
  - CMAQv4.4 with "SOA mods"
- Examined Organic Carbon (OC) at IMPROVE and SEARCH and Total Carbon Mass (TCM) at STN and SEARCH_H
- Examined various U.S. sub-domains
  - VISTAS, MRPO, MANE-VU, CENRAP, WRAP

OC at VISTAS (July 2002) IMPROVE & SEARCH

FB: -103% → -2%

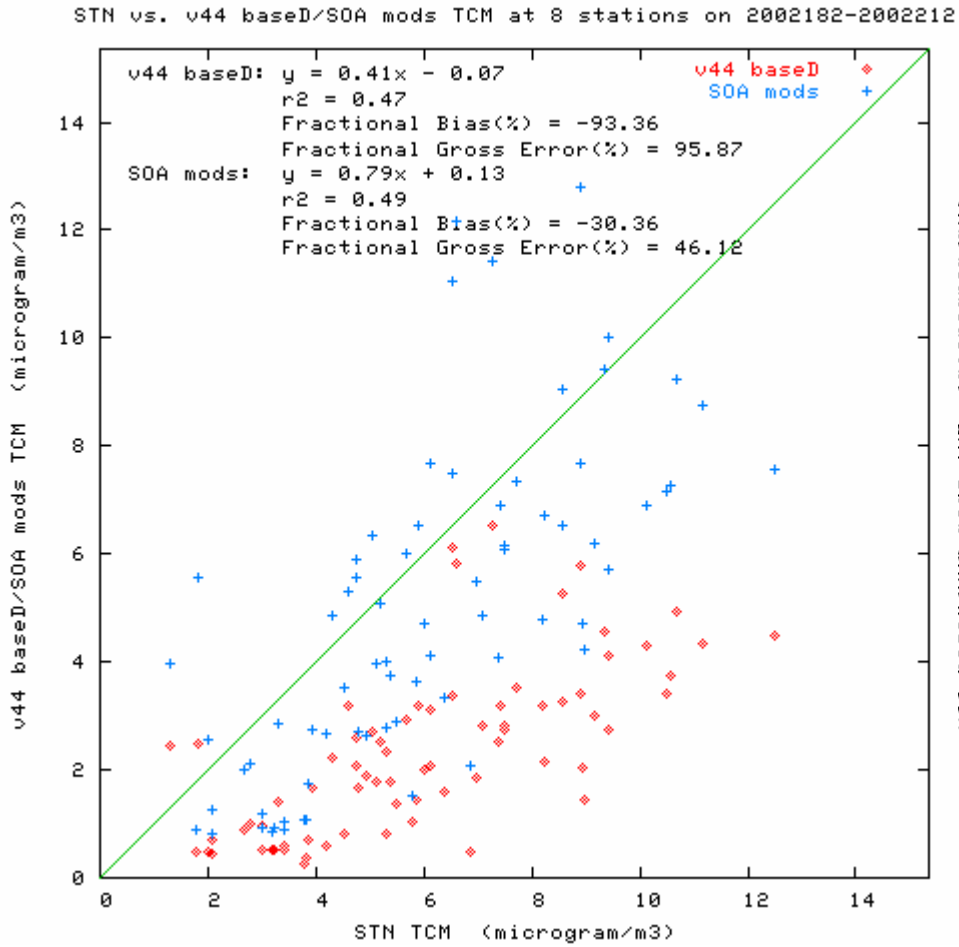
FB: -118% → -27%



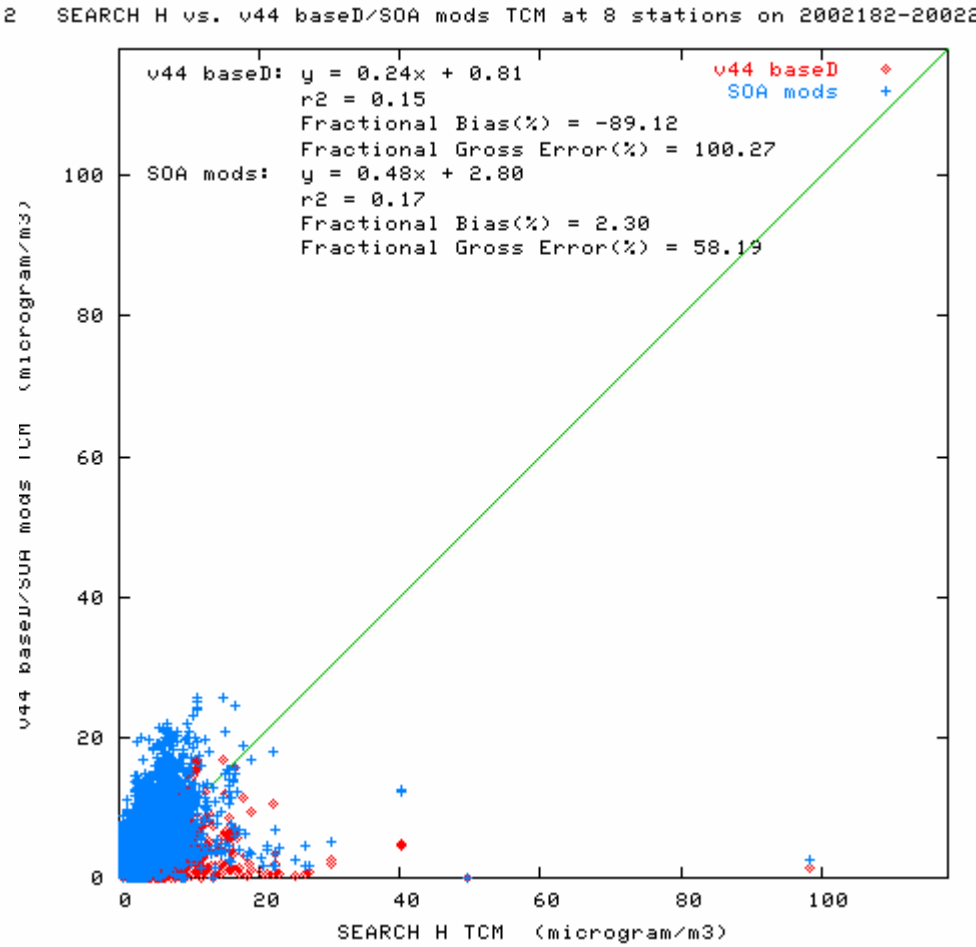


TCM at VISTAS (July 2002) STN & SEARCH_H

FB: -93% → -31%



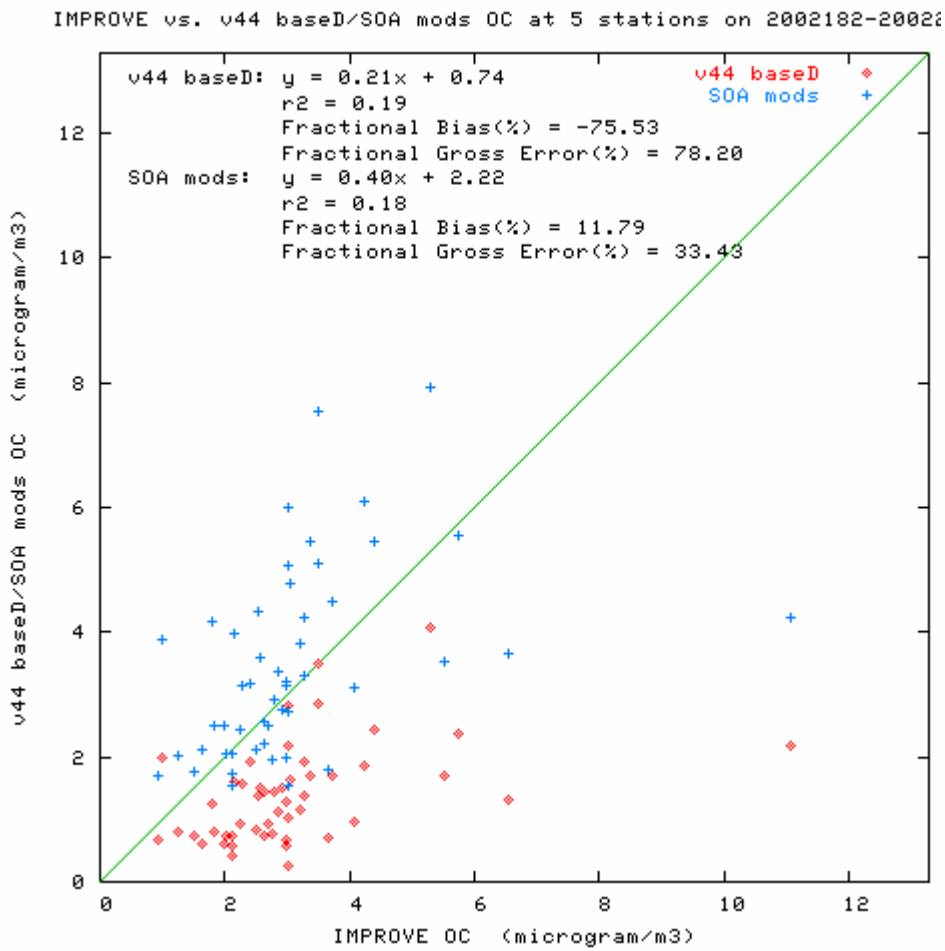
FB: -89% → +2%

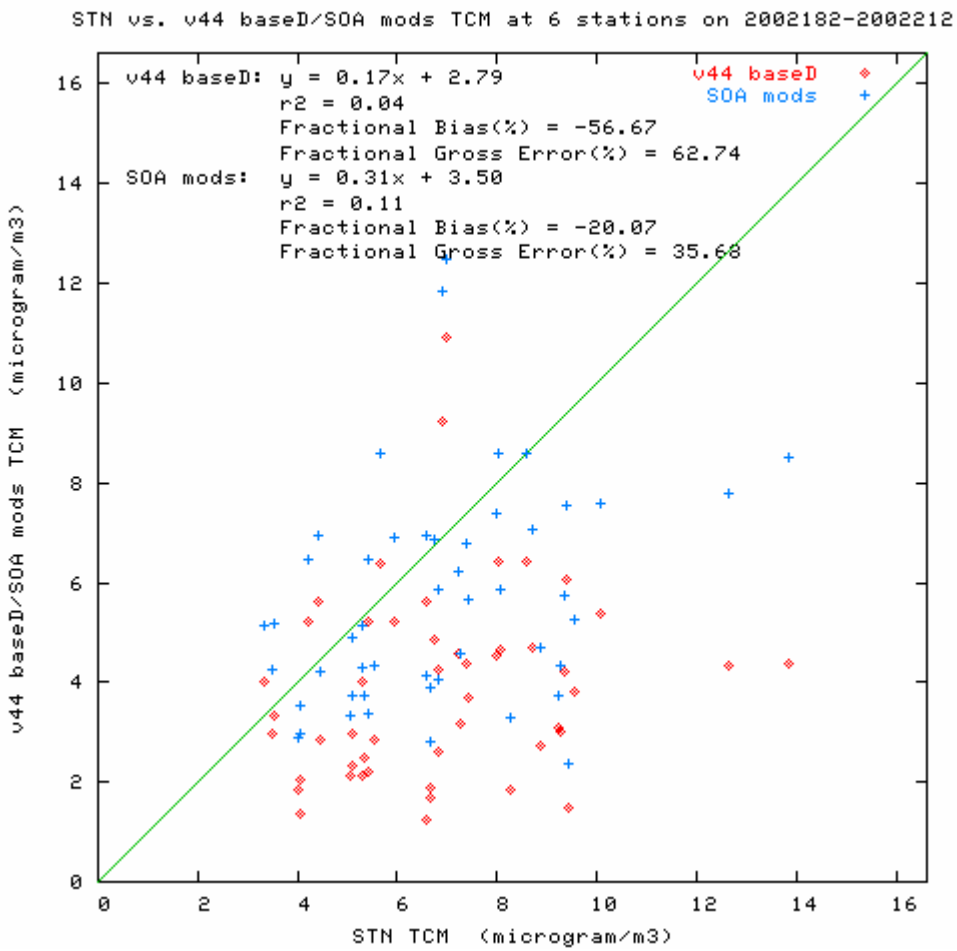


OC/TCM at MRPO (July 2002) IMPROVE & STN

OC FB: -76% → +12%

TCM FB: -57% → -20%

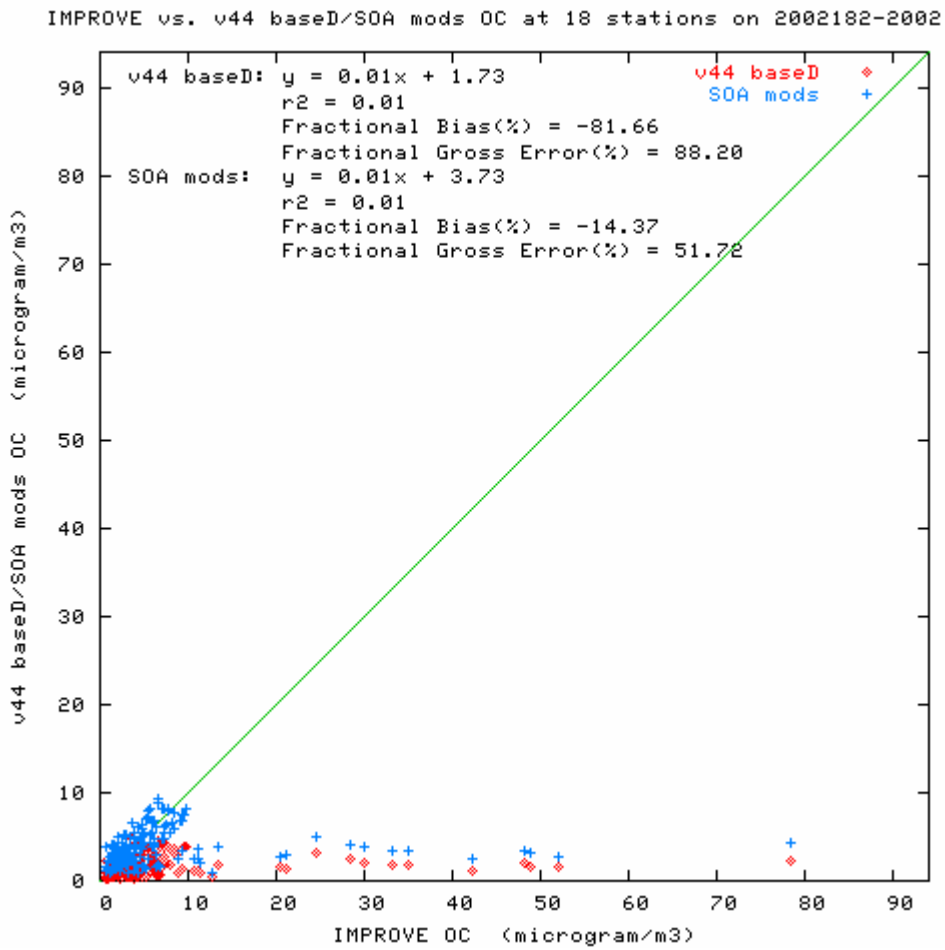


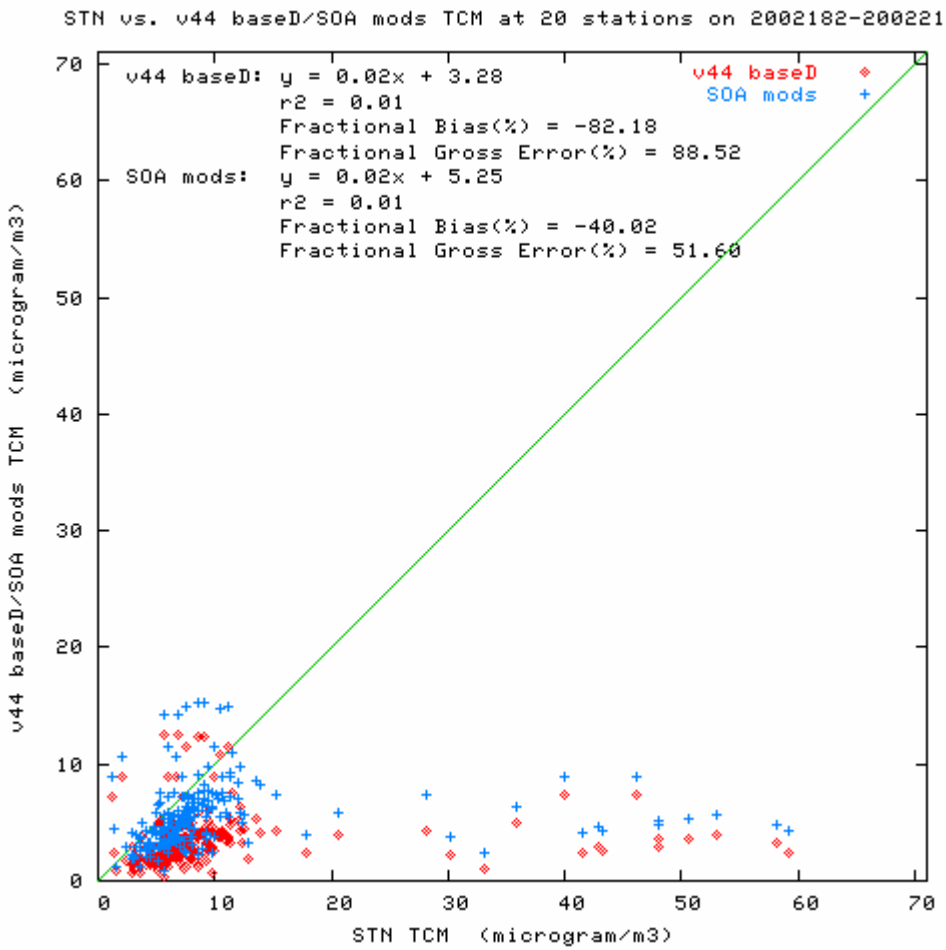


OC/TCM at MANE-VU (July 2002) IMPROVE & STN

OC FB: -82% → -14%

TCM FB: -82% → -40%

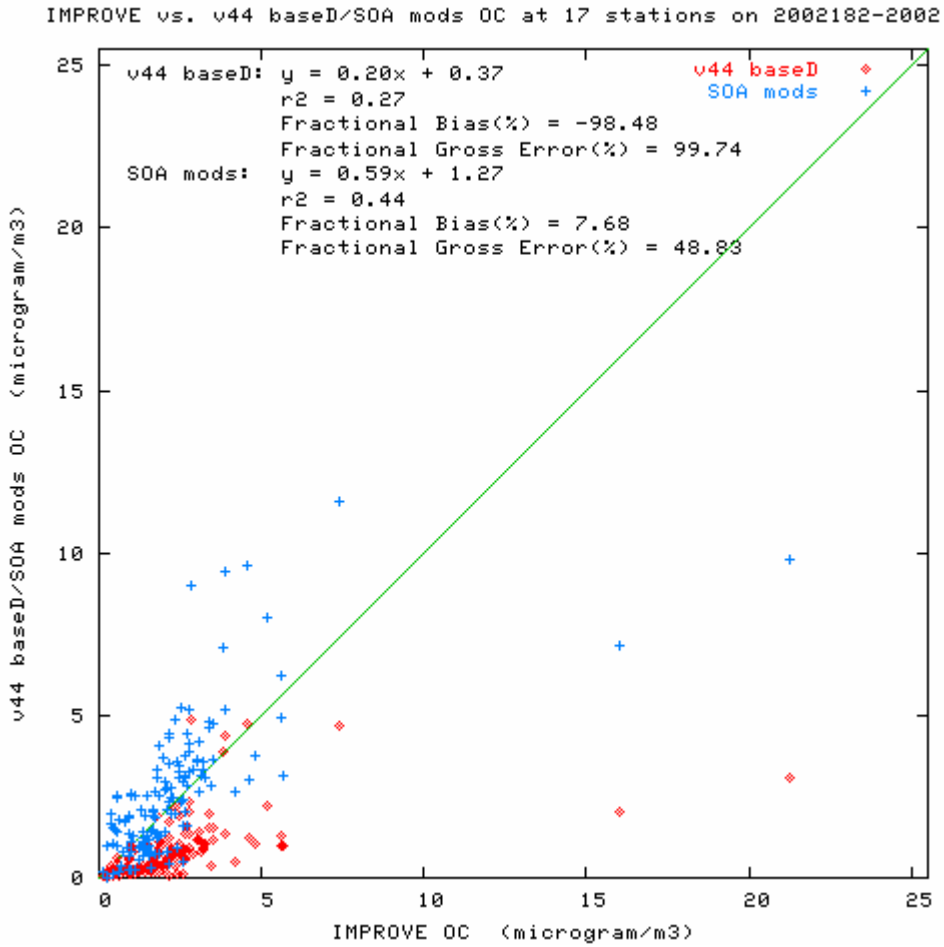


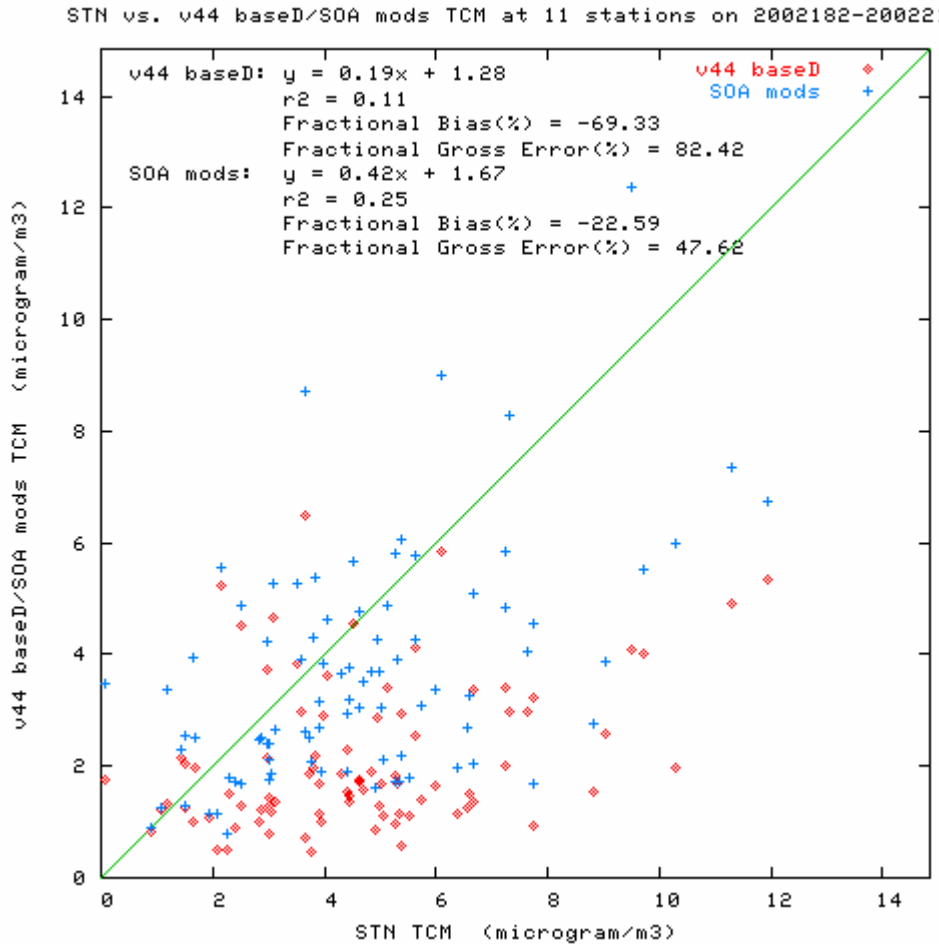


OC/TCM at CENRAP (July 2002) IMPROVE & STN

OC FB: -98% → +8%

TCM FB: -69% → -23%

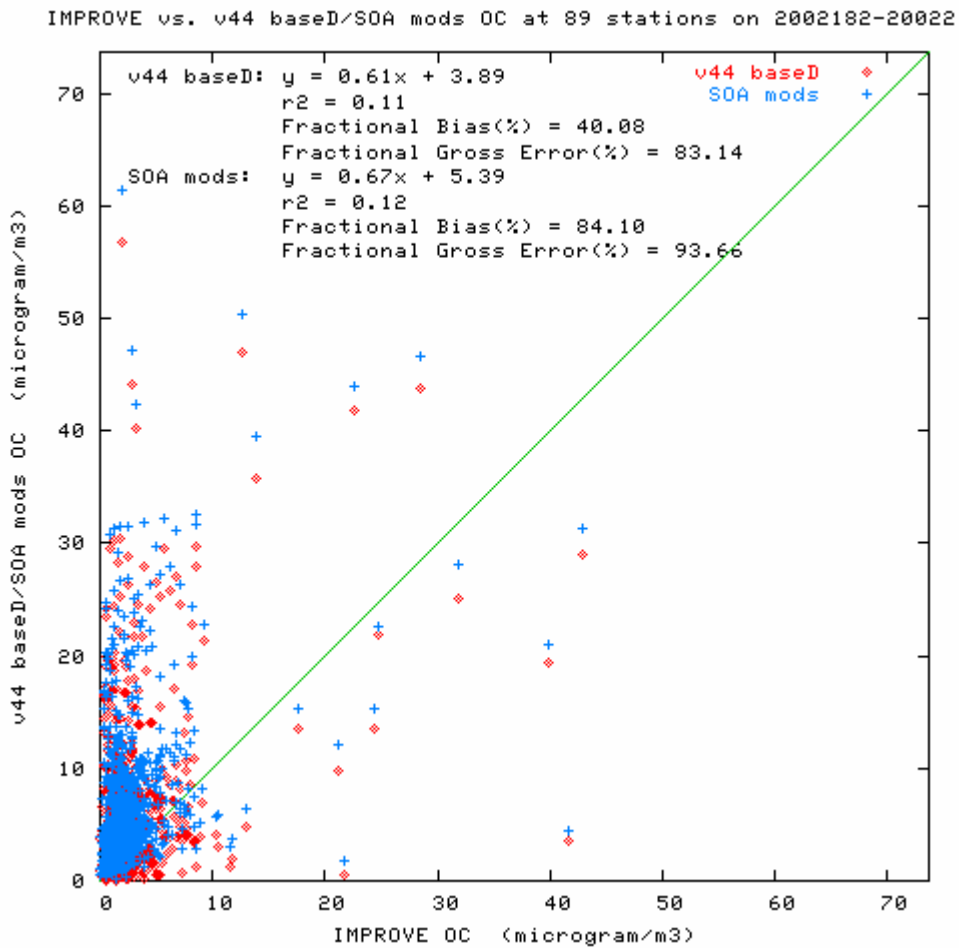


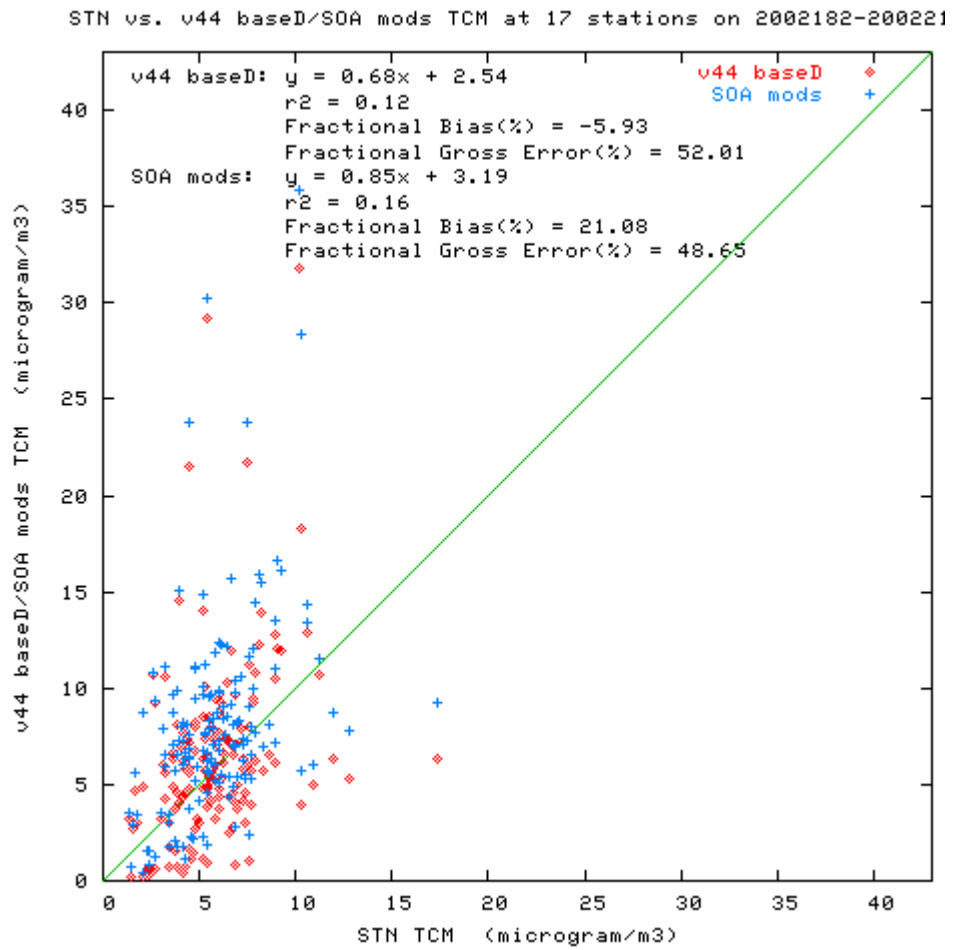


OC/TCM at WRAP (July 2002) IMPROVE & STN

OC FB: +40% → +84%

TCM FB: -6% → +21%



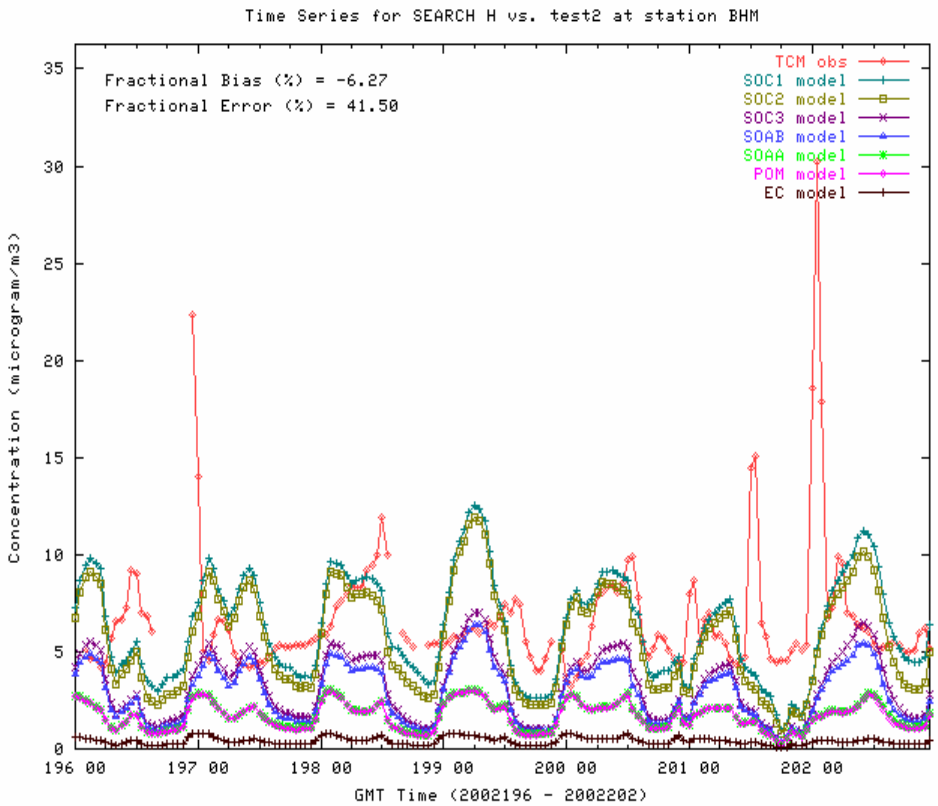


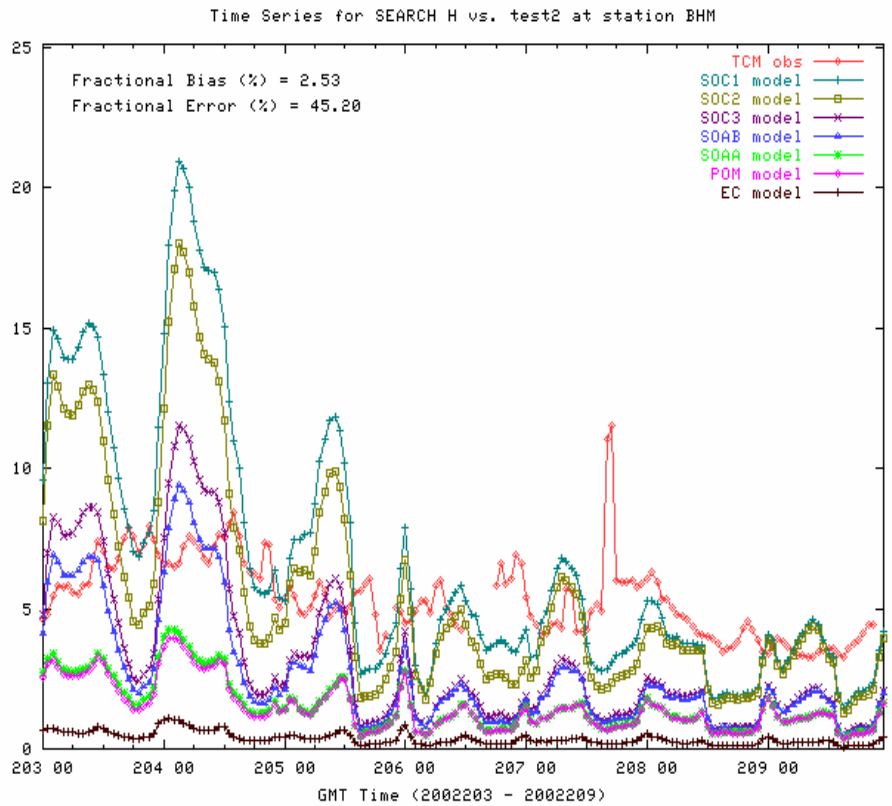
Summary of Results (July 2002)

	IMPROVE (OC)		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%

TCM (SEARCH) at Birmingham

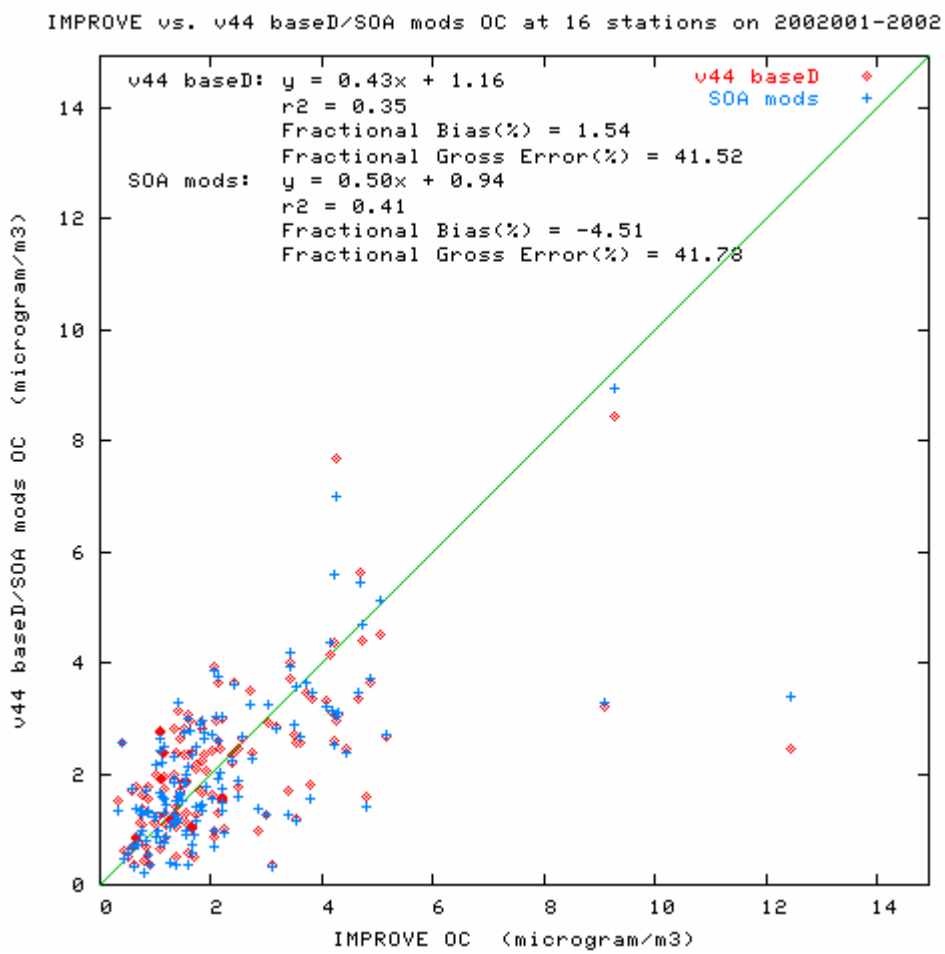




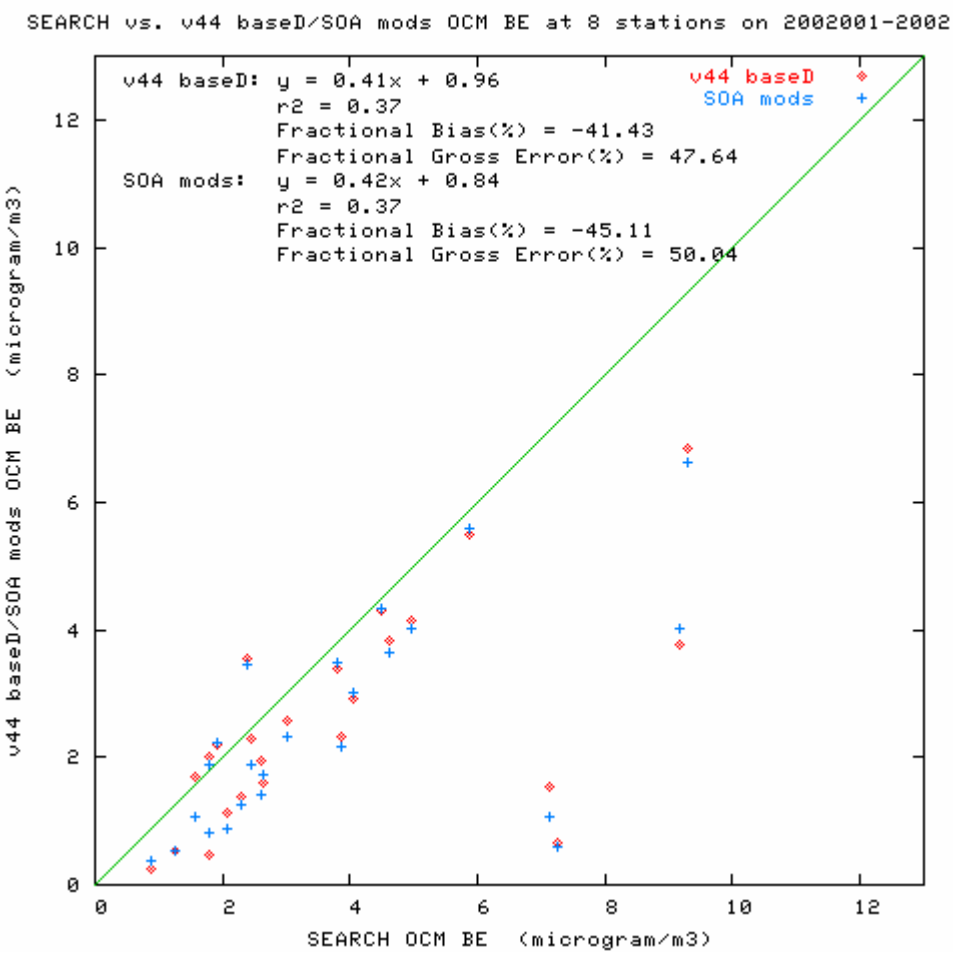
- SOC1 (Polymerized), SOC2 (Sesquiterpenes), SOC3 (Isoprene)
- Largest TCM components are SOC2, SOAB, and POM
- Diurnal variation too great

OC at VISTAS (January 2002) IMPROVE & SEARCH

FB: 2% → -5%



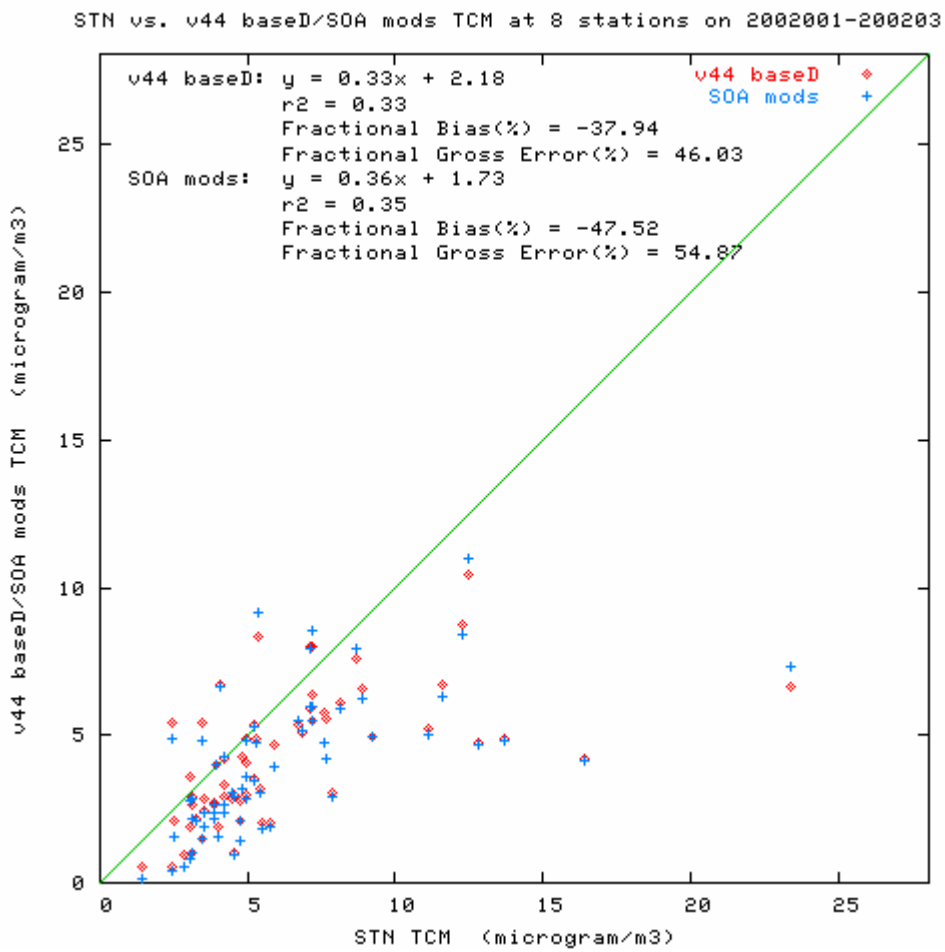
FB: -42% → -45%

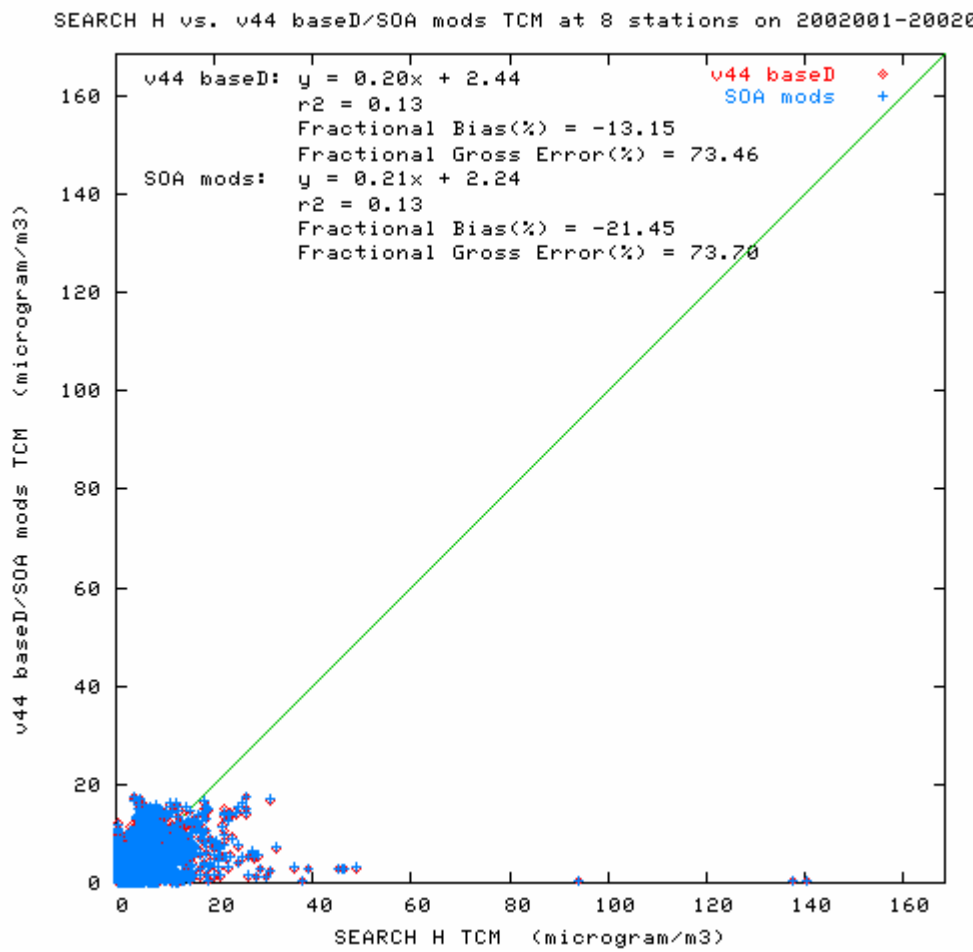


TCM at VISTAS (January 2002) STN and SEARCH_H

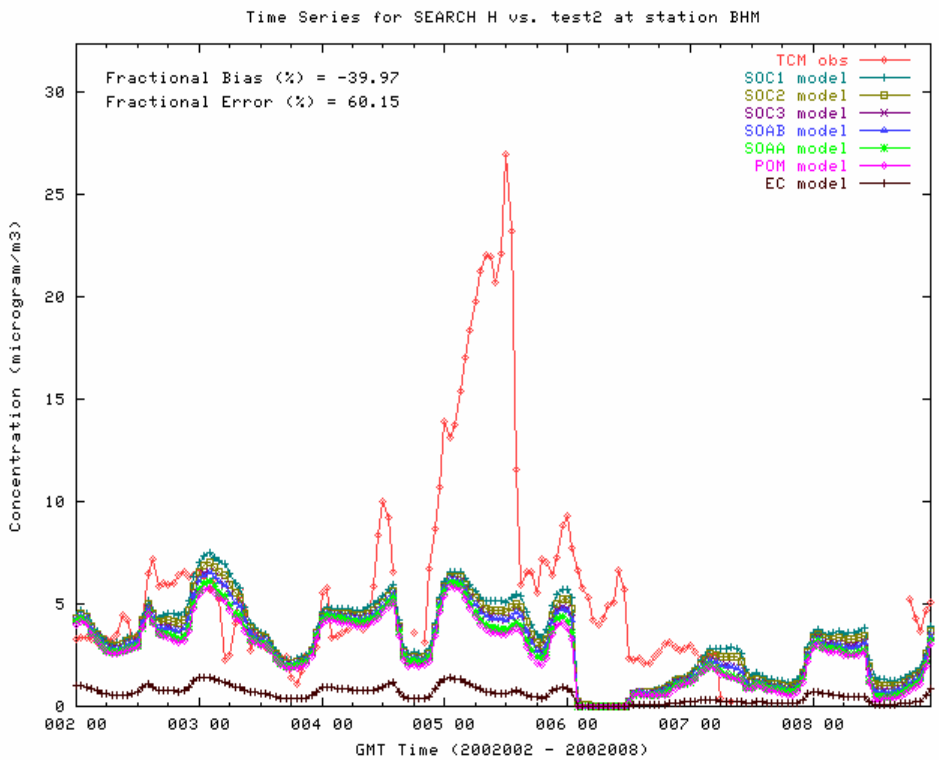
FB: -38% → -48%

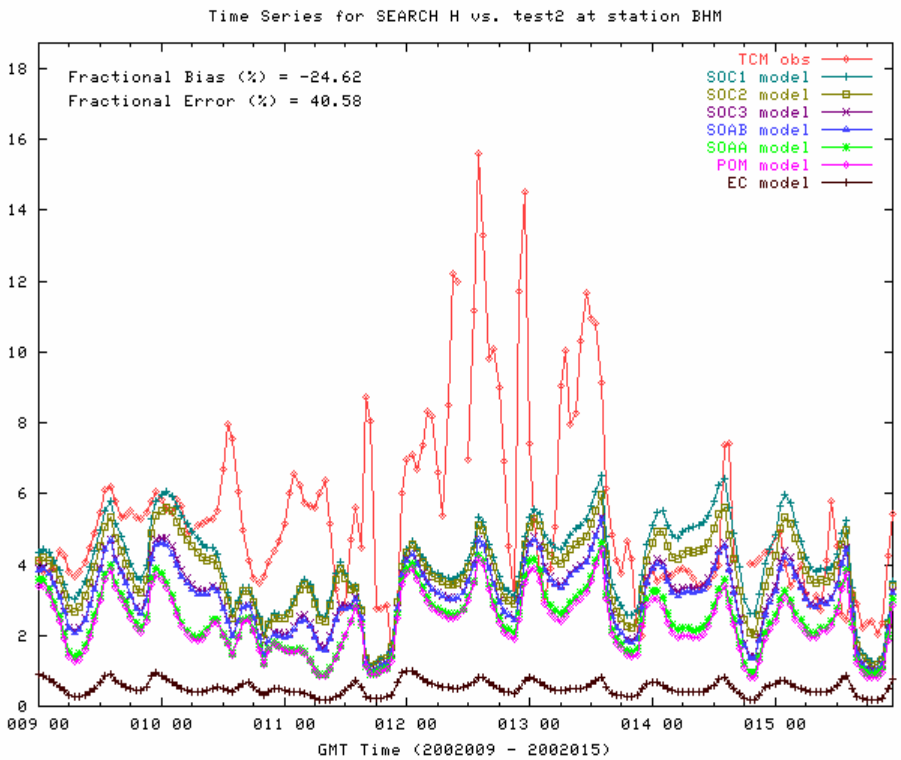
FB: -13% → -21%





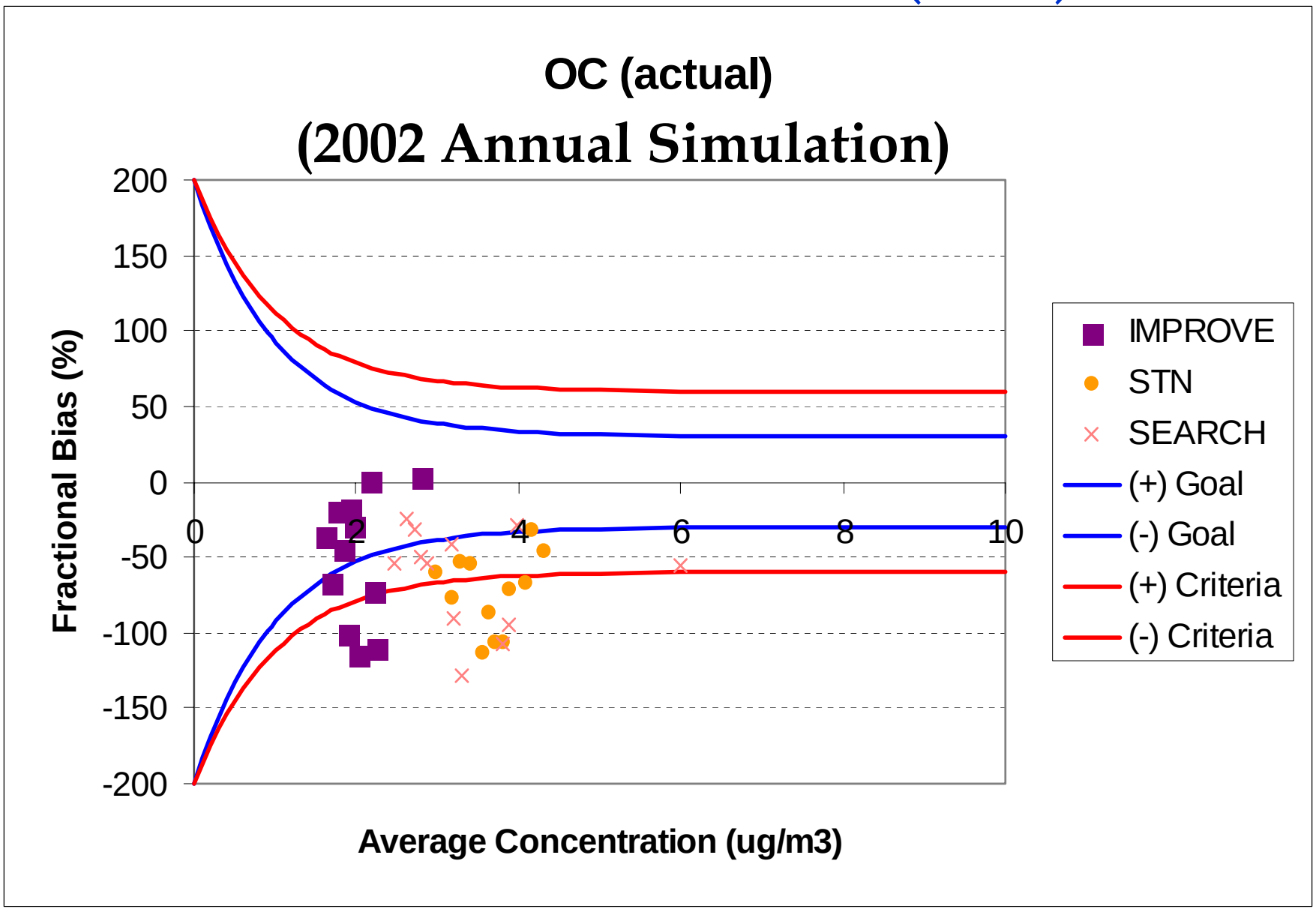
TCM (SEARCH) at Birmingham



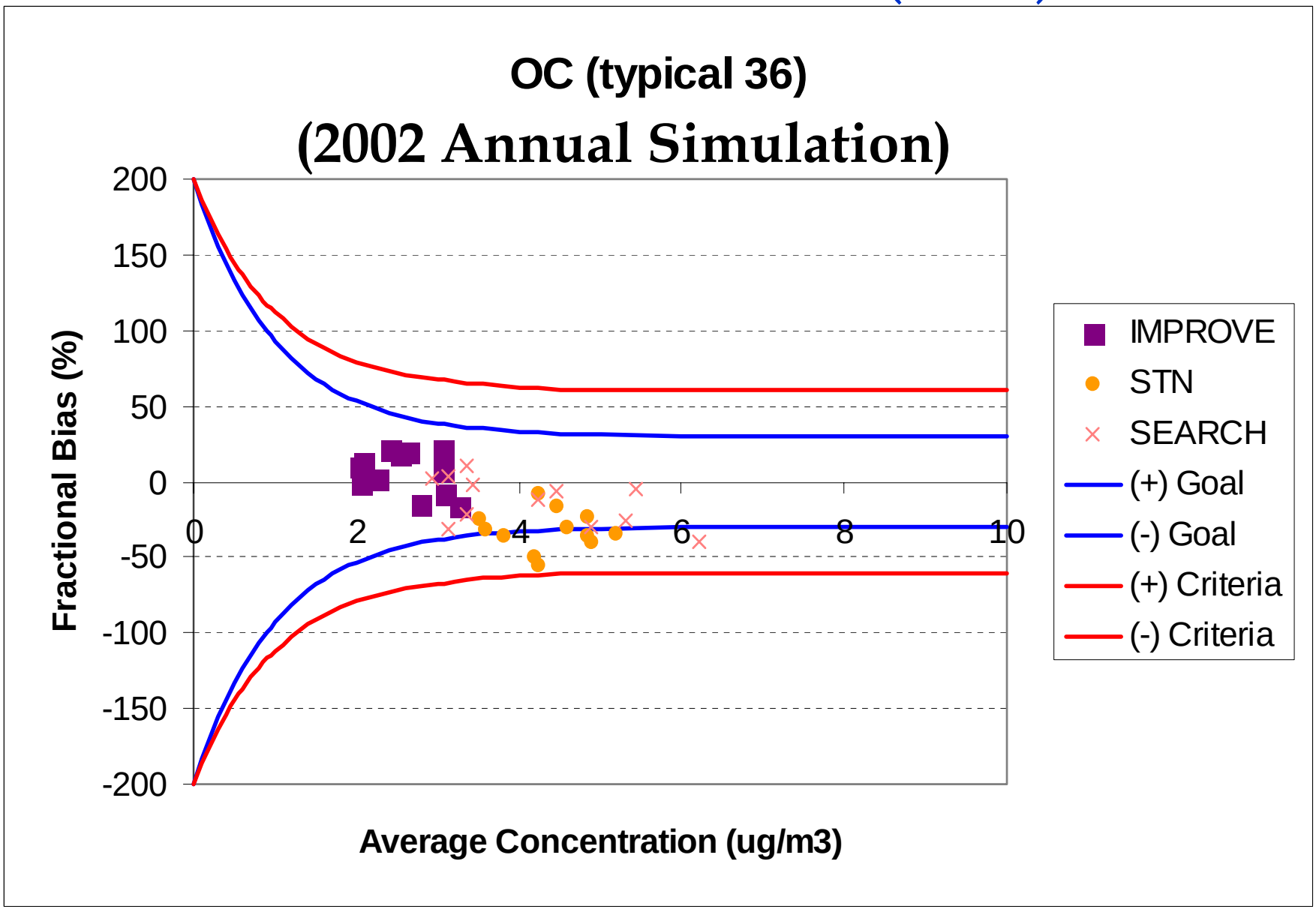


- SOC1 (Polymerized), SOC2 (Sesquiterpenes), SOC3 (Isoprene)
- POM largest component of TCM. SOA generally small.
- Large day-to-day variations not captured by model.

VISTAS Performance (OC) - old



VISTAS Performance (OC) - new



"SOA mods" Summary

- In summer, the SOA mods improves OC and TCM model performance over standard CMAQv4.4 in most RPOs, but degrades in in the WRAP subdomain
  - SOC2 (sesquiterpenes+MT2) large contributor
  - Afternoon OC/TCM peaks still too high
- In winter, the SOA mods does not significantly change the OC and TCM model performance over standard CMAQv4.4
  - POM largest contributor
  - CMAQ "SOA mods" OC and TCM < CMAQv4.4
    - Needs further investigation

Additional Analysis

- Refine SOC2/sesquiterpene treatment
- Add OVOC parameterization
  - Need to add OVOC to SMOKE emission files
  - Expect OVOC to increase OC/TCM slightly
- Add reactivity of CGs
  - More extensive code modifications to CMAQ
  - Reactivity of CGs should decrease SOA (but not SOC2) with largest reductions occurring in afternoon when modeled OC/TCM peaks are too high
- Further investigation into January OC/TCM reductions
- Investigate primary OC and EC emission inventories
  - Emissions might be too low
- Compare model results to SEARCH ^{14}C measurement data and source apportionment data
  - Biogenic/Anthropogenic/Primary/Secondary

Minimum Kz Values

Background

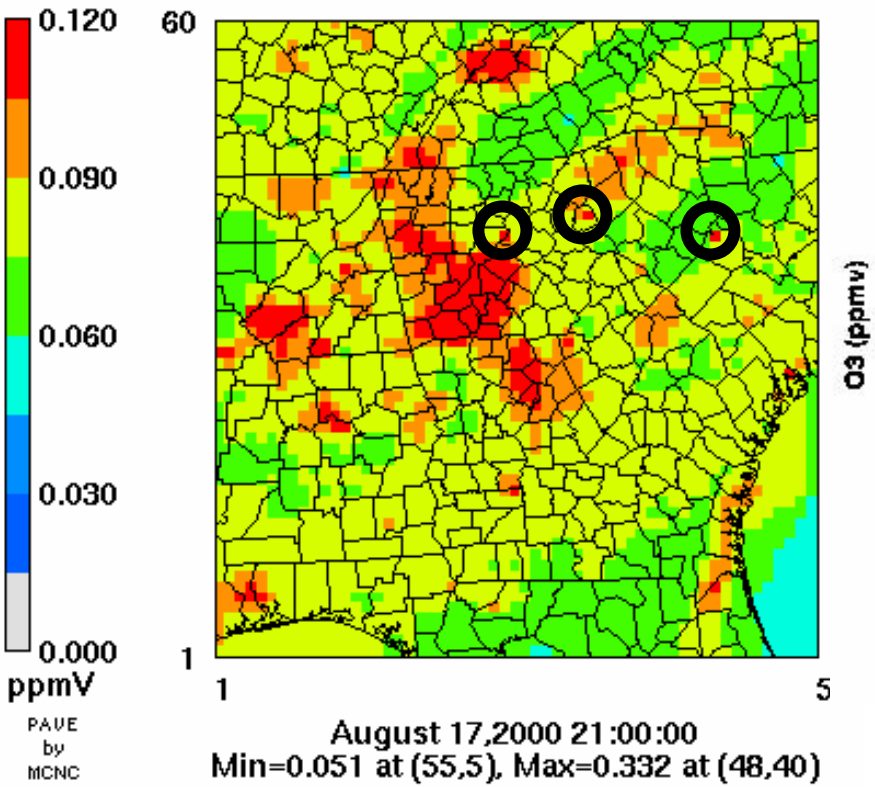
- The MCIP meteorological processors diagnosis the vertical turbulent exchange coefficients (Kz) from the MM5 meteorological variables and then CMAQ imposes a global minimum value (Kz_min) across the three-dimensional modeling grid
  - The current default Kz_min value is 1.0 m^2/s.
  - Higher Kz_min ➔ more mixing
- The value of the minimum diffusivity (Kz_min) plays an important role in the vertical distribution of emissions especially during nocturnal hours or other stable periods with limited mixing
  - Values that are too low can lead to over predictions of mass (concentrations) in the lowest model layers
  - Values that are too high can lead to over-mixing of emissions through very deep layers

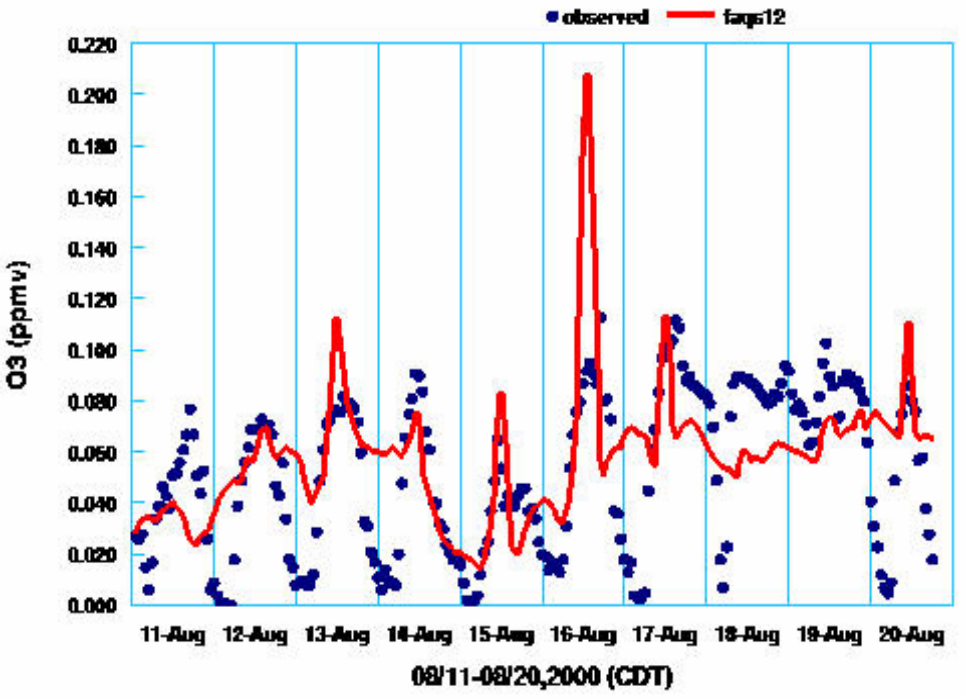
GaTech Kz_min Experiment

Species	Periods	Pairs	1.0	0.3	0.1	0.03	0.0001
O3	1am~ 6am	5712	88.48	57.22	33.65	21.85	17.03
O3	7pm~12pm	5682	33.19	20.97	12.67	9.66	8.94
NO	1am~ 6am	247	-96.12	-75.84	-38.55	-1.94	25.99
NO	7pm~12pm	269	-81.10	-33.36	21.26	57.09	81.58
CO	1am~ 6am	1226	-39.04	-14.37	14.09	34.12	50.99
CO	7pm~12pm	1220	-32.86	-14.08	0.67	7.01	10.40

- Night-time 12 km NMB by using different Kz_min values (m^2/s) in CMAQ for August 11-20, 2000
- Typically, Kz_min has small impact on daytime ozone
- An optimal Kz_min may lie between 0.1 and 0.3 m^2/s

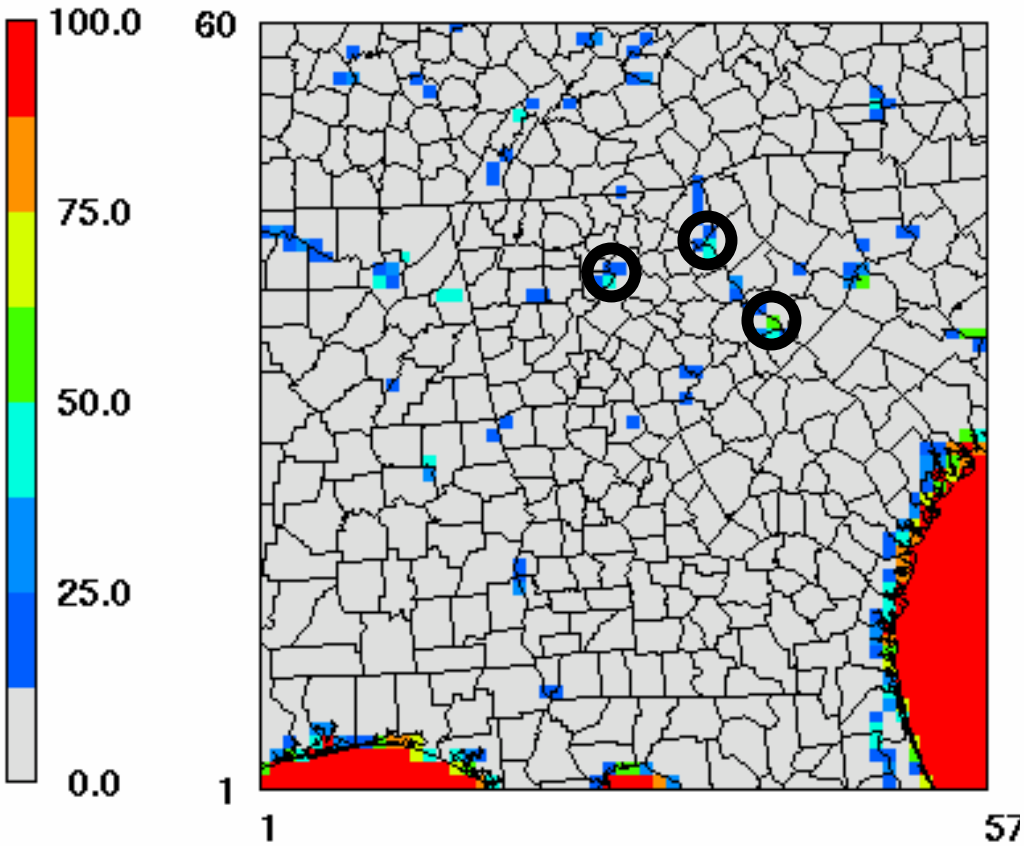
Ozone Concentrations



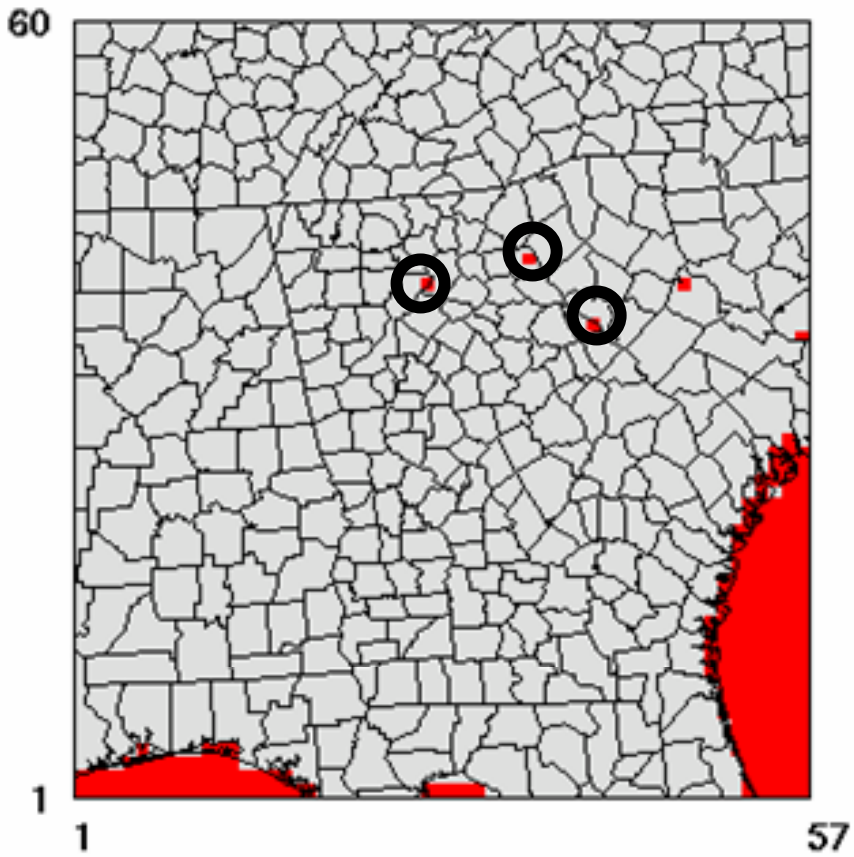


- Localized, high ozone peaks during the day found by reducing Kz_min

Surface Met. Parameters

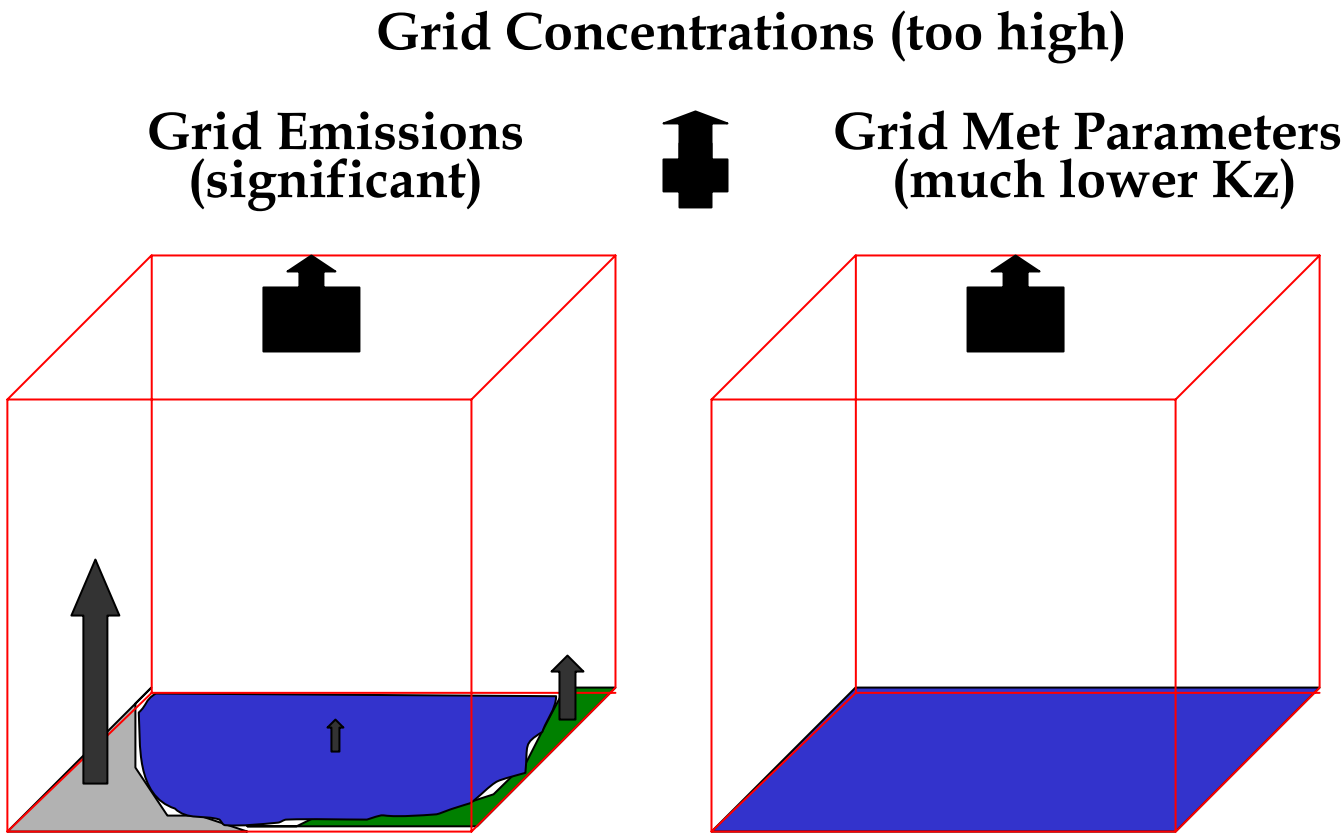


USGS Water Fractions in 12 km



MM5 OSU LSM Assigns Dominate Landuse to Grid Cell ➔ Pure Water Cell

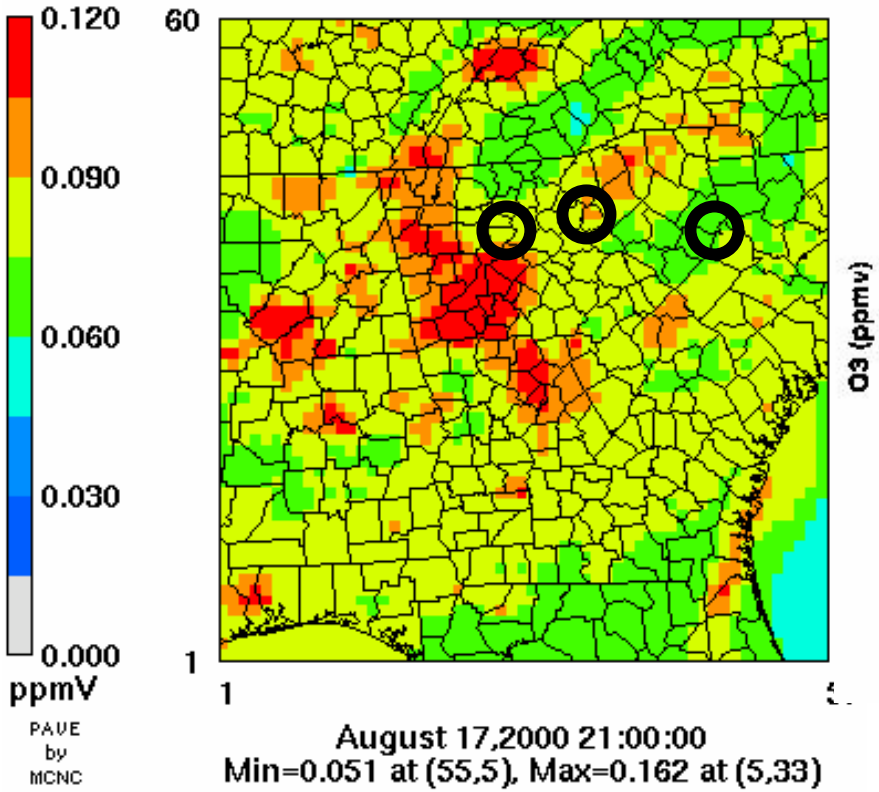
Emissions Trapped Near Surface

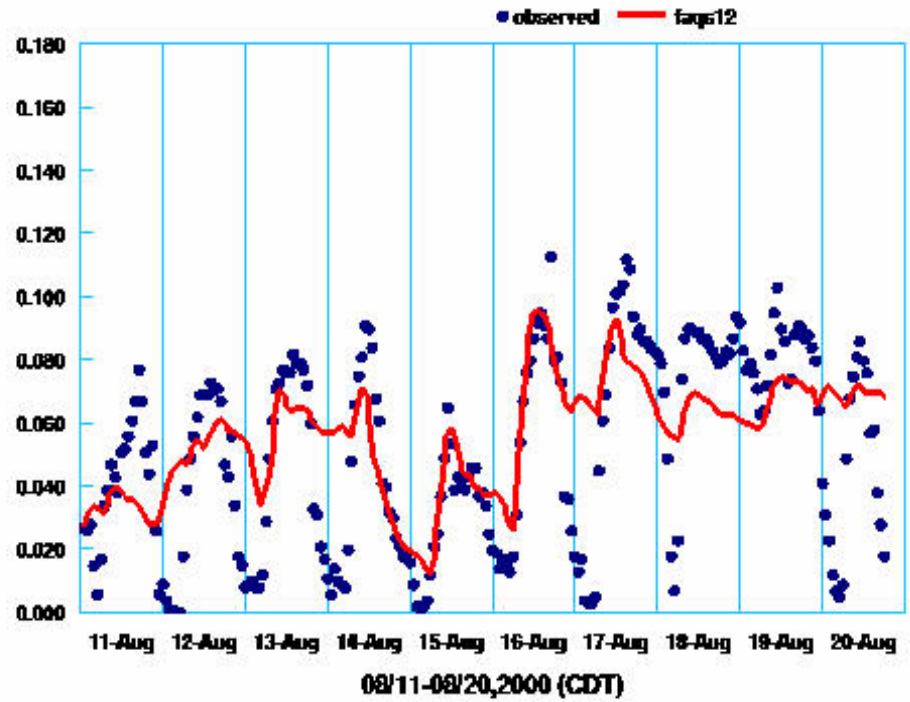


Possible Solutions

- Aggregating surface meteorological parameters from the fractional landuse for each grid cell in the meteorological modeling.
- Smoothing the Kz in CMAQ for those grid cells over the mixed landuse with water by averaging the Kz of this grid cell with its surrounding grid cells.

Ozone Concentrations



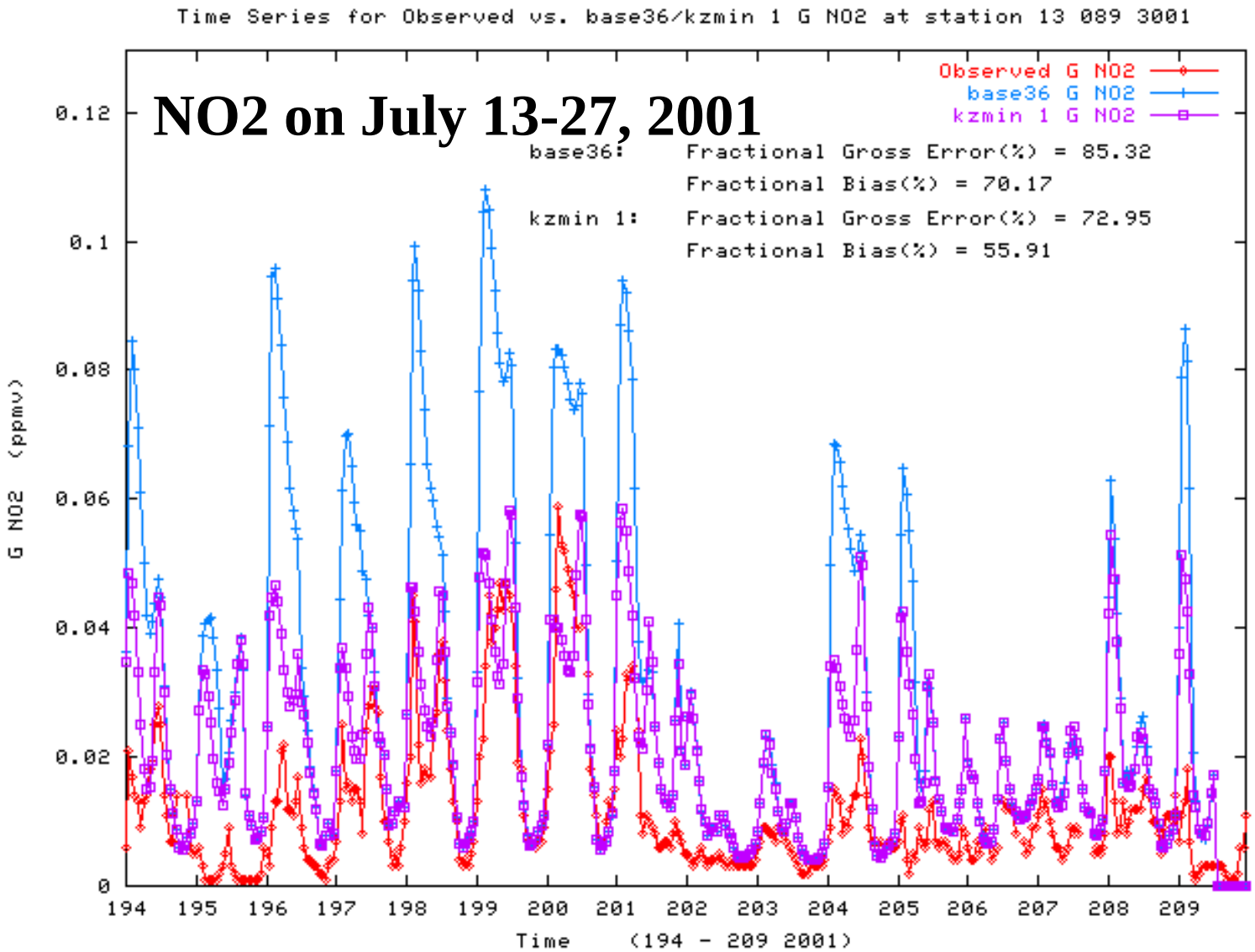


- A 9-cell averaging method was used in CMAQ to smooth Kz

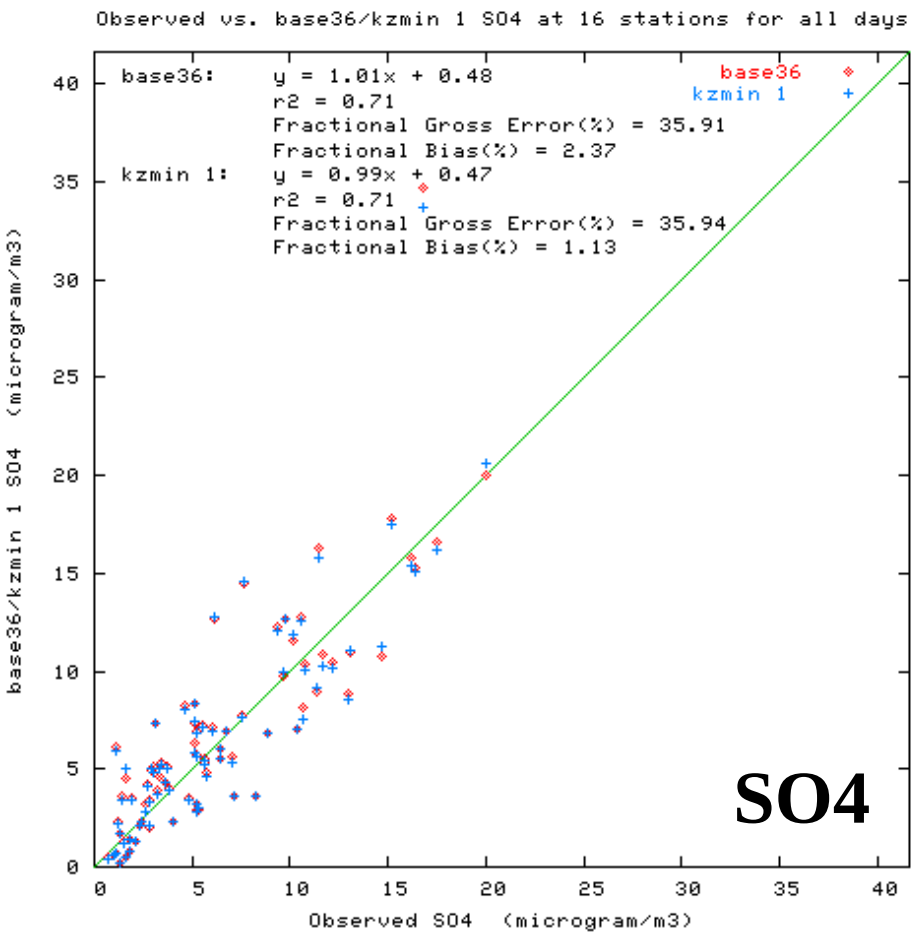
VISTAS Kz_min Sensitivities

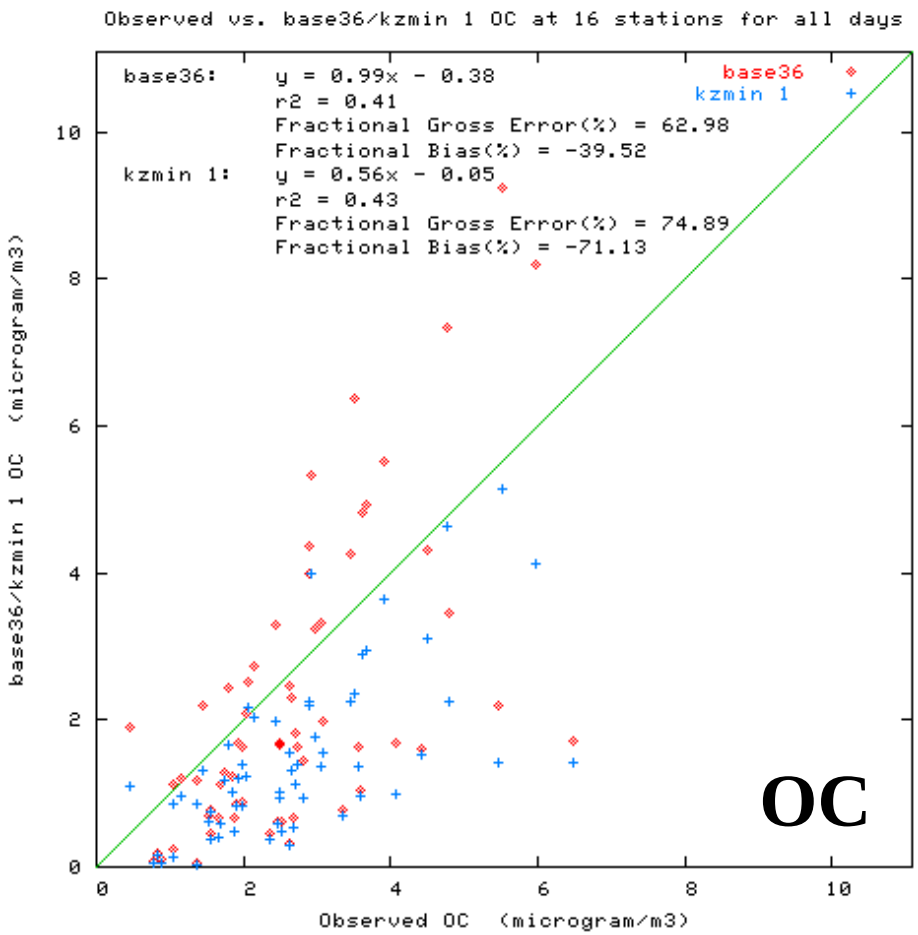
- Examined Kz_min=1.0 vs Kz_min=0.1
- January 1-20 (2002), July 13-21 (1999), July 13-27 (2001)
- Gas Phase Species (Kz_min=0.1)
  - Better night-time ozone performance at urban sites
  - Night-time over predictions of NO2 and CO
- PM Species (Kz_min=0.1)
  - Minimal impact on most species
  - Major impact on Organic Carbon (OC)
- Minimum PBL Height Sensitivity
  - Results similar to Kz_min=1.0

Kz_min=0.1 vs. Kz_min=1.0

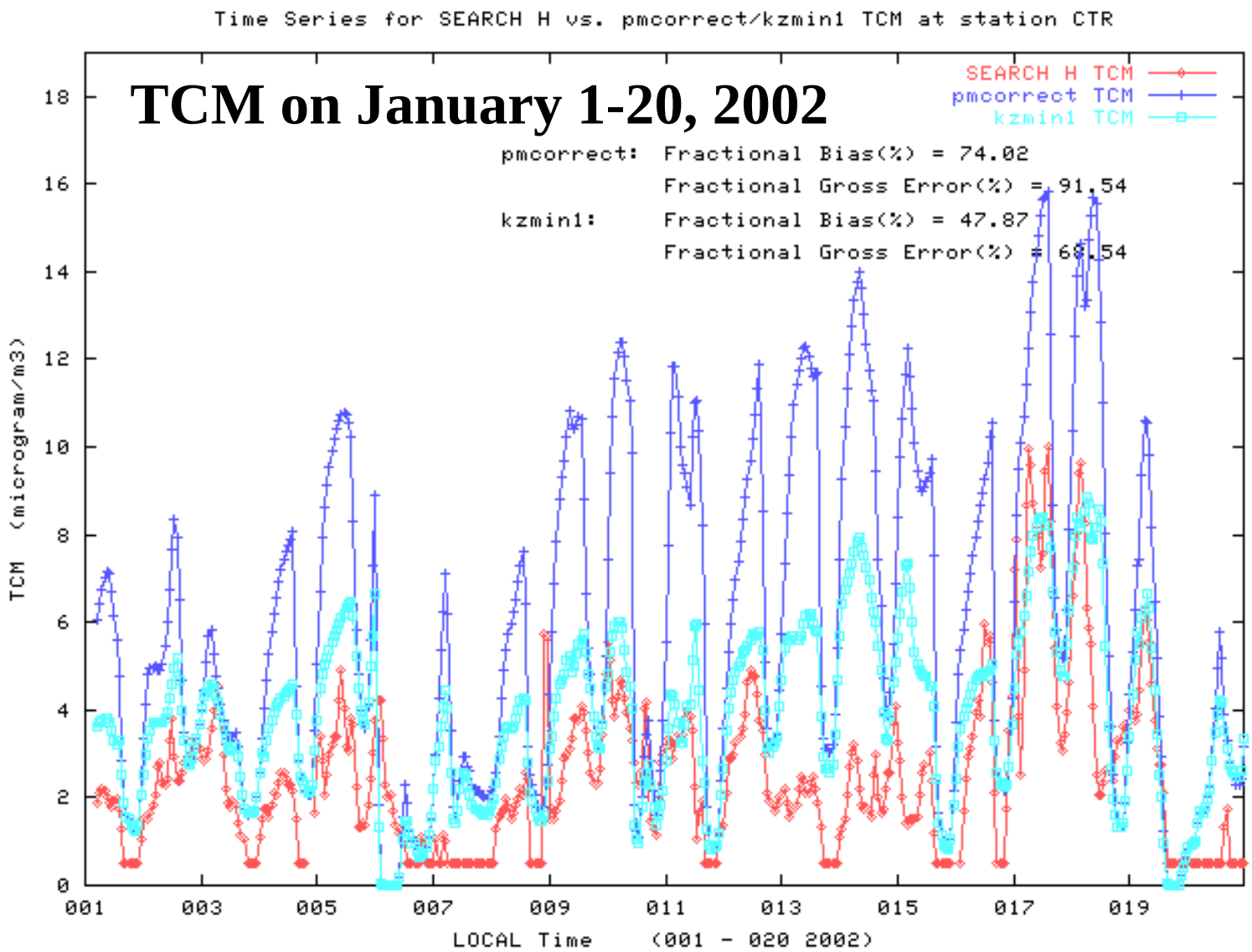


Kz_min=1.0 vs. Kz_min=0.1

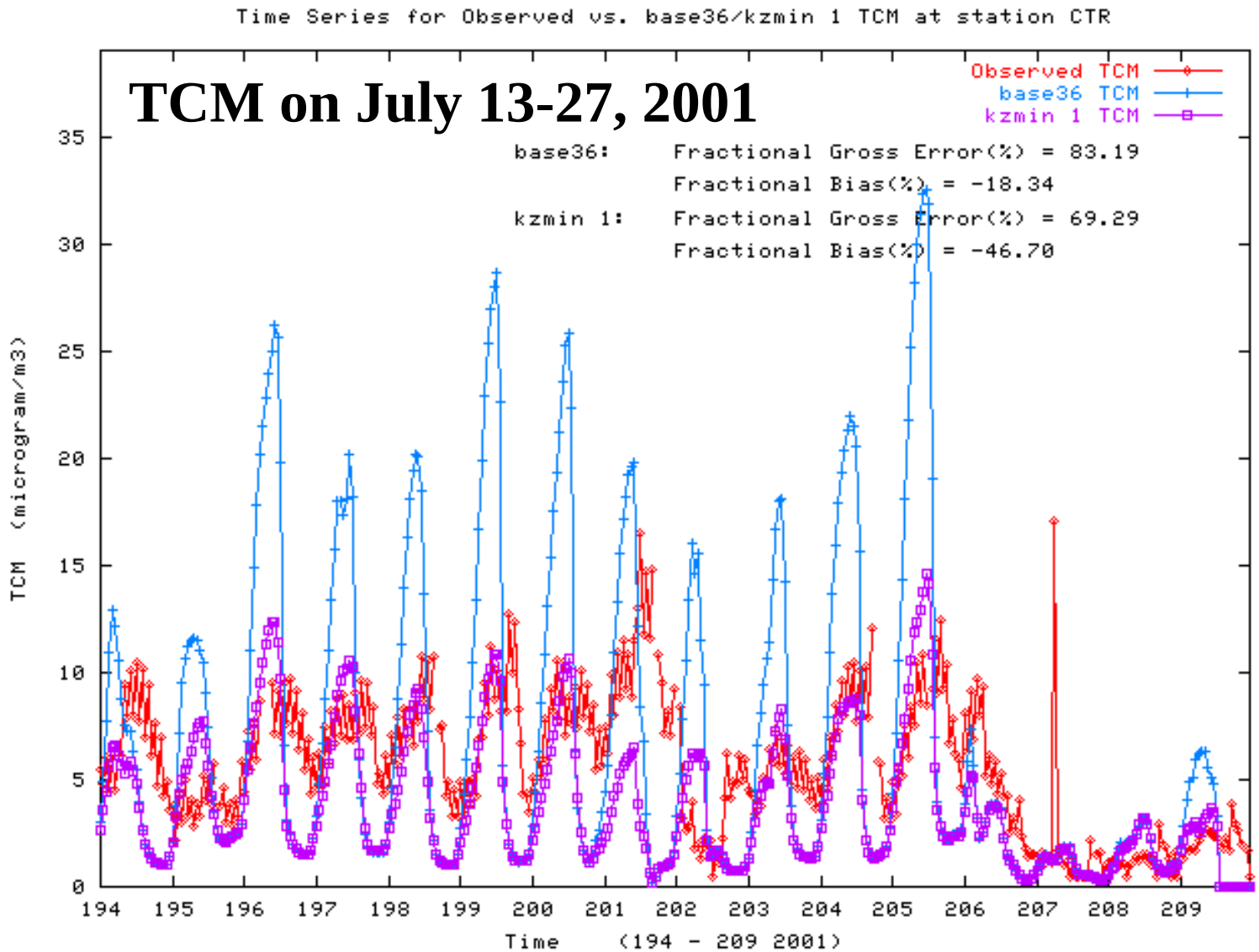




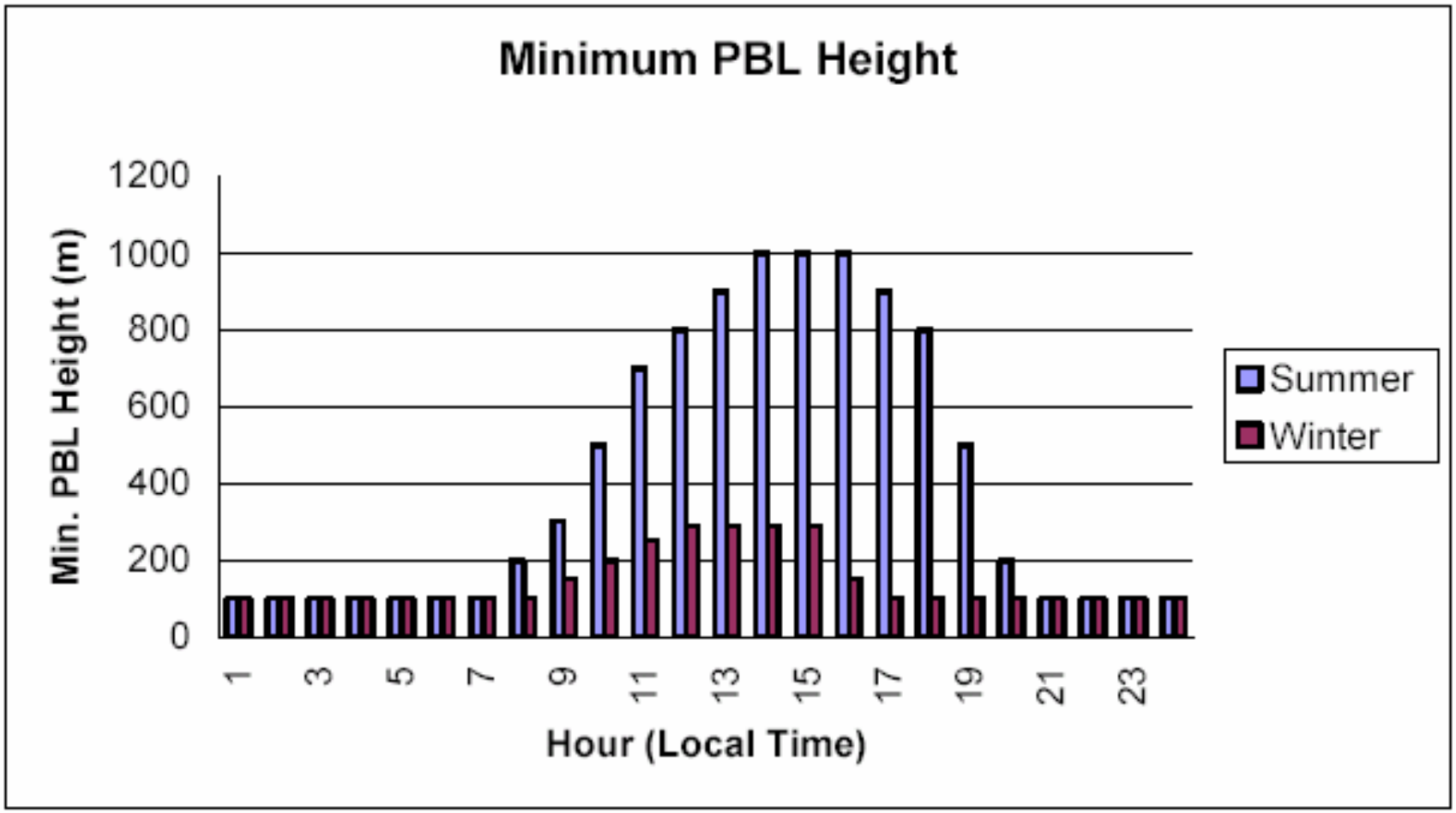
Kz_min=0.1 vs. Kz_min=1.0



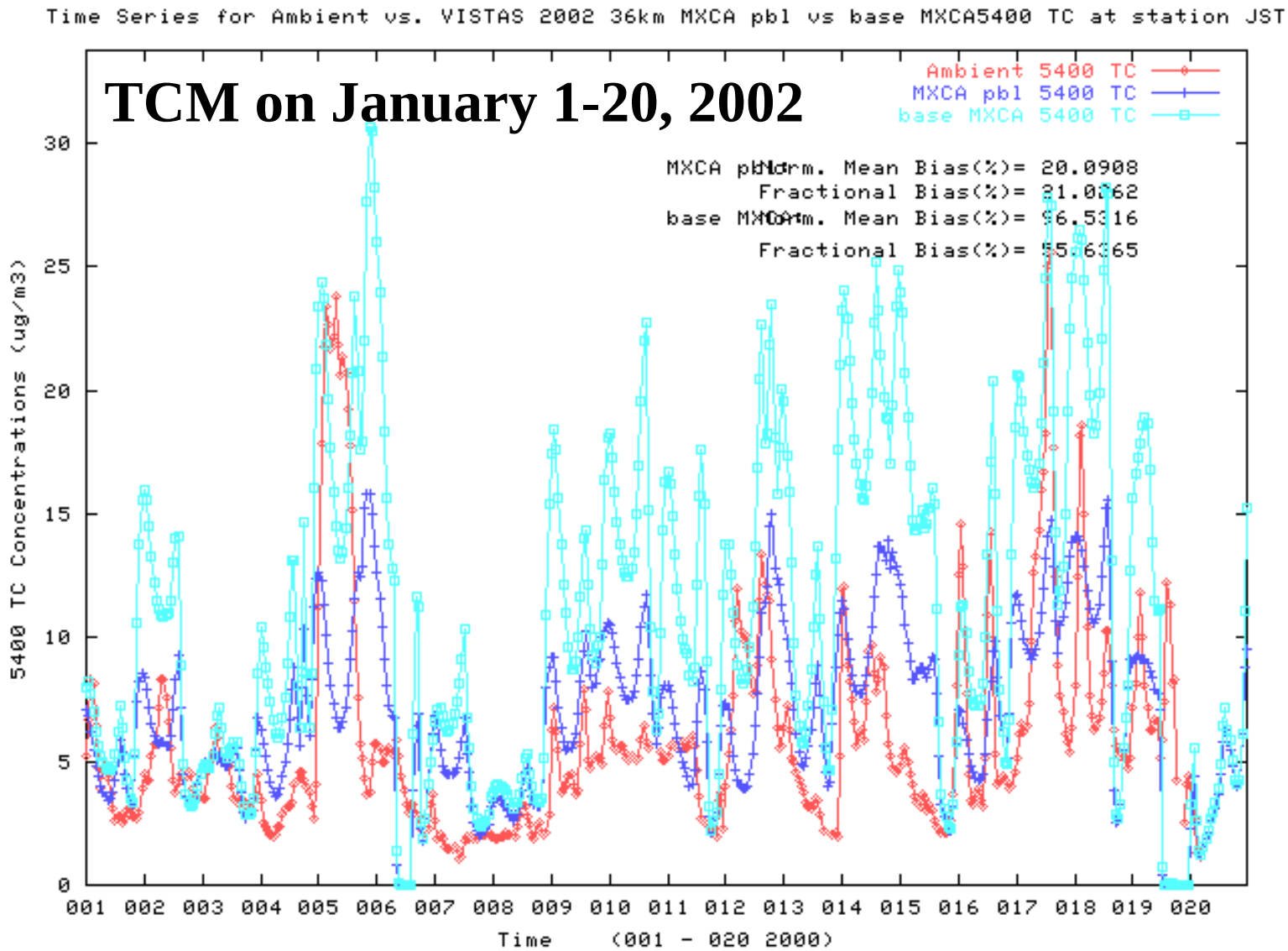
Kz_min=0.1 vs. Kz_min=1.0



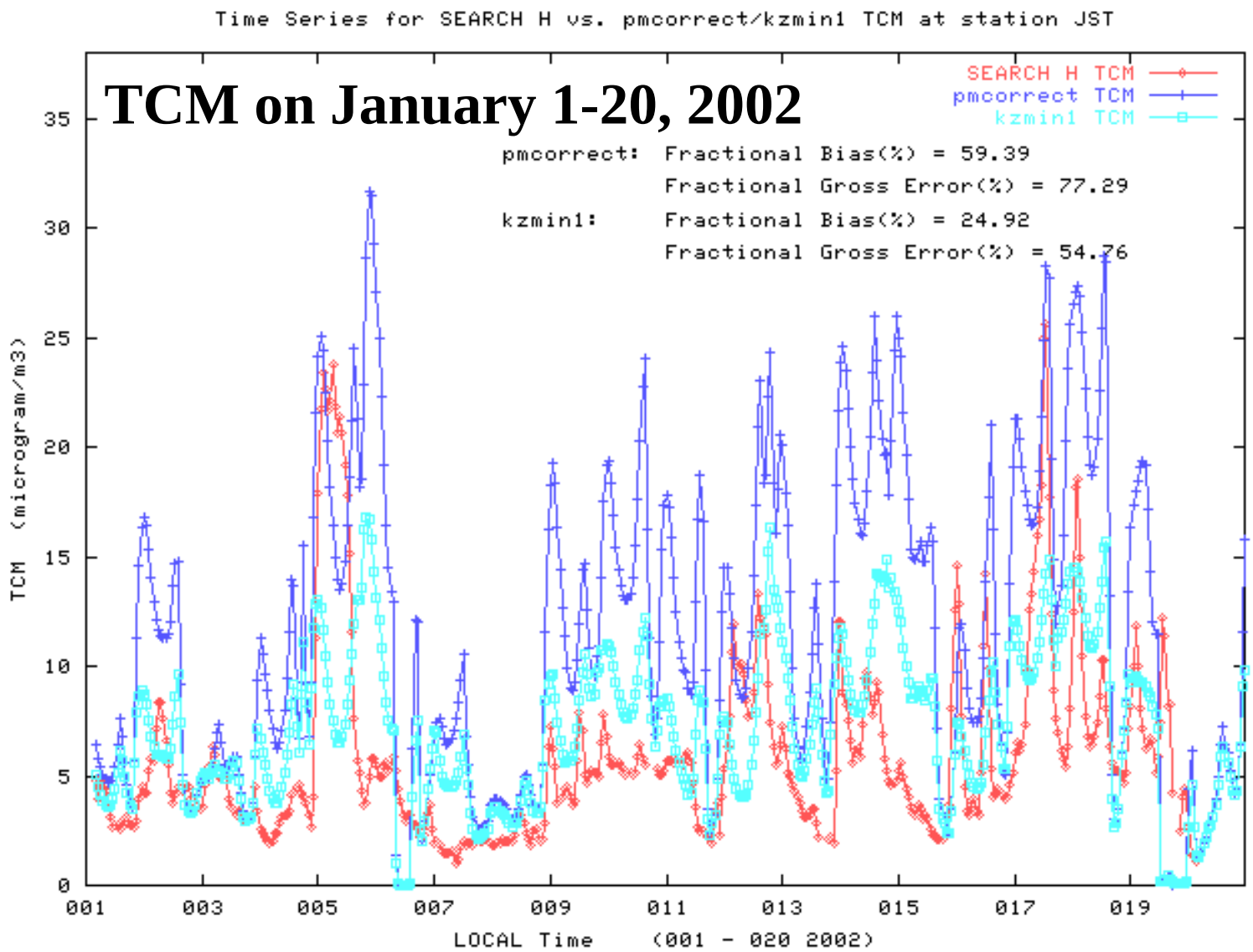
PBL Height Sensitivity



PBL_min vs. Kz_min = 0.1

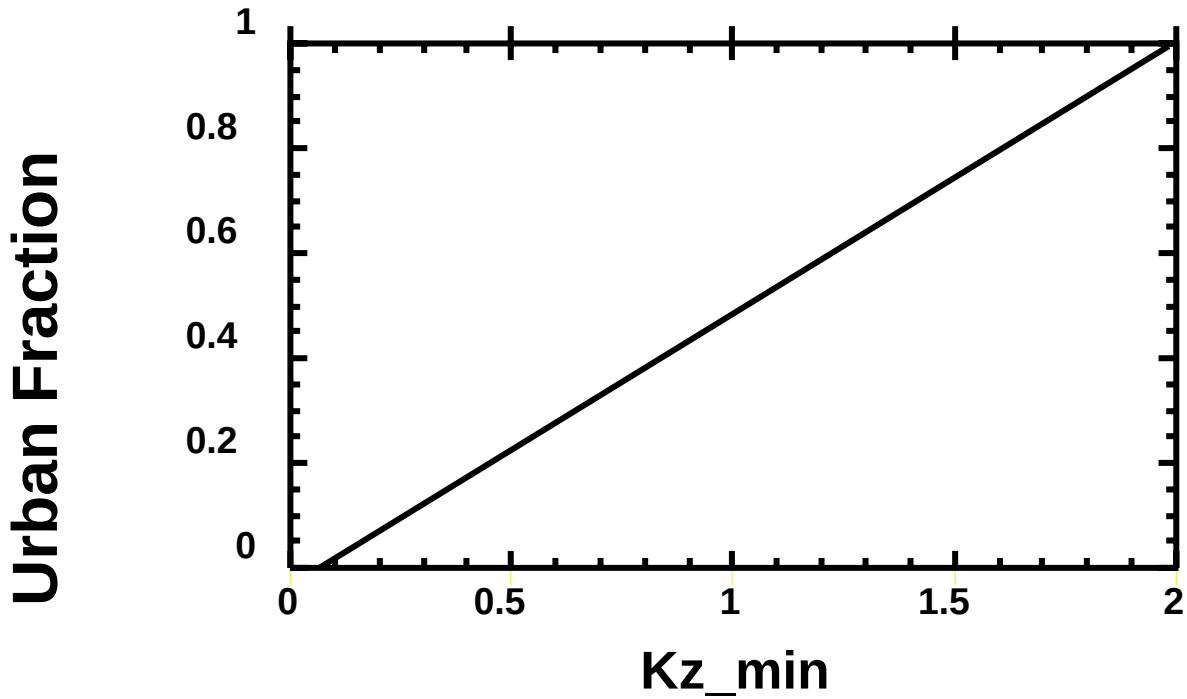


Kz_min = 1.0 vs. Kz_min = 0.1



EPA's AQF version of CMAQ

- Minimum K_z according to Urban Land Use



Kz_min Summary

- Analysis by GT suggests an optimal Kz_min may lie between 0.1 and 0.3 m^2/s
  - Did not evaluate PM species
  - Artificially high surface ozone values were found resulting from the OSU land surface model
    - A 9-cell averaging method was used to smooth Kz
- Analysis by VISTAS found Kz_min had major impact on hourly OC concentrations
  - Increasing minimum PBL heights had similar impact as increasing Kz_min
- EPA implementing Kz_min that varies with Urban Land Use