Reconciling Reported HRVOC Emissions with Ambient Measurements, Update

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Background

- **Historically, reported emissions of VOCs have been insufficient to explain concentrations measured in the HGB area.**

- **Specifically, Highly Reactive VOCs (HRVOCs – Ethene, Propene, Butenes, and 1,3-Butadiene) may have been under-reported by as much as an order of magnitude.**

- **TexAQS II data suggest that the discrepancy between reported emissions and observed concentrations of ethene are smaller than was the case in 2000. The discrepancy for propene appears to have changed little.**

Background

- **Since 2003, the HGB area has had an extensive network of Automatic Gas Chromatographs, which measure ambient concentrations of several hydrocarbon species. In 2005 and 2006, twelve sites operated in Harris (8), Galveston (1), and Brazoria (3) counties.**

- **This work uses the Auto-GC data from 2005 and 2006 to attempt to reconcile the reported emissions with measured concentrations.**

CAMx Ozone Modeling in SIP Development
The Big Picture

Base Case	**Day-specific emissions; replicate what actually happened**
Baseline Case	**Typical emissions; used in RRF to predict future design values**
Future Base Case	**Apply future growth + on-the-books controls to estimate future ozone**
Control Strategy Testing	**Determine control strategies that will effectively reduce ozone**
SIP	**Document modeling procedures**

Background (Cont.)

- **Emissions data (tons/day) are fundamentally incommensurate with ambient concentration data (parts/billion carbon, or ppbC), i.e., they cannot be directly compared.**
- **A variety of models have been developed to estimate ambient concentrations resulting from specified emission rates, including CAMx, and the Industrial Source Complex (ISC) model.**
- **The ISC model is relatively simplistic (compared to CAMx), so hundreds of ISC runs can be completed in the time required for a single run of CAMx.**

The ISC Model

- **ISC is widely used in modeling for air permit applications.**
  - **Input: Emission rates from point, area, and mobile sources, stack parameters, wind speed and direction, mixing depth, ambient temperature, and stability class**
  - **Assumptions: Steady-state conditions, straight-line winds, no atmospheric chemistry, Gaussian dispersion of airborne contaminants**
  - **Output: Hourly pollutant concentrations at specified locations**

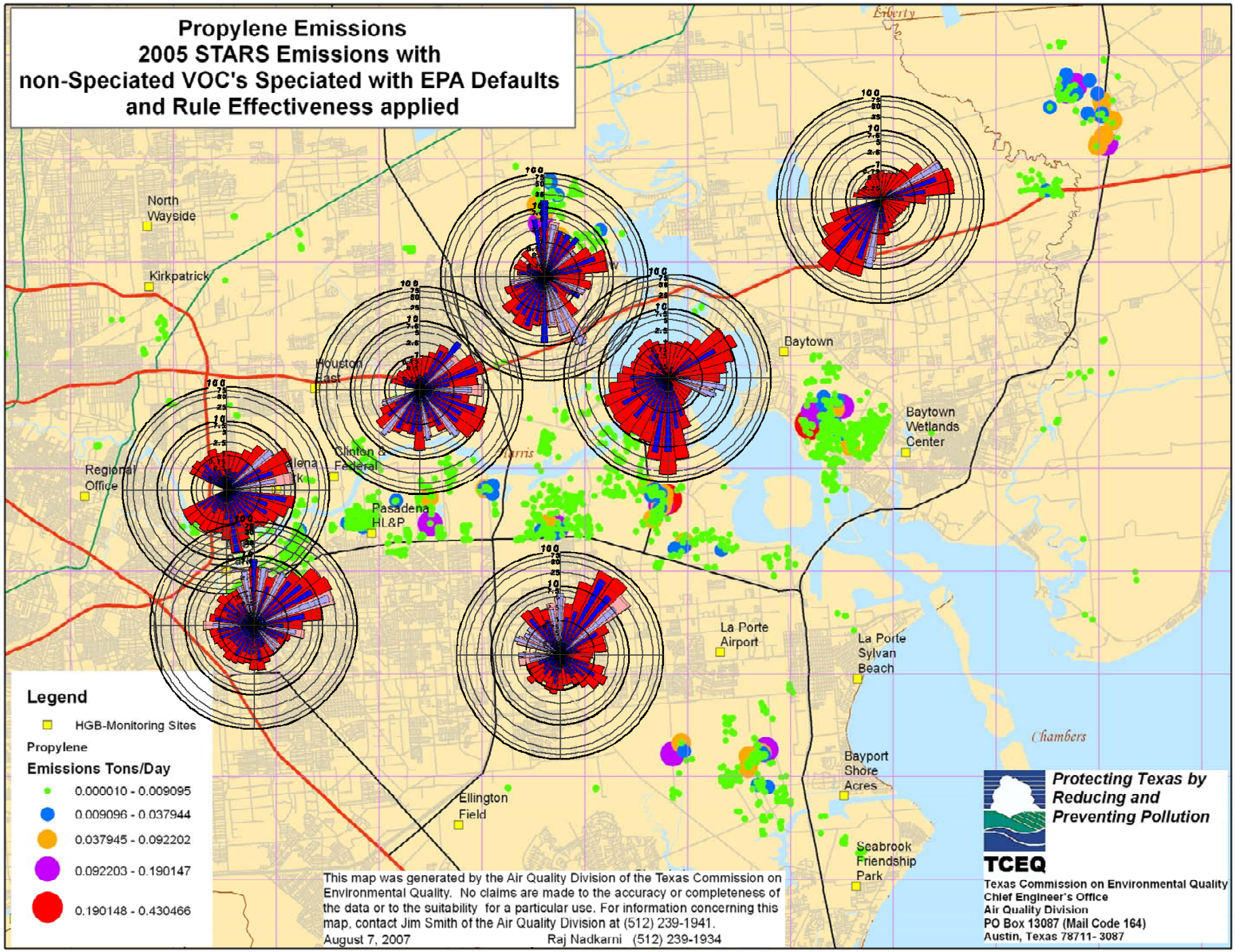
The ISC Model (Cont.)

- **Used Version 3 of the short-term form of ISC (ISC-ST3) for each hour in 2005 and 2006 using archived meteorological data, provided that wind direction was relatively constant for at least two hours:**
  - **Sinuosity ≥ 0.95. Sinuosity is the straight-line distance between a source and receptor, divided by the length of the path taken by an air parcel traveling from the source to the receptor. If the parcel travels in a straight line, then sinuosity = 1.0.**
  - **Maximum deviation between any two recorded wind directions is ≤ 15° over two hours (i.e. the entire path of the air parcel lies within a 15° "wedge" with vertex at the receptor).**

The ISC Model (Cont.)

- **Used the emissions data created for the 2005 and 2006 CAMx base case modeling runs:**
  - **2005 and 2006 STARS extracts**
  - **Complete speciation**
  - **Rule-effectiveness adjusted**
  - **Note: does not capture most temporal variability in point source hydrocarbon emissions.**

- **Median modeled concentrations were calculated at each HGB Auto-GC location and compared with median monitored concentrations.**


Propylene Emissions
2005 STARS Emissions with
non-Speciated VOC's Speciated with EPA Defaults
and Rule Effectiveness applied
North Wayside
Kirkpatrick
Houston East
Clinton & Federal
Regional Office
Pasadena HL&P
Baytown
Baytown Wetlands Center
La Porte Airport
La Porte Sylvan Beach
Bayport Shore Acres
Ellington Field
Seabrook Friendship Park
Liberty
Harris
Chambers
Legend
HGB-Monitoring Sites
Propylene
Emissions Tons/Day
0.000010 - 0.009095
0.009096 - 0.037944
0.037945 - 0.092202
0.092203 - 0.190147
0.190148 - 0.430466
This map was generated by the Air Quality Division of the Texas Commission on Environmental Quality. No claims are made to the accuracy or completeness of the data or to the suitability for a particular use. For information concerning this map, contact Jim Smith of the Air Quality Division at (512) 239-1941.
August 7, 2007
Raj Nadkarni (512) 239-1934
Protecting Texas by Reducing and Preventing Pollution
TCEQ
Texas Commission on Environmental Quality
Chief Engineer's Office
Air Quality Division
PO Box 13087 (Mail Code 164)
Austin, Texas 78711- 3087

ISC Results

- **Comparing the ISC-modeled and monitored concentrations at the Auto-GC sites indicates discrepancies between what one would have expected to see (ISC-modeled concentrations) and what was actually seen (monitored concentrations).**
- **The wind roses generally point to areas from whence these discrepancies may arise, but don't indicate distances or pinpoint sources.**
- **This approach does not directly address how well reported emissions agree with actual emissions.**

The Potential Source Contribution Function

- **The Potential Source Contribution Function (PSCF) is a technique for locating source regions associated with high monitored pollutant concentrations.**

- **Back trajectories were calculated for each location and hour, with locations output every five minutes. (These trajectories were used to compute the sinuosity values discussed earlier.)**

PSCF (Cont.)

- **When a trajectory point lands in a grid cell (a "hit"), the cell counter is incremented by one. It is possible under light wind conditions for a grid cell to accumulate several "hits" for a single trajectory.**

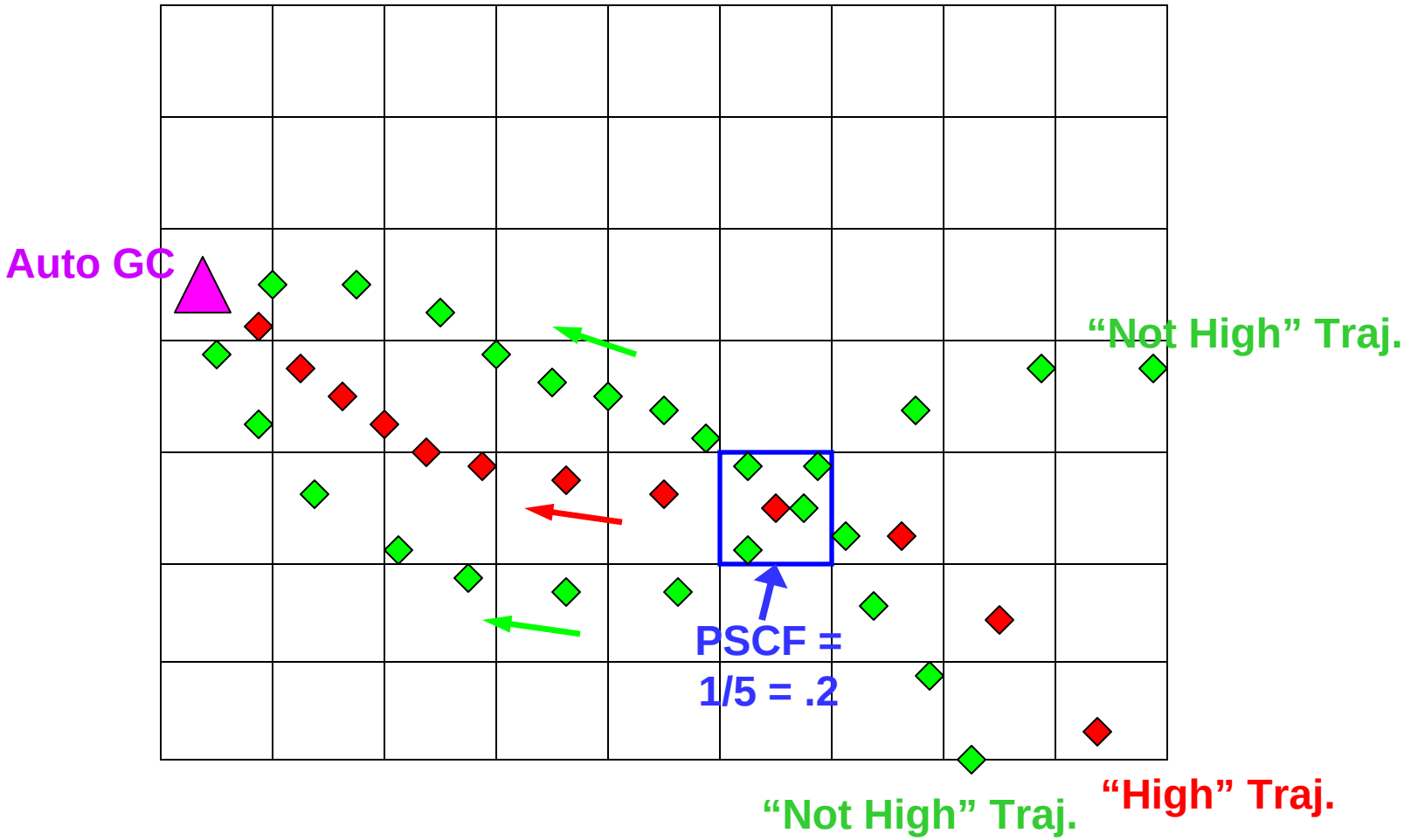
- **For each "Hit" in a grid cell, a value of "High" or "Not High" is assigned, depending on the measured pollutant concentration at the end of the path (an Auto-GC in this case).**

PSCF (Cont.)

- **Finally, the number of "Highs" in each grid cell is divided by the total number of "Hits" to produce the PSCF value – the estimated probability that an air parcel passing through the grid cell will be associated with a high pollutant concentration.**

- **Xie and Berkowitz (2006) defined a "High" monitored concentration as one above the 75% percentile for that pollutant at that monitor.**

PSCF Illustration



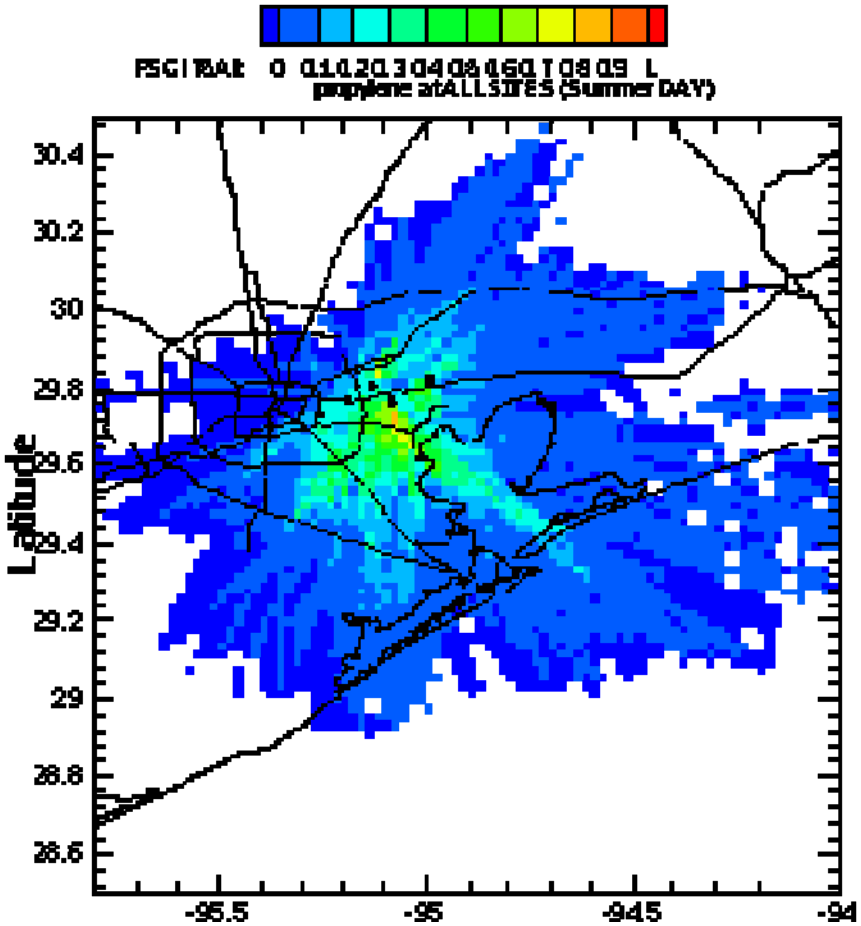
PSCF (Cont.)

- **The following graphics, reproduced from Xie and Berkowitz, show the PSCF analysis for propene at the Channelview auto-GC, (right), and a combined analysis for five auto-GCs (left) for 2003 summer daytime observations. This analysis used six-hour back trajectories.**

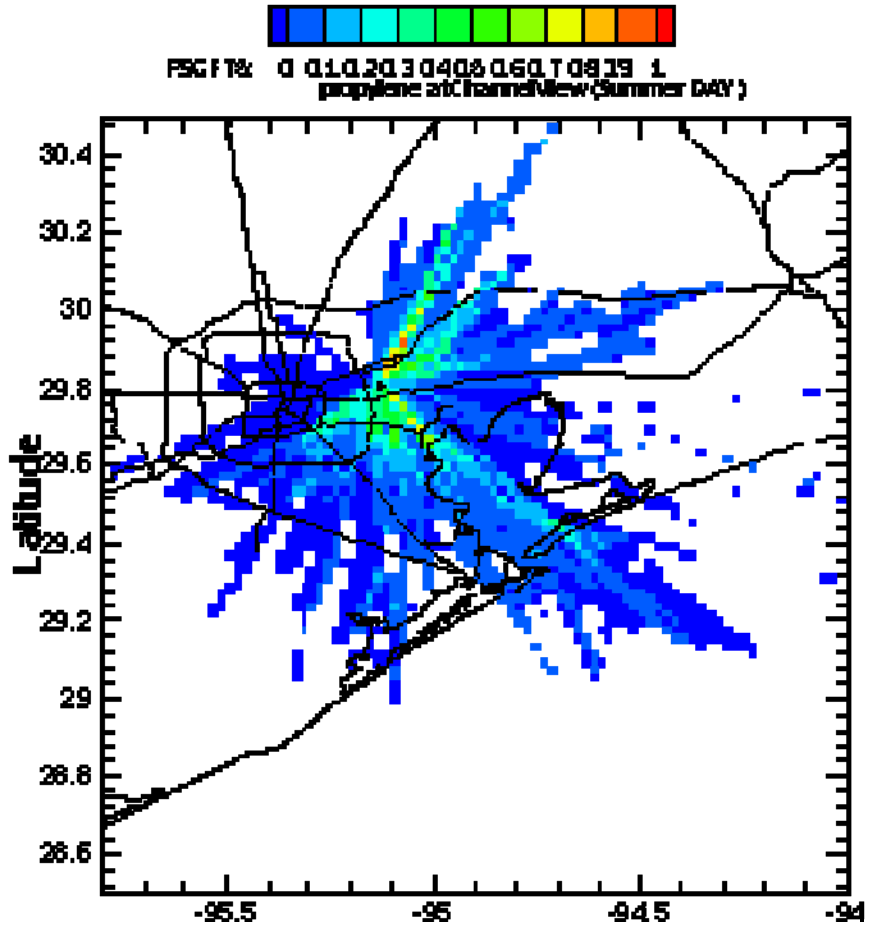
- **The shading in the plots represents the empirical probability that an air parcel passing through a specific location will deliver a high (i.e. greater than the 75th percentile) concentration of propene to the Channelview site (right-hand plot), or to any site (left-hand plot).**

2003 Summer Daytime PSCF Probabilities for Propene at Channelview and Combined for Five Sites

Five Auto-GC Sites



Channelview



PSCF Results

- **The analysis shows that at Channelview, most high-probability trajectories come from East-to-Northeast and from Southwest-to Southeast – corresponds well with emission source locations.**

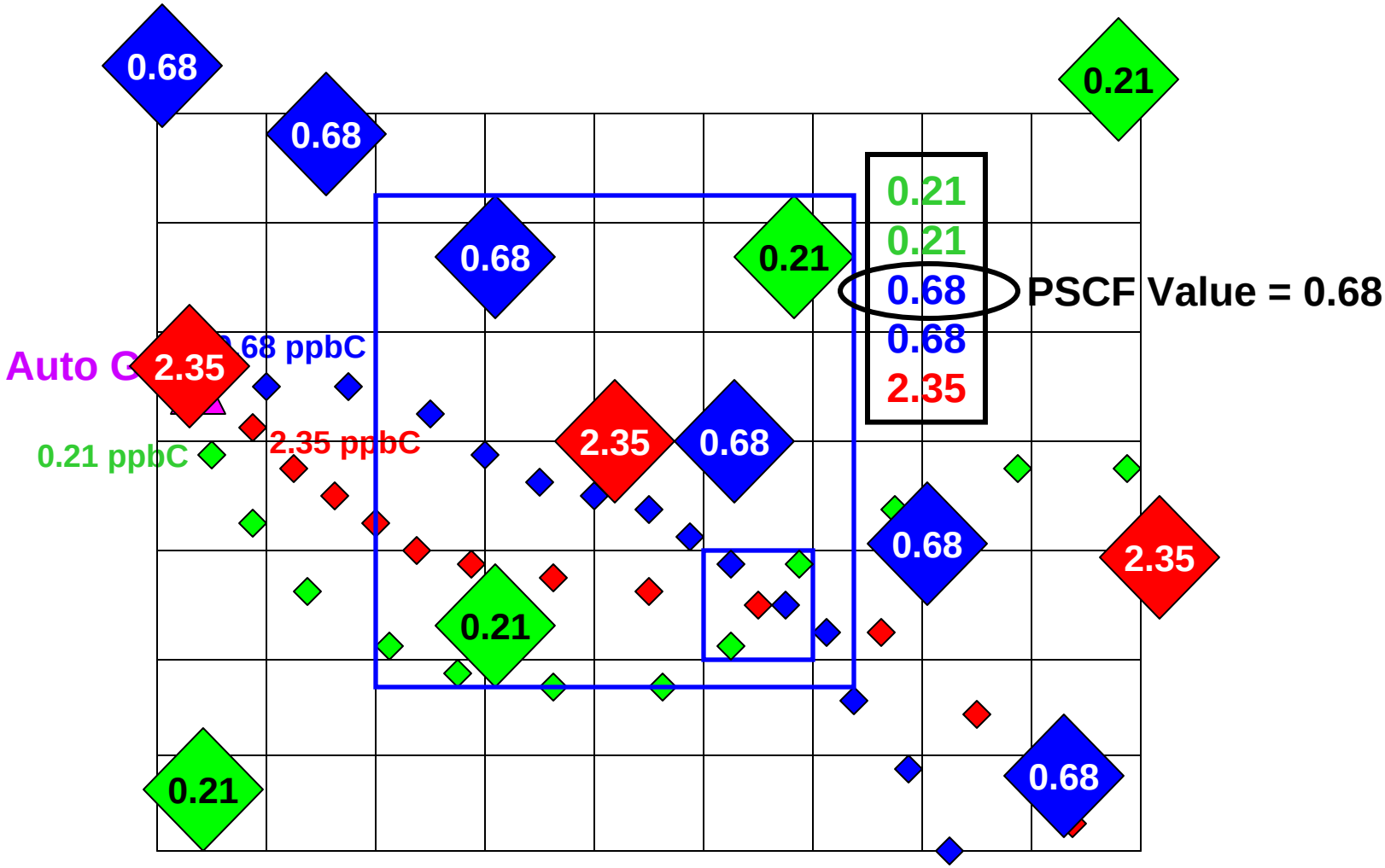
- **The method points toward known sources, but also shows long "tails" beyond sources (artifact).**

- **Combining analysis for all monitors can help pinpoint sources, reduce tailing.**

PSCF – Type 2

- **PSCF helps locate source regions associated with high monitored concentrations, but can't by itself quantify emissions.**
- **As an alternative to the Xie-Berkowitz approach, we assigned the actual concentration values to the grid cells (instead of "High" or "not High"), then took the grid cell median value. This can be done for a single monitor or for all monitors.**
- **This analysis was limited to the straight trajectories used in the ISC analysis discussed earlier.**

PSCF Type 2 Illustration



PSCF – Type 2

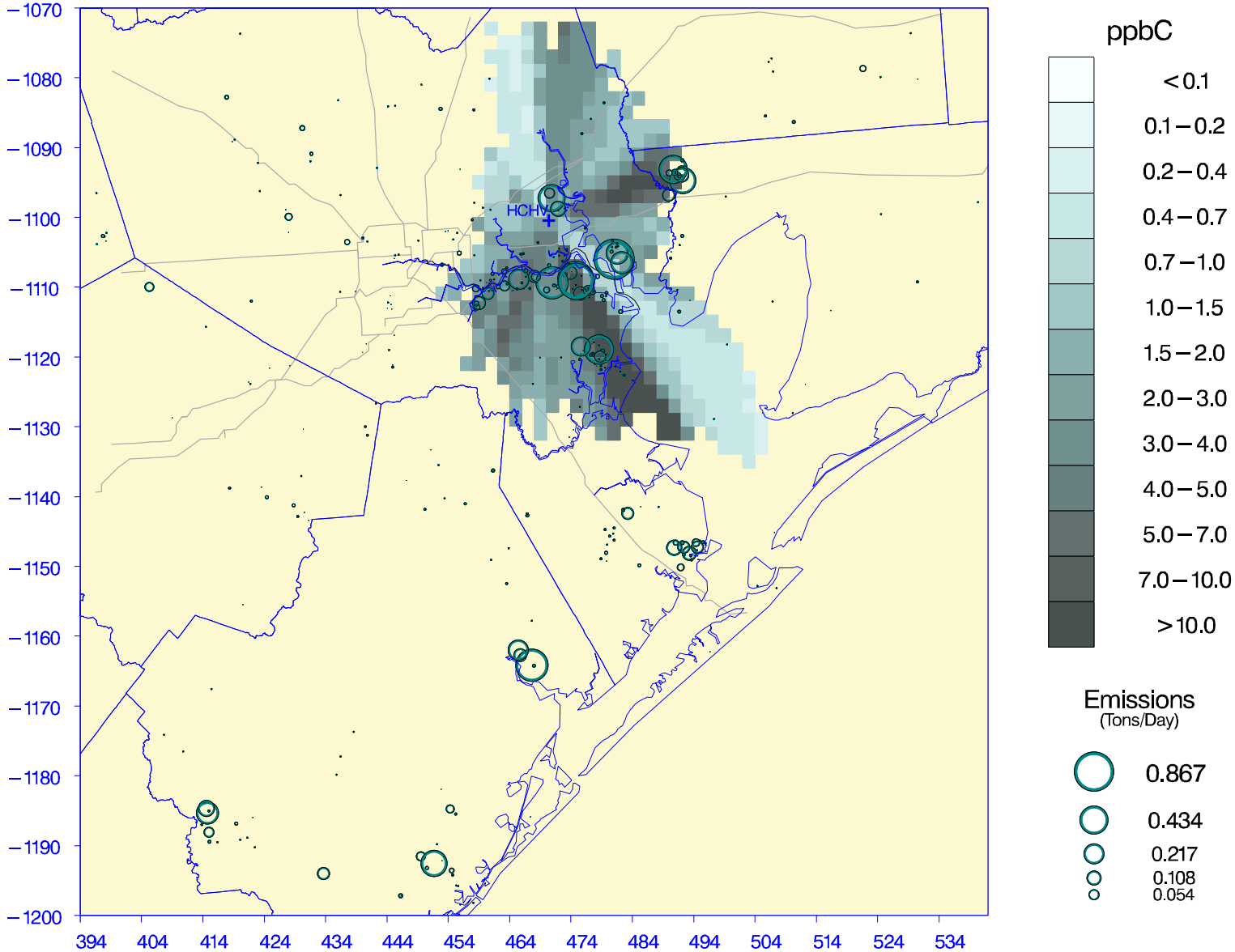
- **The median cell values have the same units as the measurements (ppbC), and are referred to as "pseudo-concentrations".**

- **The next two graphics show 2005 propene pseudo-concentrations for Channelview only, then for all 12 auto-GC sites.**

PSCF for Monitored Propene

Channelview, 2005 2H Back Traj, WDMax 15, 2 Km Grid, Iteration 1

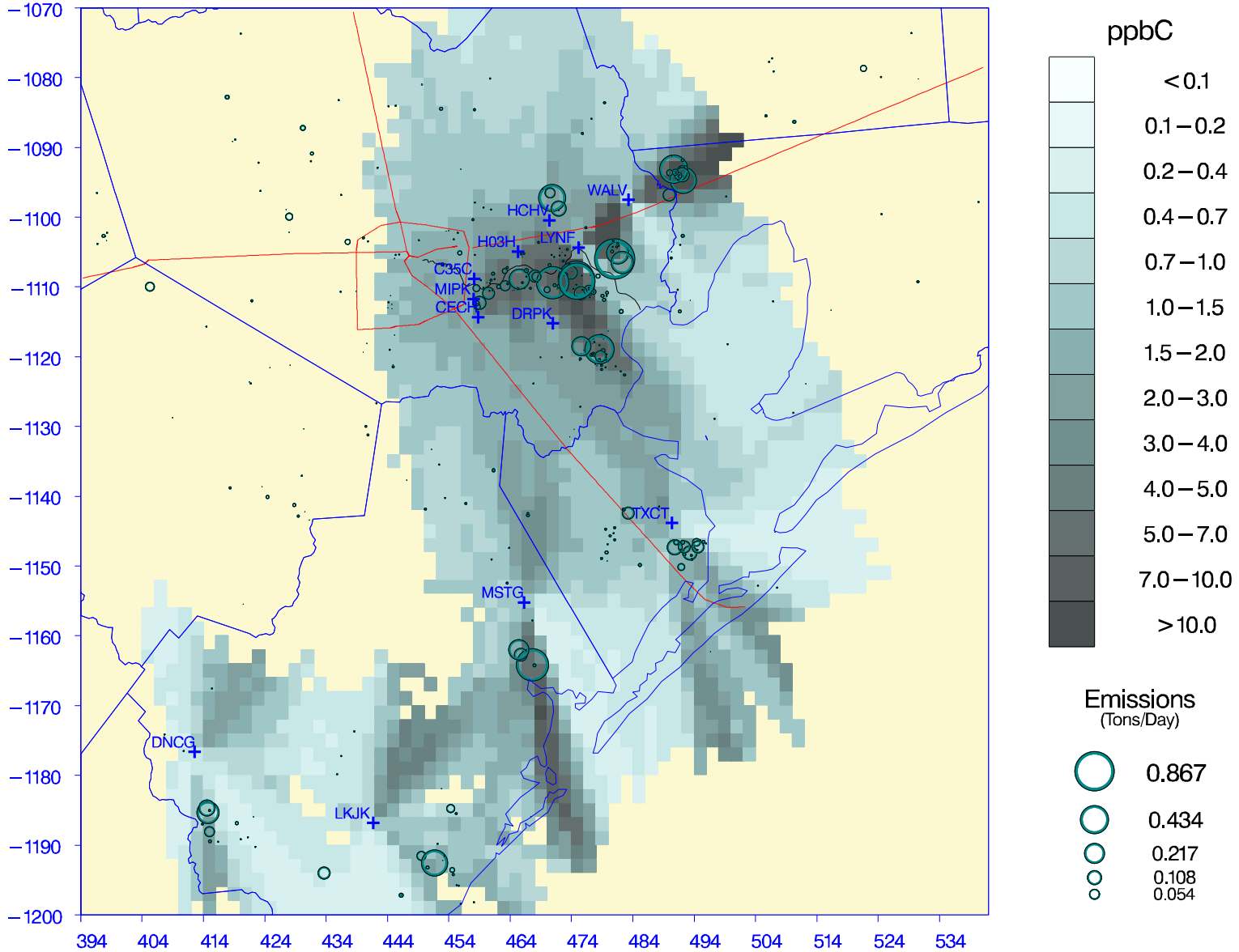
Cells with at least 40 Trajectory Points



PSCF for Monitored Propene

Twelve HGB Area Sites, 2005 2H Back Traj, WDMax 15, 2 Km Grid, Iteration 1

Cells with at least 100 Trajectory Points, Unreconciled Area Sources



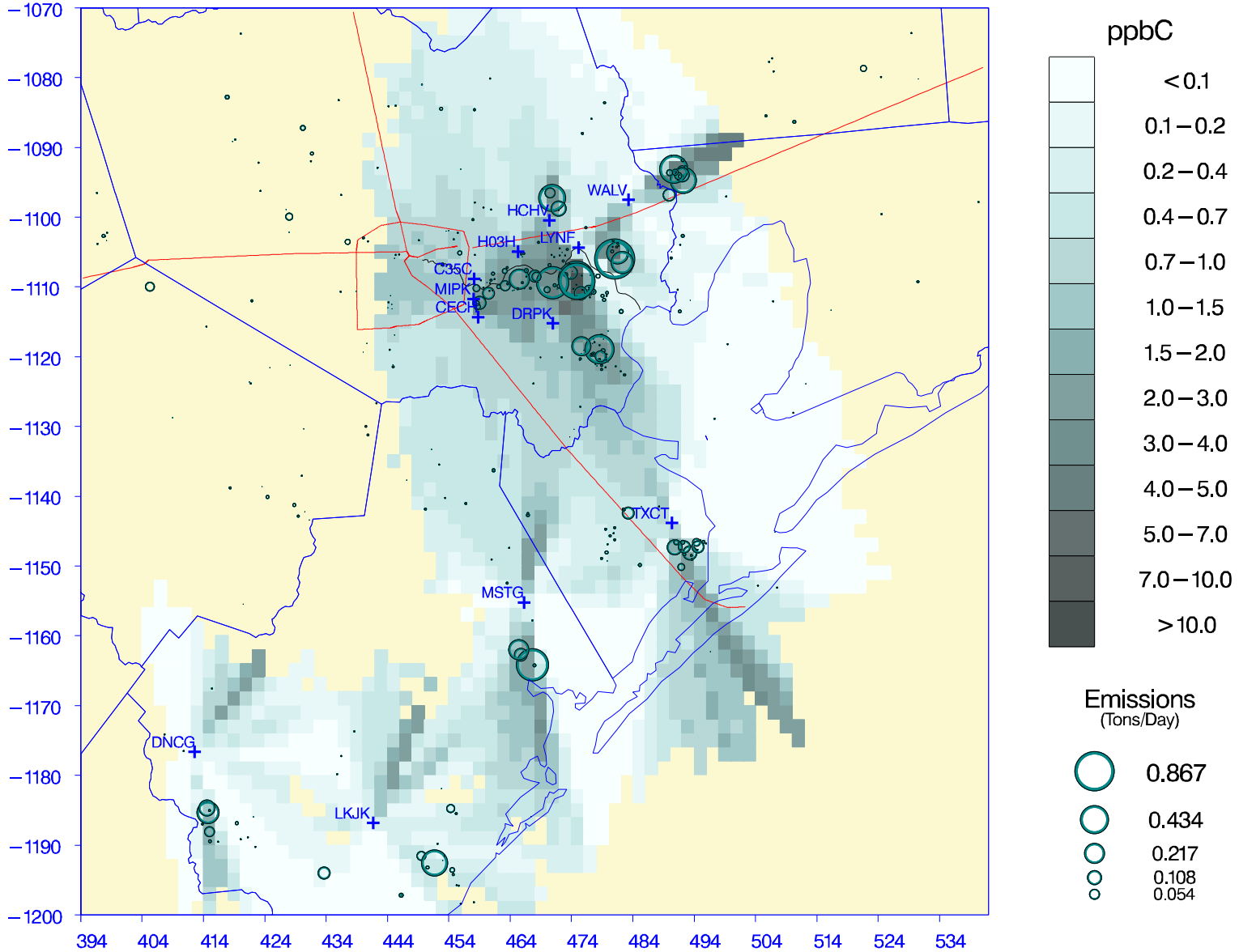
PSCF – Type 2 (Cont.)

- **To see what the Type 2 map would be expected to look like with the reported emissions, the measured concentrations at the Auto-GC sites can be replaced with the ISC-modeled concentrations at the same locations.**

PSCF for ISC Modeled Propene

Twelve HGB Area Sites, 2005 2H Back Traj, WDMax 15, 2 Km Grid, Iteration 1

Cells with at least 100 Trajectory Points, Unreconciled Area Sources



PSCF – Type 2 (Cont.)

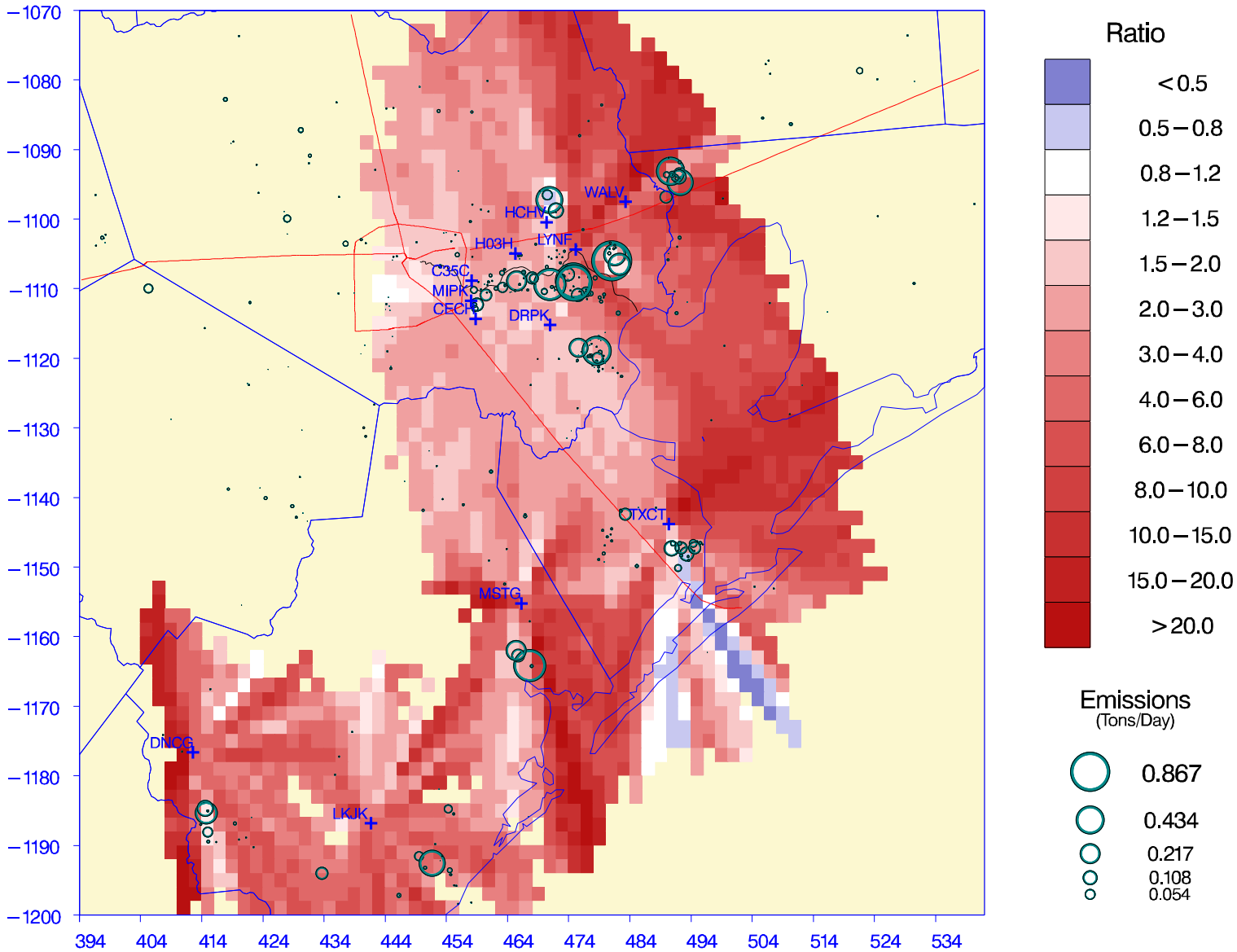
- **The monitored data generally show higher pseudo-concentrations than ISC indicates would be expected, based on the reported emissions.**

- **Taking the ratio by grid cell of the monitor-based pseudo-concentrations to the ISC-modeled pseudo-concentrations yields a dimensionless emission reconciliation factor (ERF) for each grid cell.**

PSCF Ratio (Mon/ISC) for Propene

Twelve HGB Area Sites, 2005 2H Back Traj, WDMax 15, 2 Km Grid, Iteration 1

Cells with at least 100 Trajectory Points, Unreconciled Area Sources



Emission Reconciliation

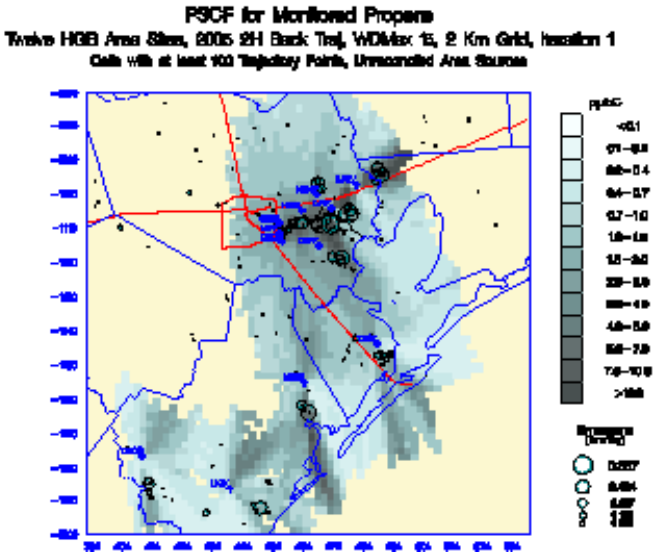
- **The next logical step is to multiply the emissions in each grid cell by the cell's ERF.**
  - **Applied to point sources only**
  - **Implemented by adding ground-level fugitive-type emissions**
  - **In a few cells, the ERF's are < 1.0; in those cases, emissions were left unchanged**

- **For 2005, the RE-adjusted propene emissions increased from approximately 10 tpd to approximately 25 tpd after reconciliation (150% increase).**

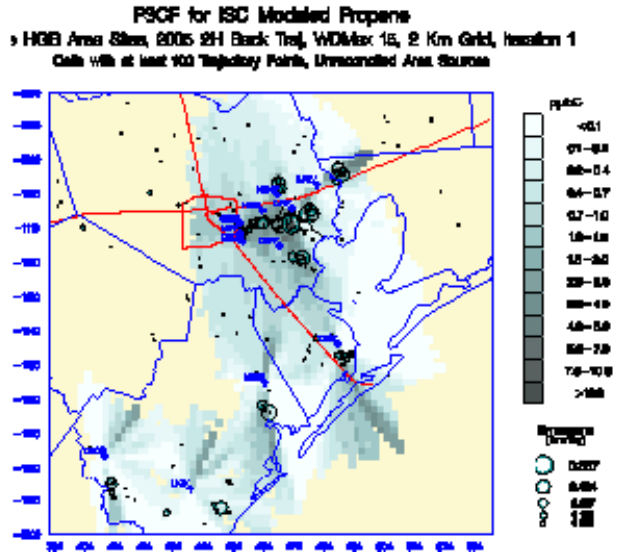
Emission Reconciliation

- **Reconciled emissions should match better with monitored data than unreconciled emissions. Re-running ISC using reconciled emissions should produce a "whiter" map of ERFs.**

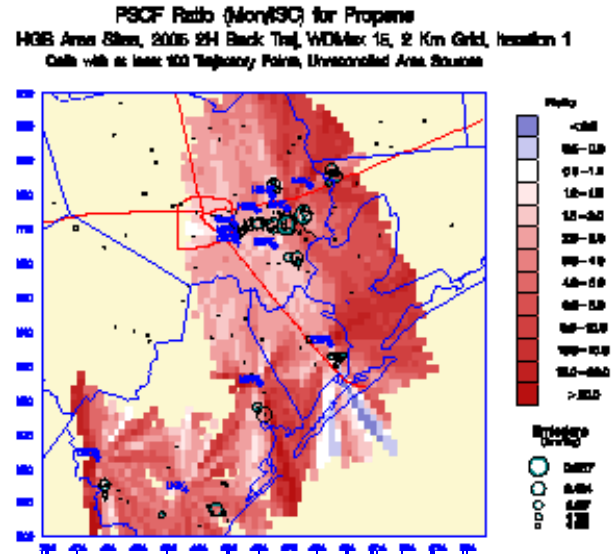
Monitored



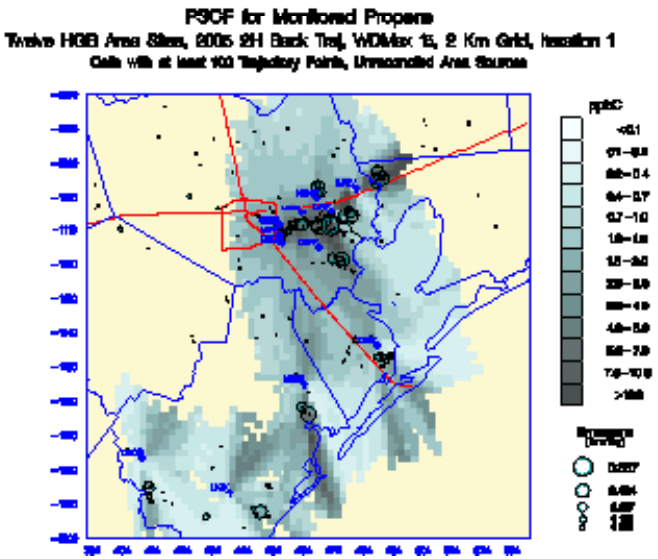
Modeled-Unreconciled



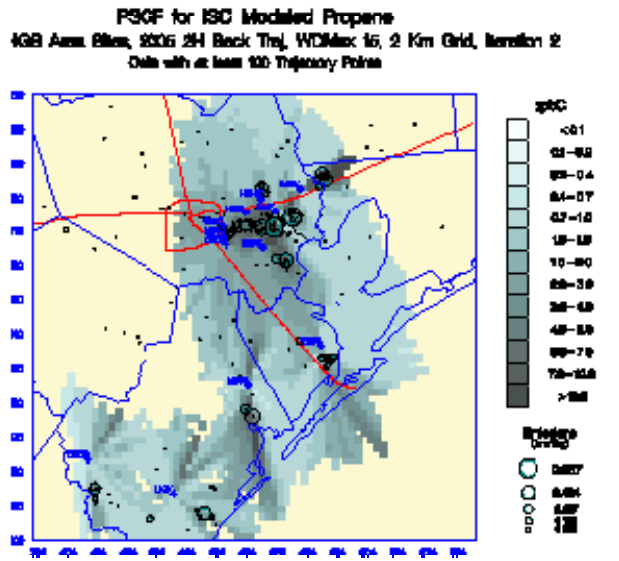
ERFs-Unreconciled



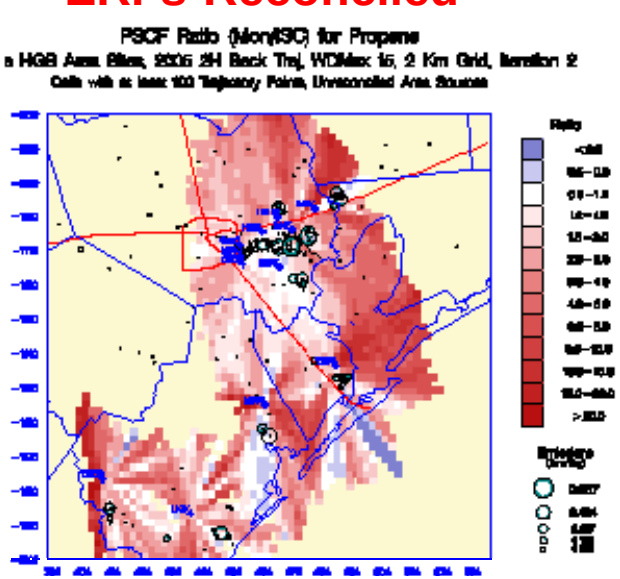
Monitored



Modeled-Reconciled



ERFs-Reconciled

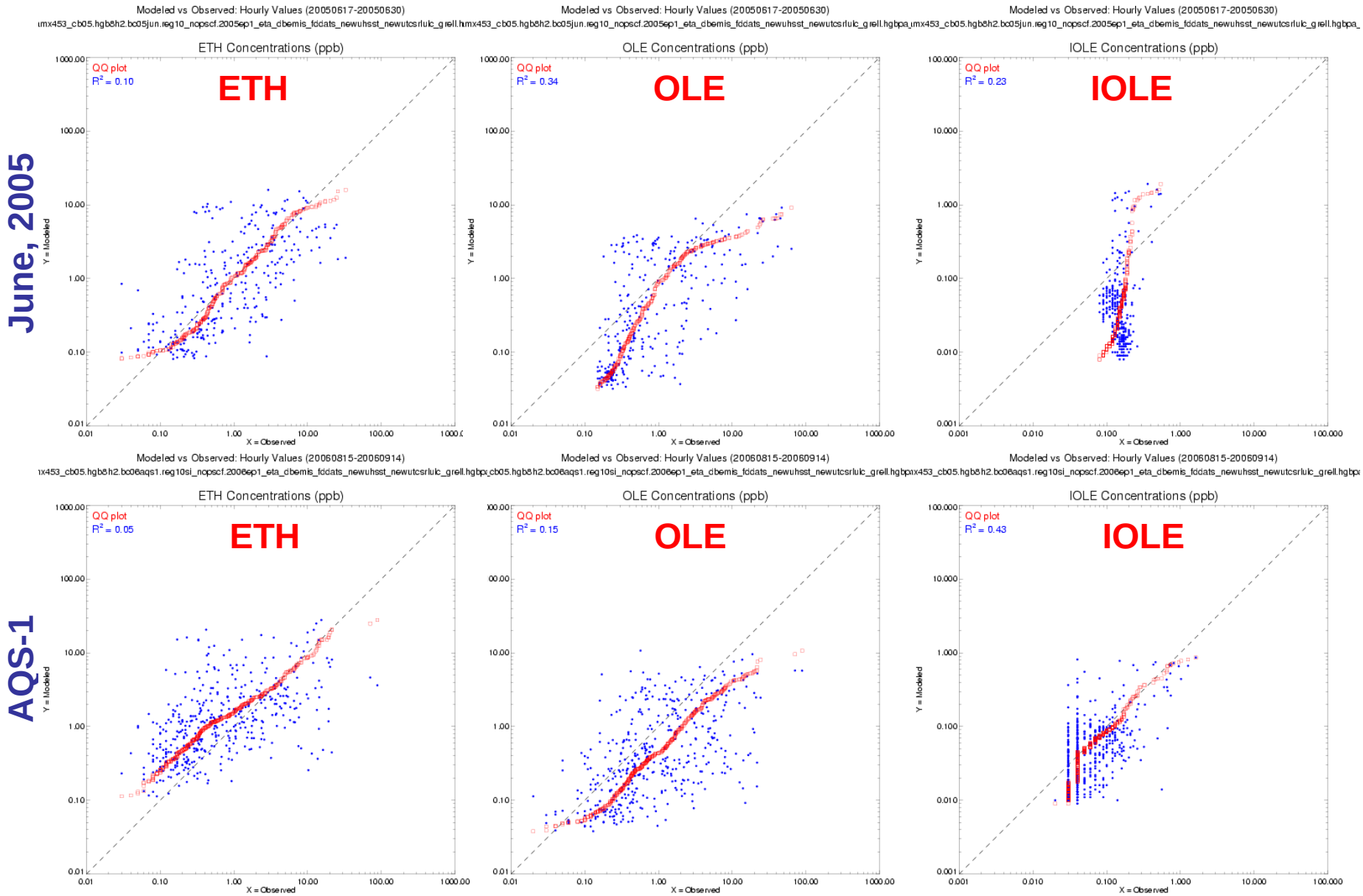


Emission Reconciliation Summary

HRVOC Species	2005			2006		
	RE-Adjusted Reported Emissions	Reconciled Emissions	Percent Change	RE-Adjusted Reported Emissions	Reconciled Emissions	Percent Change
Propene	10.03	25.07	149.8%	9.65	21.92	127.1%
Ethylene	10.96	18.72	70.8%	10.10	15.80	56.4%
1,3-Butadiene	2.22	3.02	35.7%	1.53	1.97	28.3%
1-Butene	2.59	3.96	52.8%	2.70	3.13	16.2%
t-2-Butene	0.58	1.38	135.4%	0.50	1.55	210.9%
c-2-Butene	0.33	0.74	126.8%	0.54	0.86	58.1%
TOTAL	26.72	52.89	97.9%	25.02	45.23	80.7%

CAMx HRVOC Model Performance - Wallisville

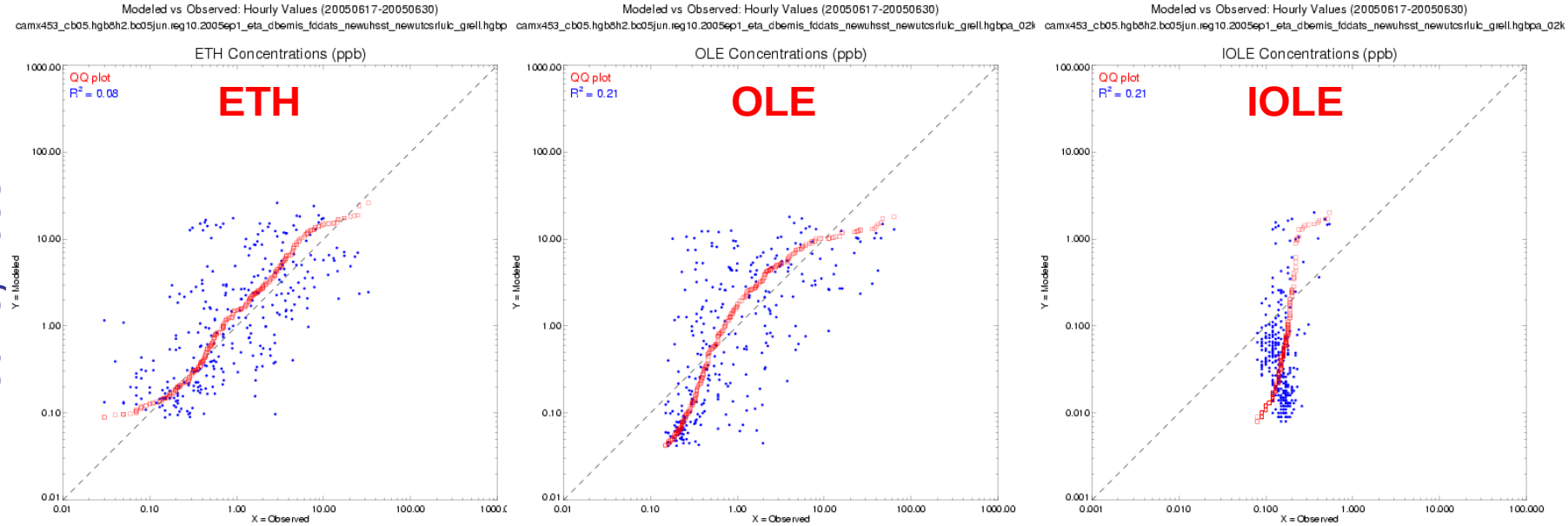
Unreconciled Emissions



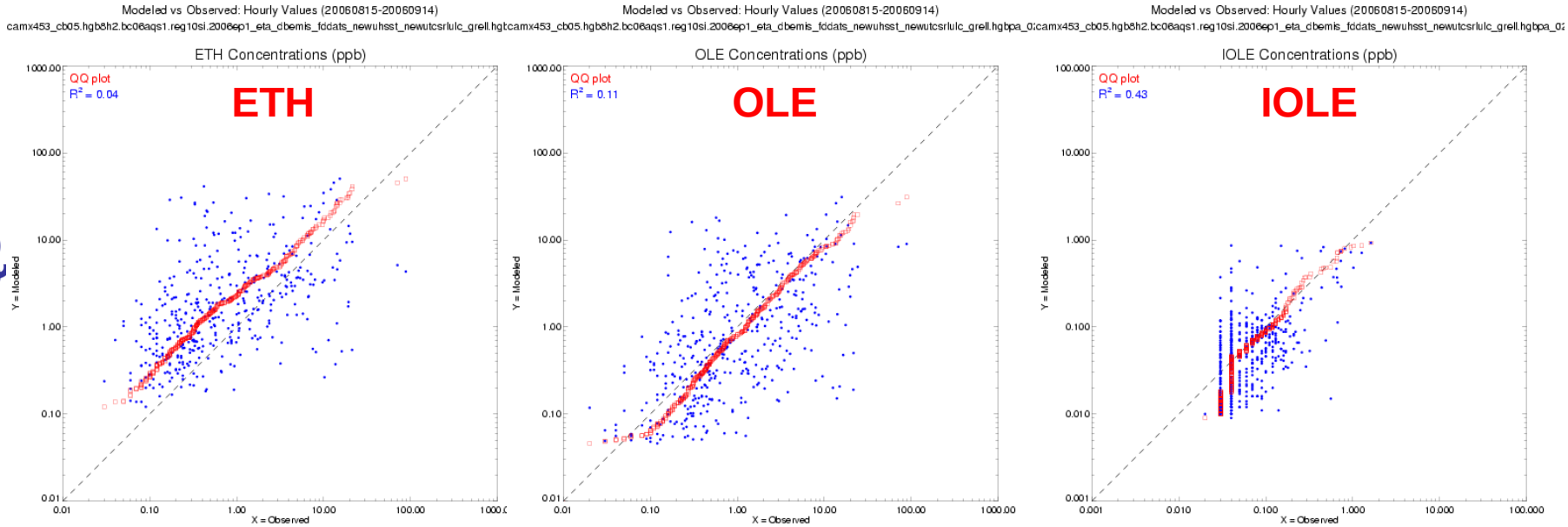
CAMx HRVOC Model Performance - Wallisville

Reconciled Emissions

June, 2005

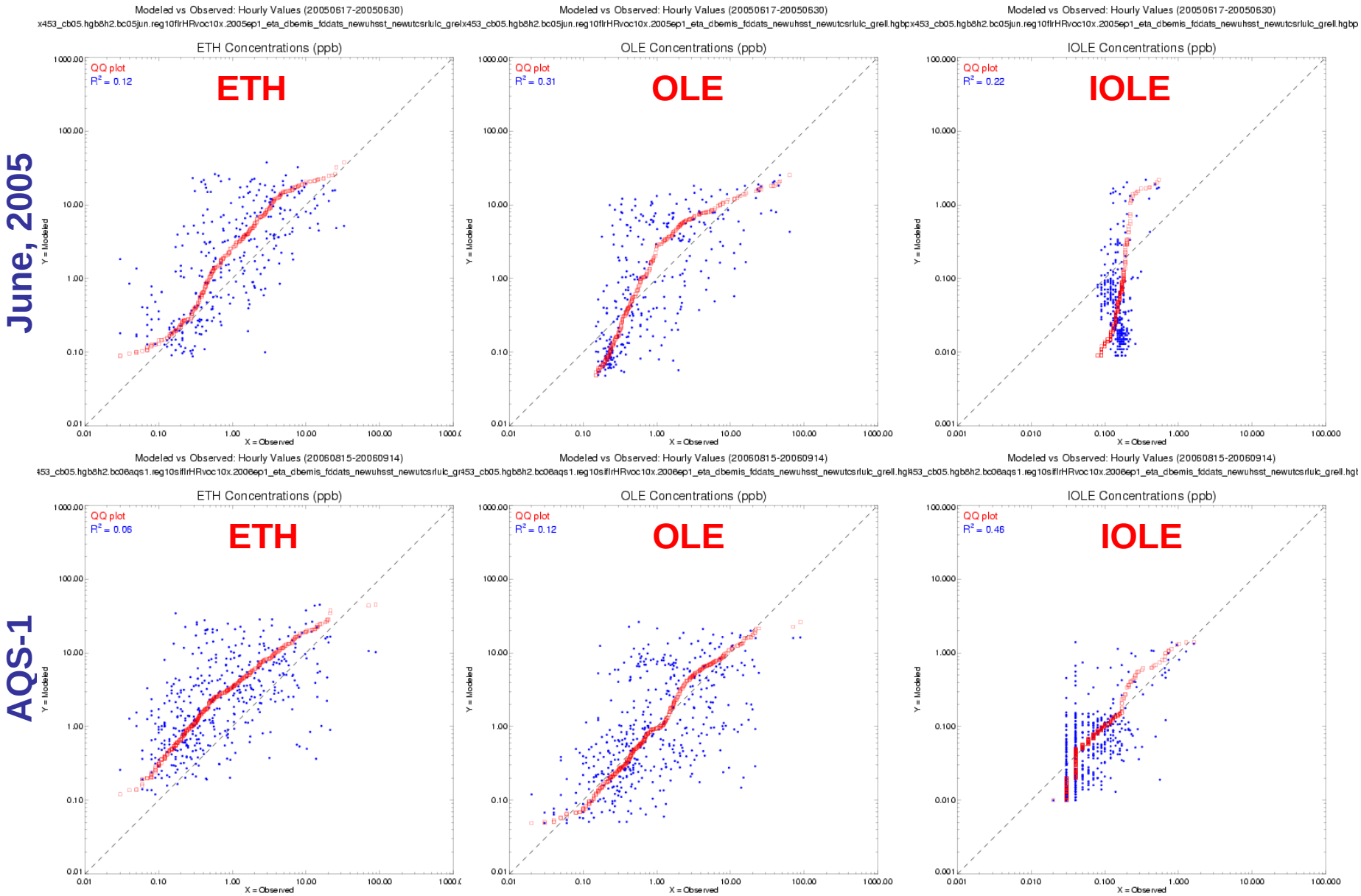


AQS-1



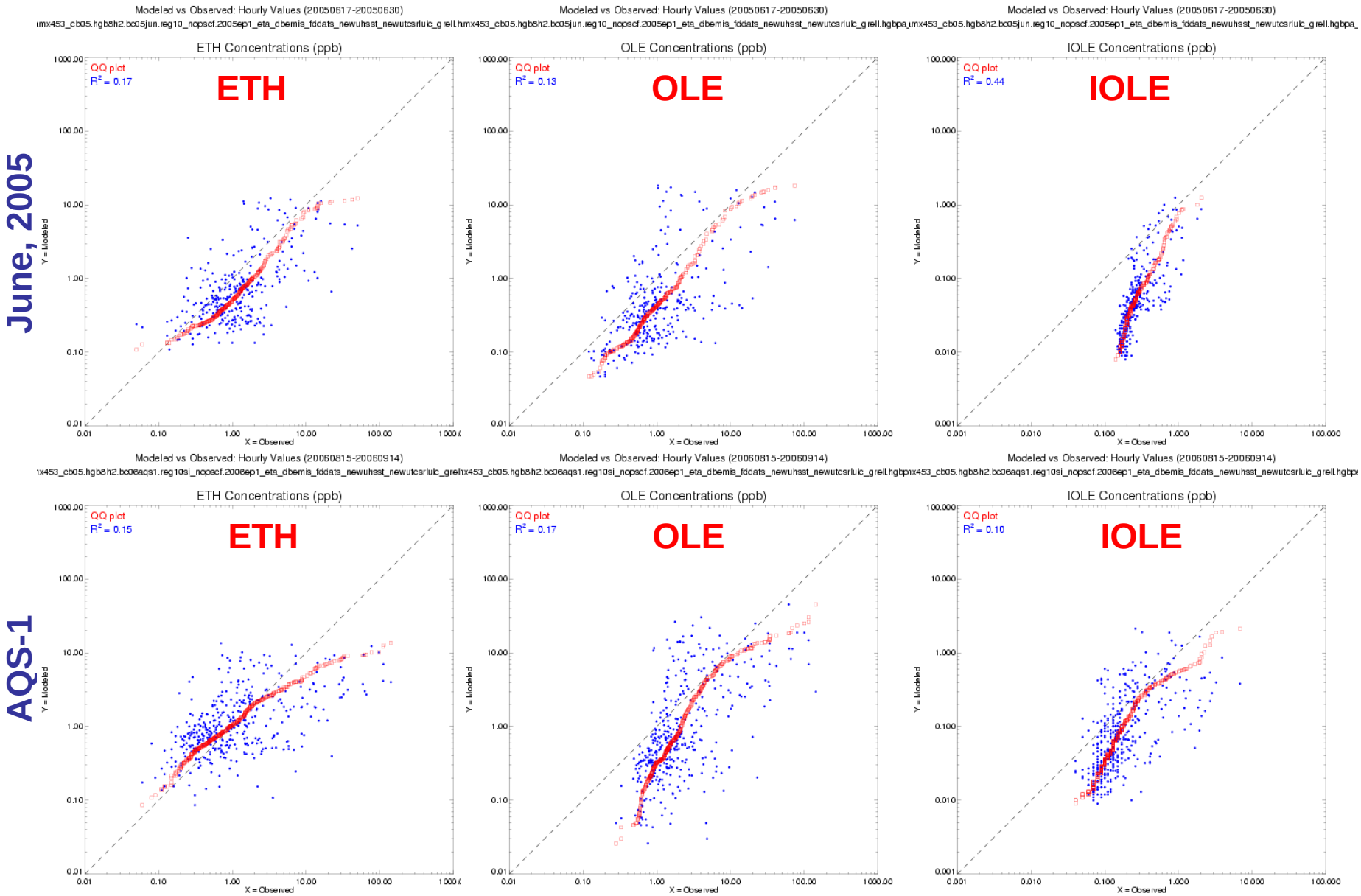
CAMx HRVOC Model Performance - Wallisville

10X Flare HRVOC Sensitivity



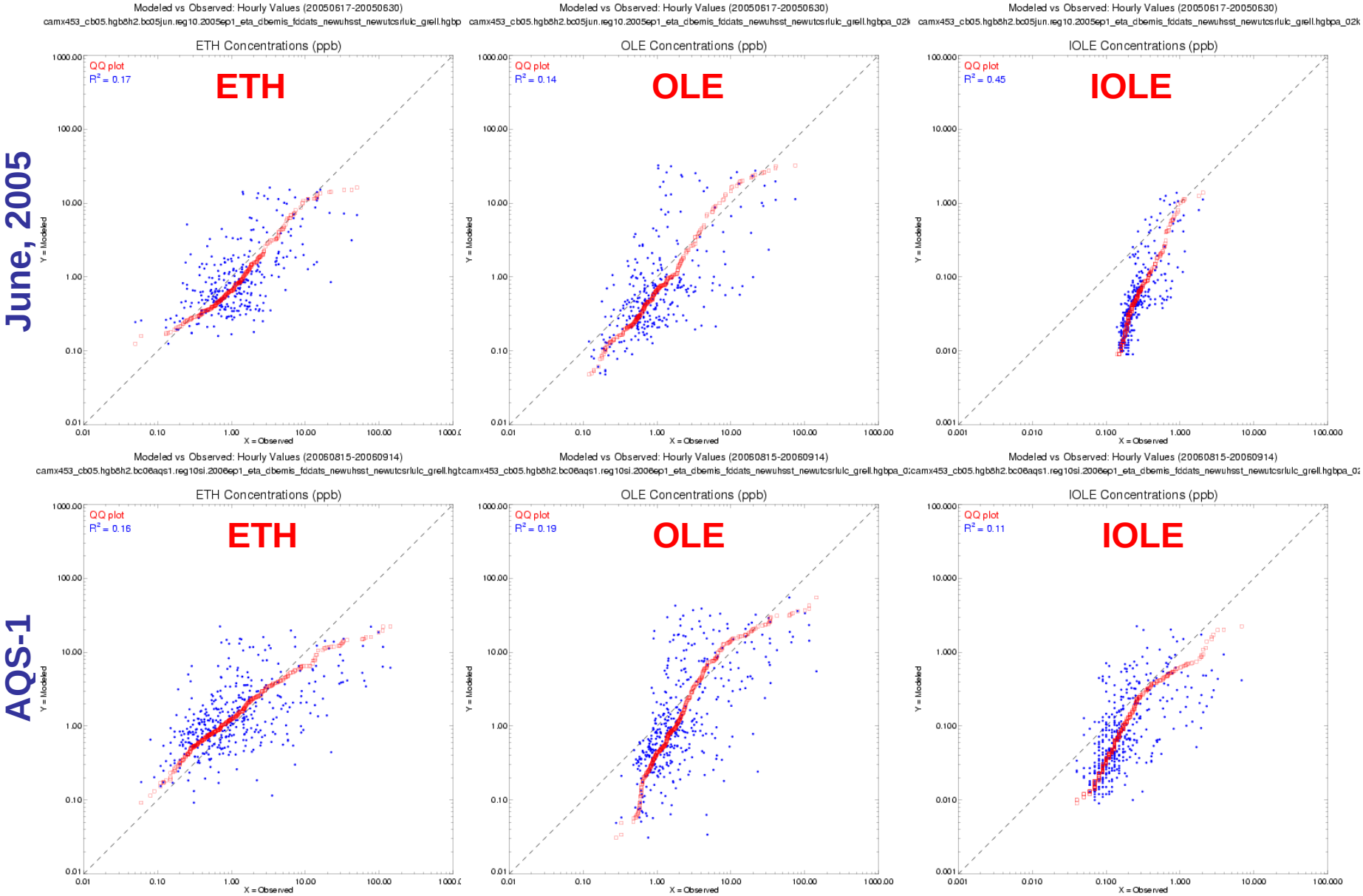
CAMx HRVOC Model Performance – Deer Park

Unreconciled Emissions



CAMx HRVOC Model Performance – Deer Park

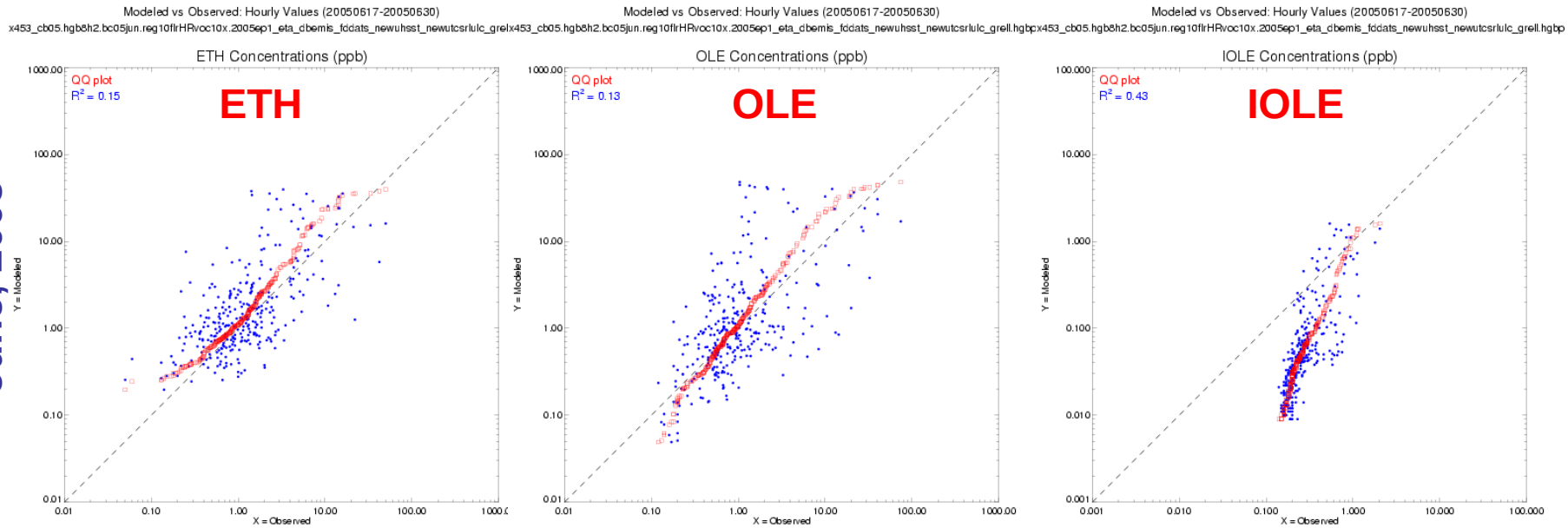
Reconciled Emissions



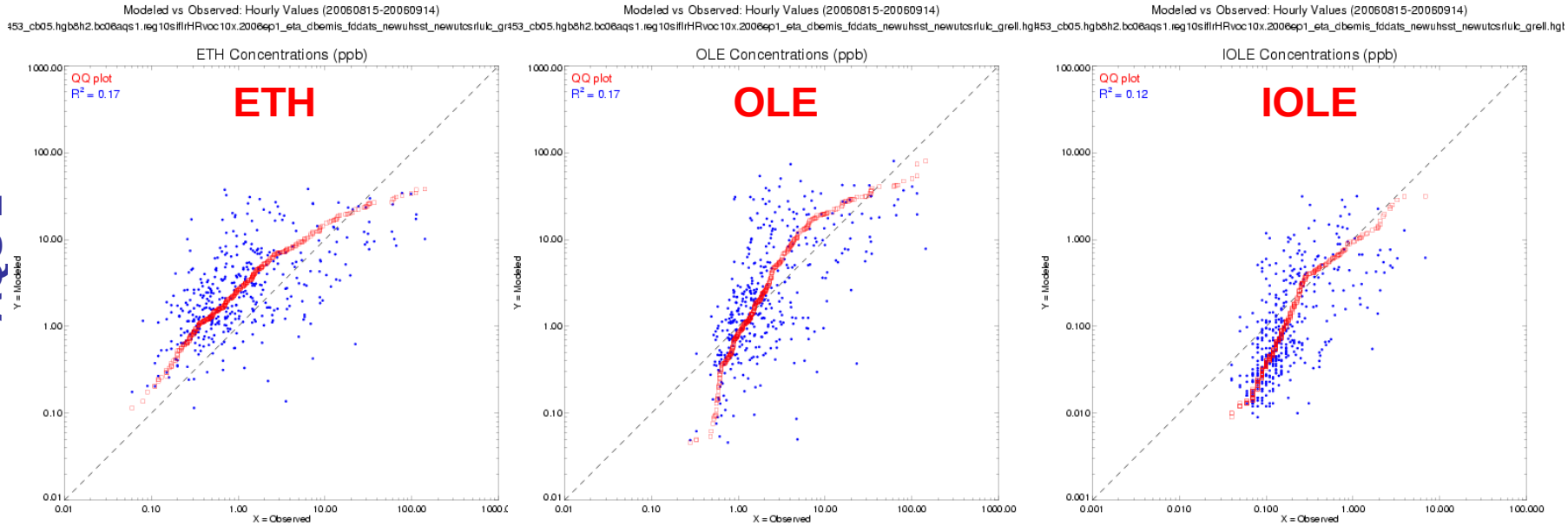
CAMx HRVOC Model Performance – Deer Park

10X HRVOC Sensitivity

June, 2005



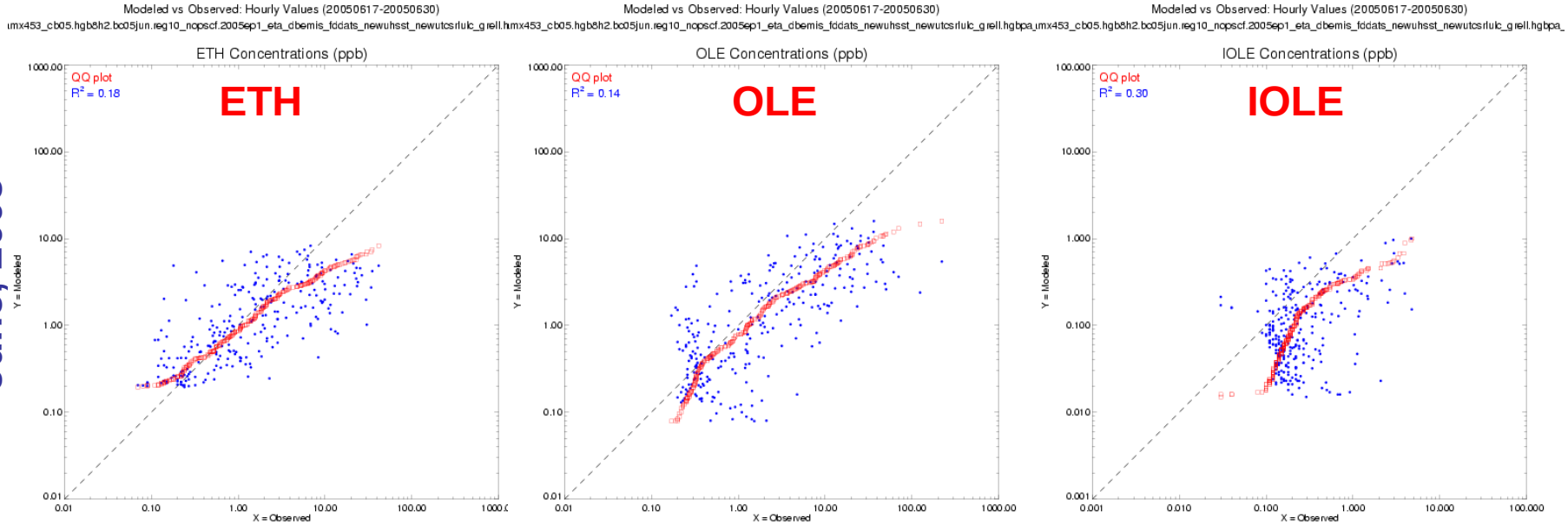
AQS-1



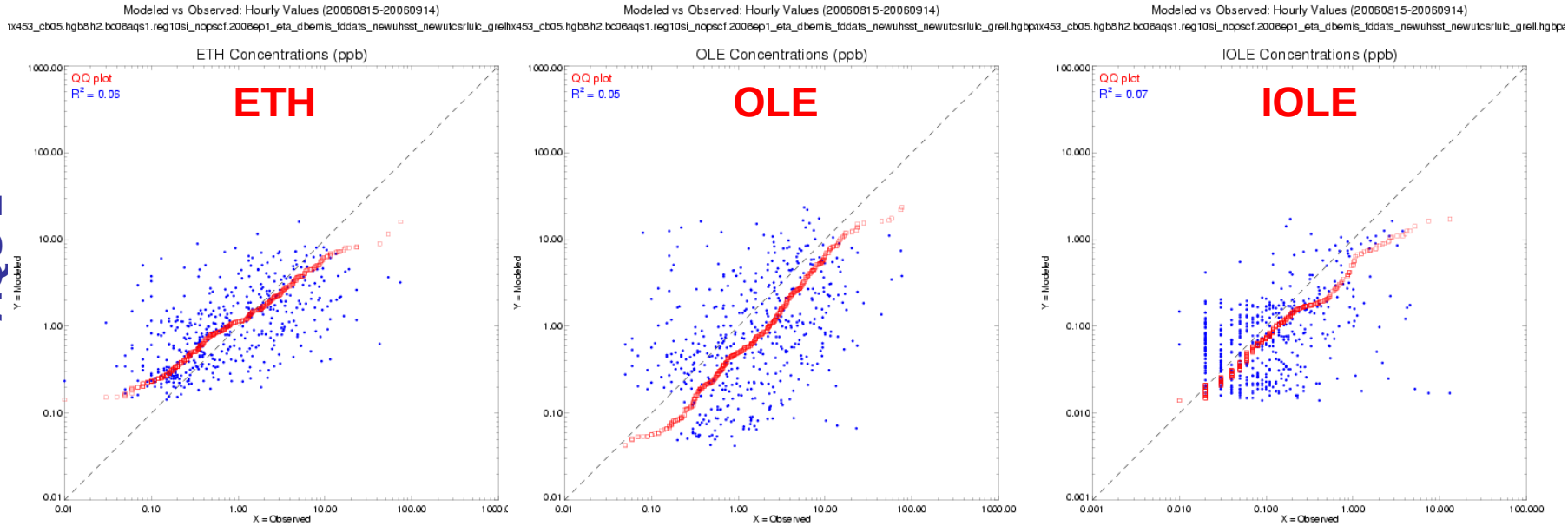
CAMx HRVOC Model Performance – Lynchburg Ferry

Unreconciled Emissions

June, 2005

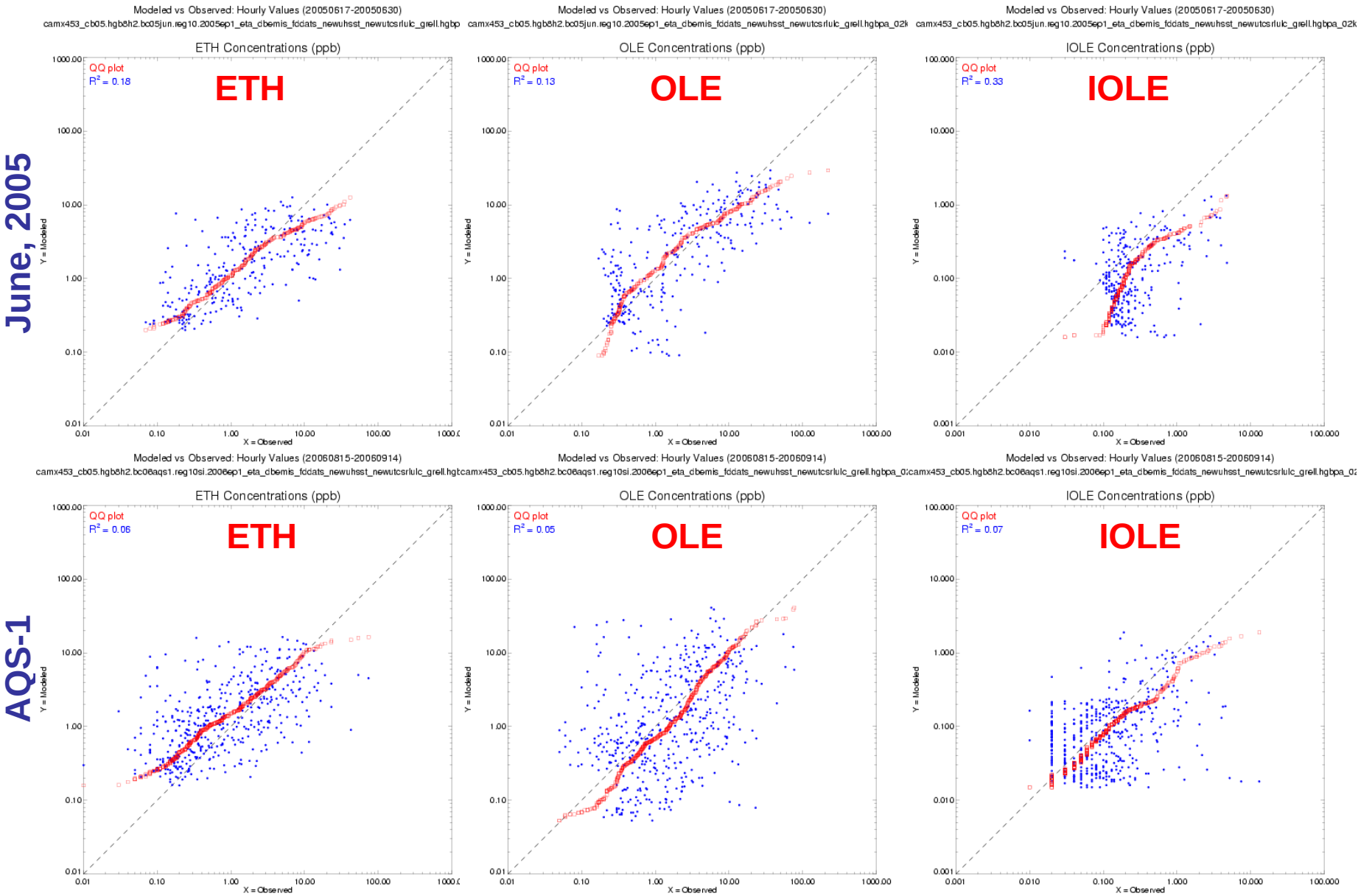


AQS-1



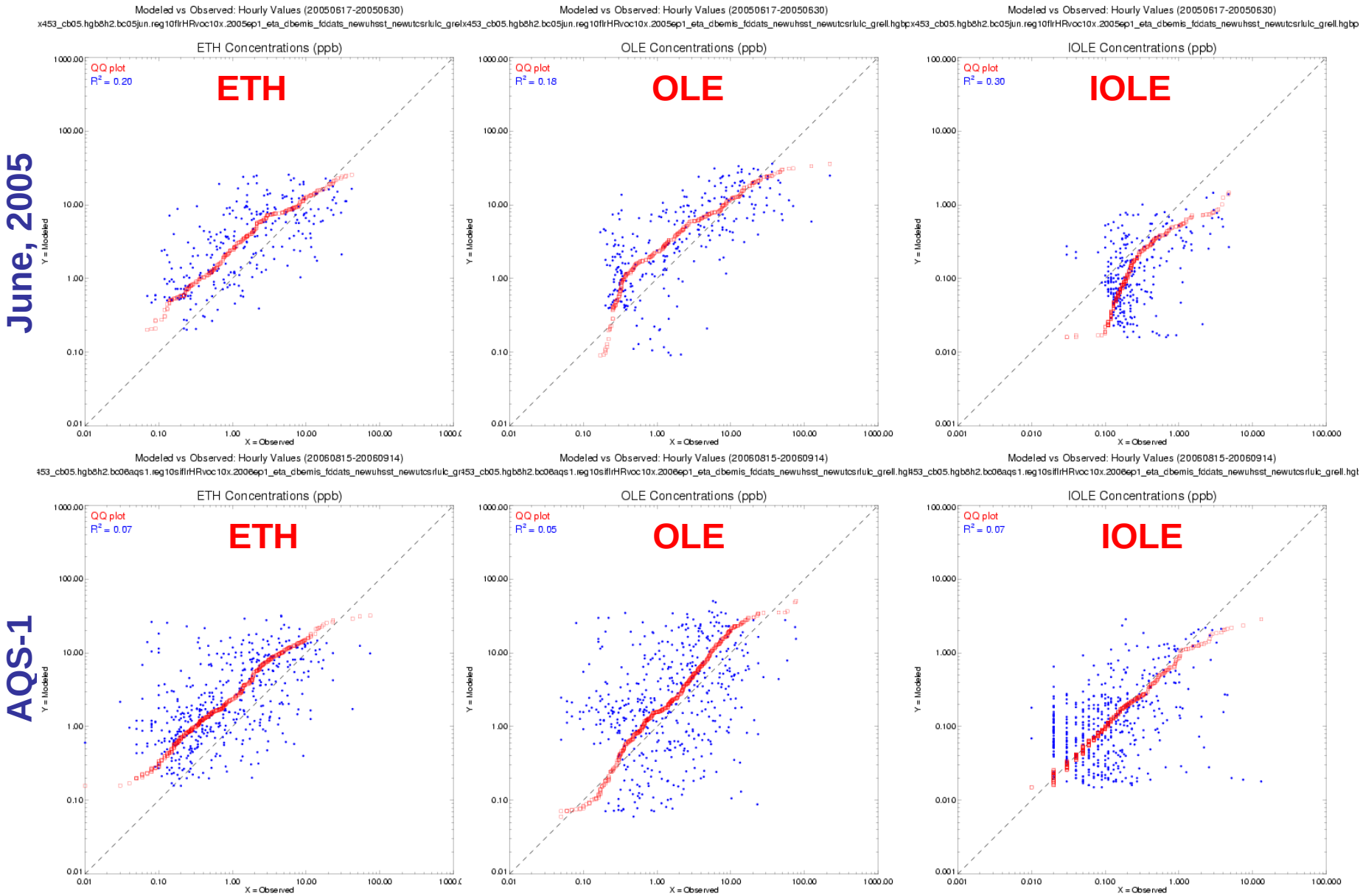
CAMx HRVOC Model Performance – Lynchburg Ferry

Reconciled Emissions



CAMx HRVOC Model Performance – Lynchburg Ferry

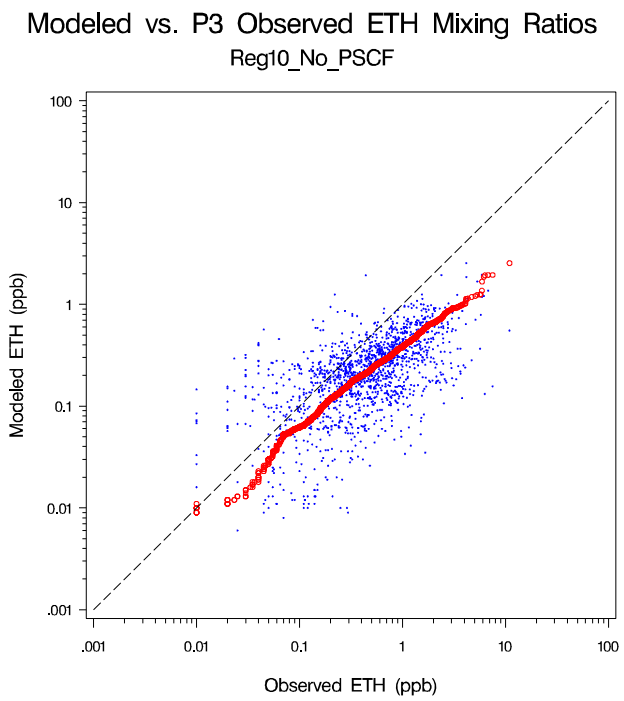
10X Flare HRVOC Sensitivity



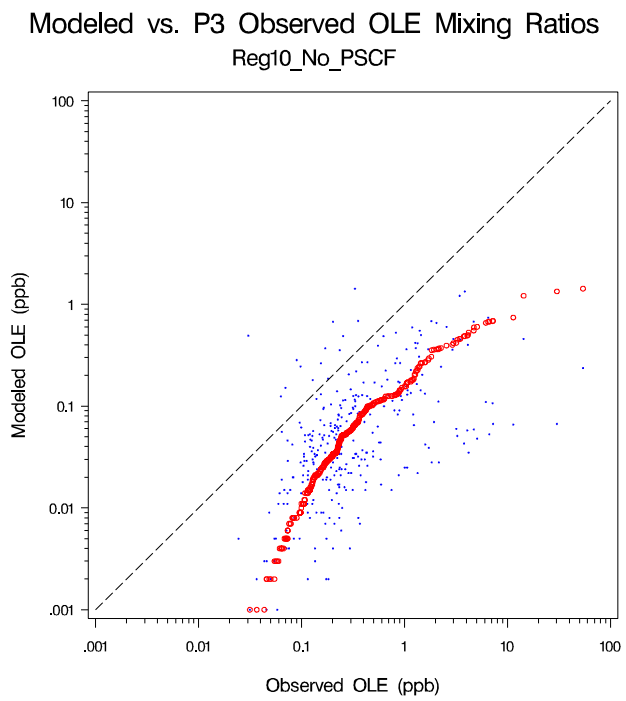
CAMx HRVOC Model Performance – NOAA P3 All Flights August 31 – October 12, 2006, HG 2-Km Subgrid

Unreconciled Emissions

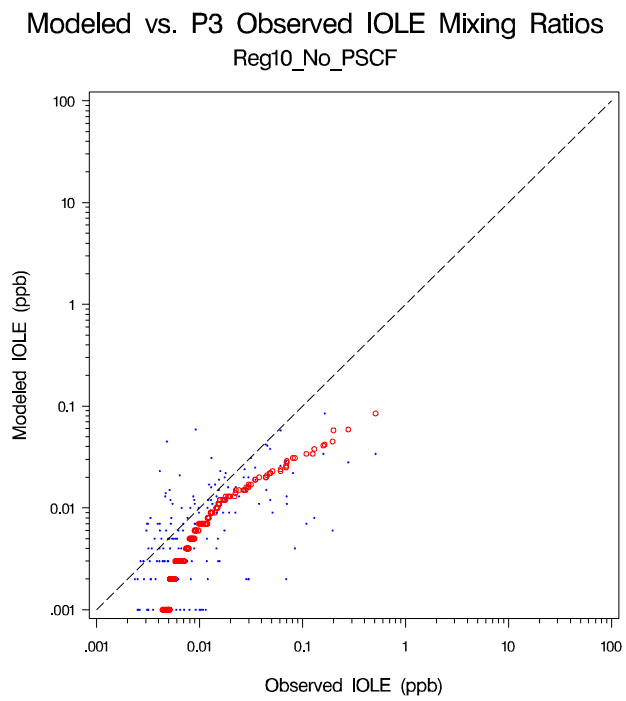
ETH



OLE



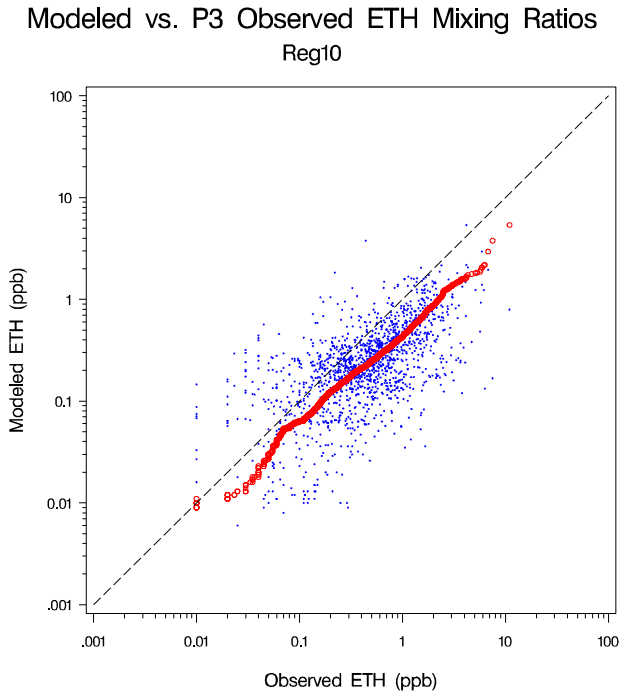
IOLE



CAMx HRVOC Model Performance – NOAA P3 All Flights August 31 – October 12, 2006, HG 2-Km Subgrid

Reconciled Emissions

ETH



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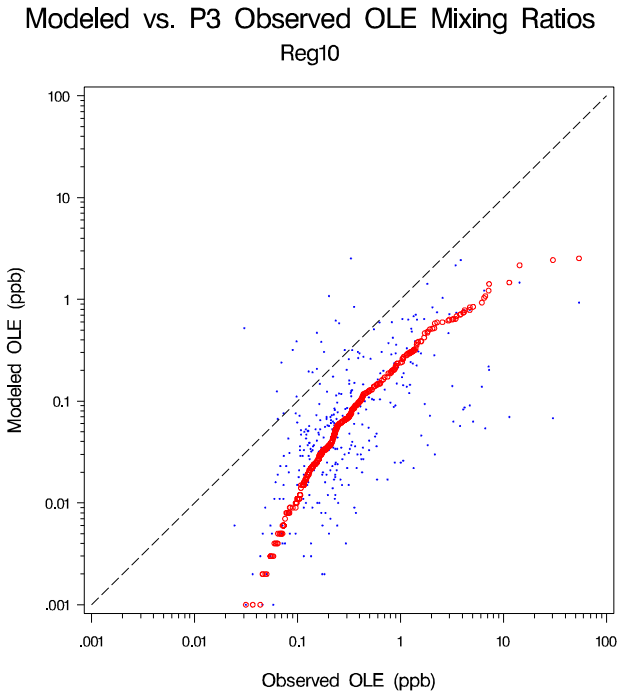

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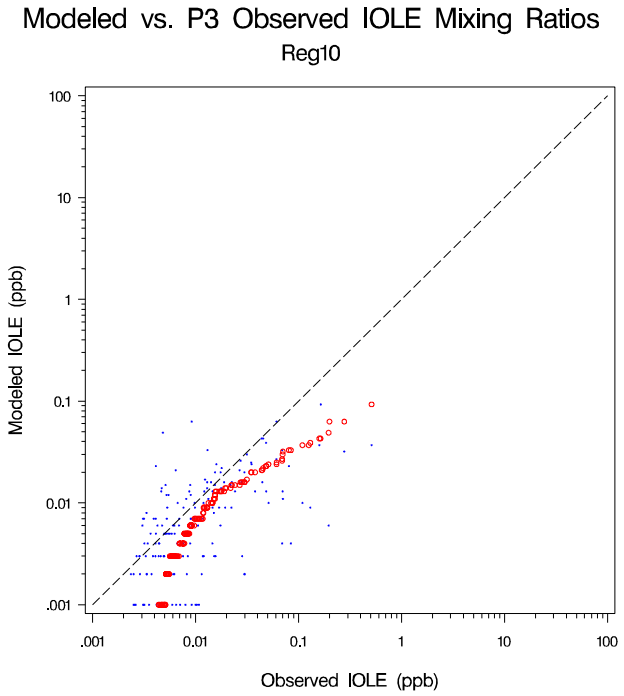
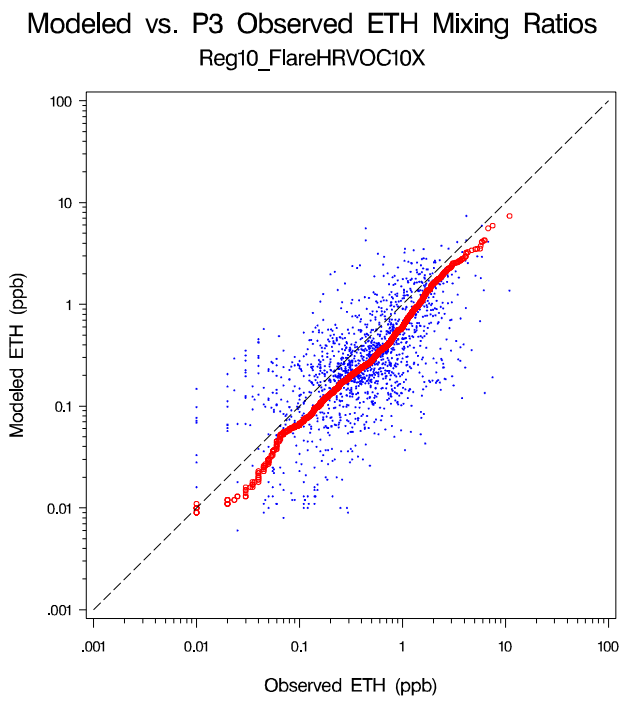


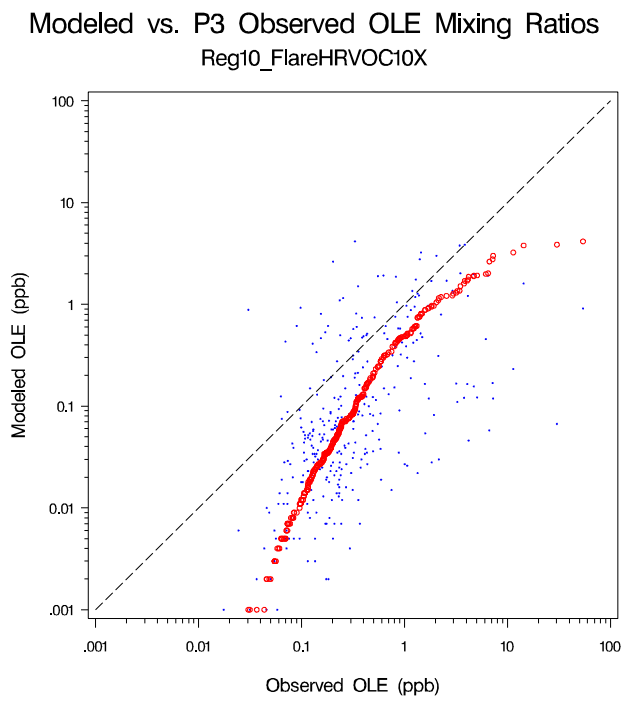
CAMx HRVOC Model Performance – NOAA P3 All Flights Aug. 31 – Oct. 12, 2006, HG 2-Km Subgrid

10X Flare HRVOC Sensitivity

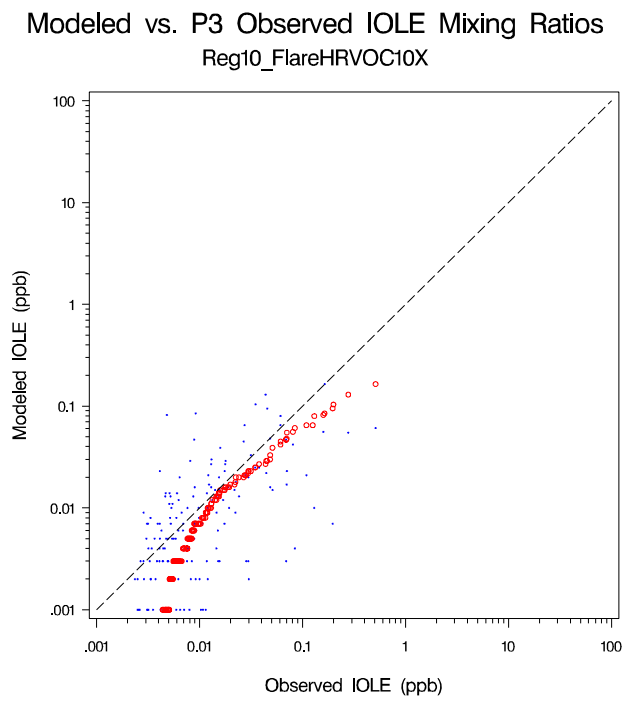
ETH



OLE



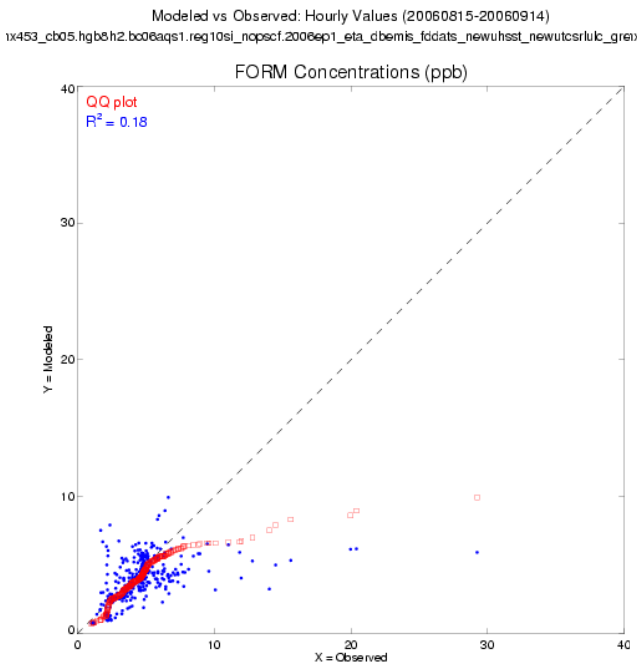
IOLE



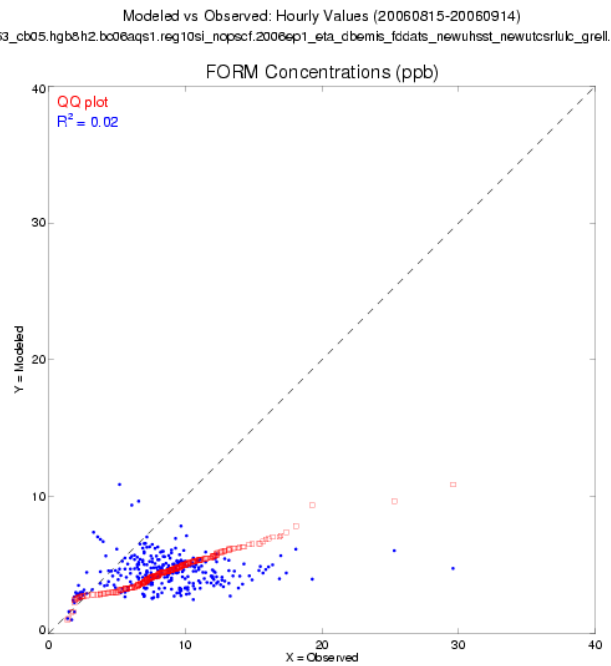
CAMx Formaldehyde Model Performance

Unreconciled Emissions

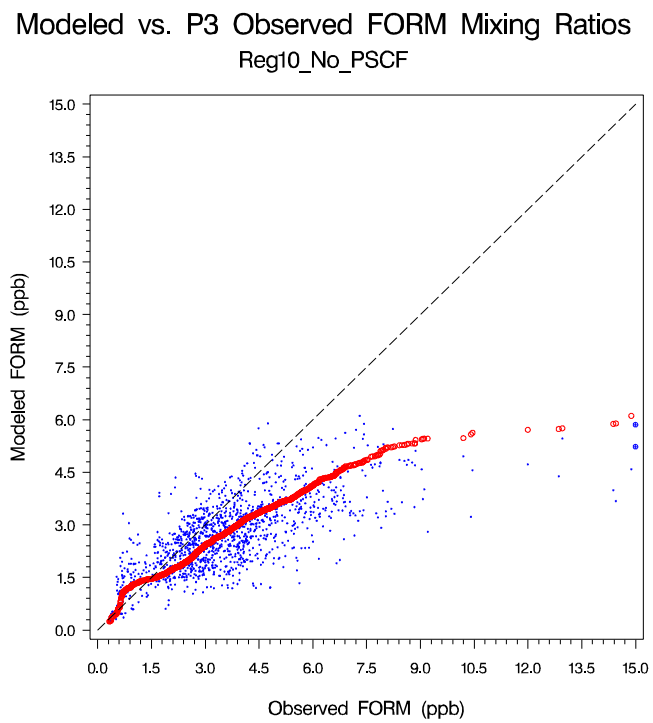
Moody Tower, AQS-1



Lynchburg Ferry, AQS-1



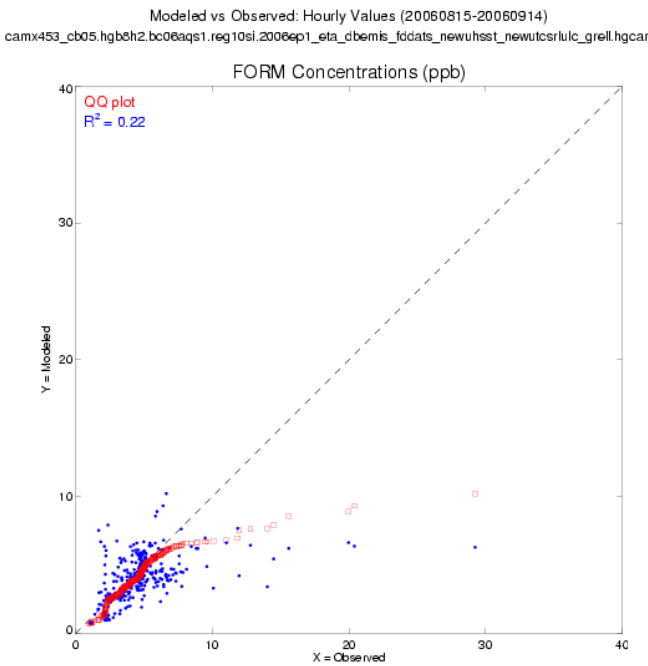
NOAA P3



CAMx Formaldehyde Model Performance

Reconciled Emissions

Moody Tower, AQS-1



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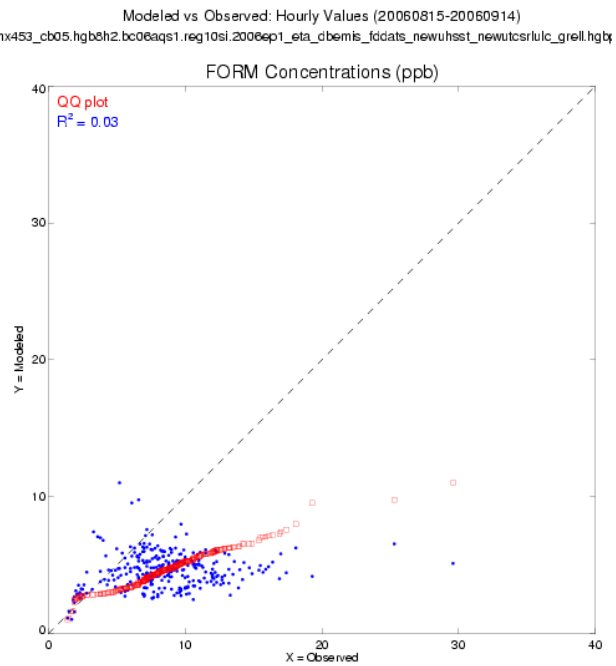

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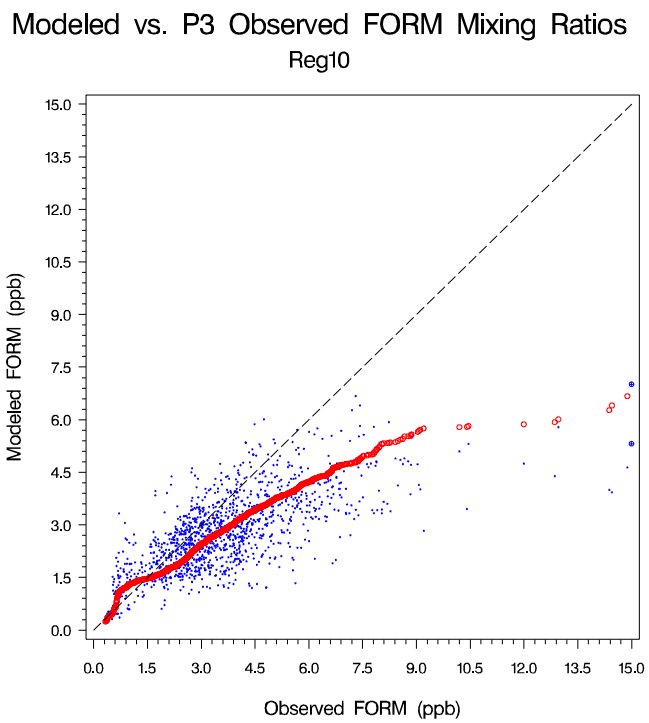
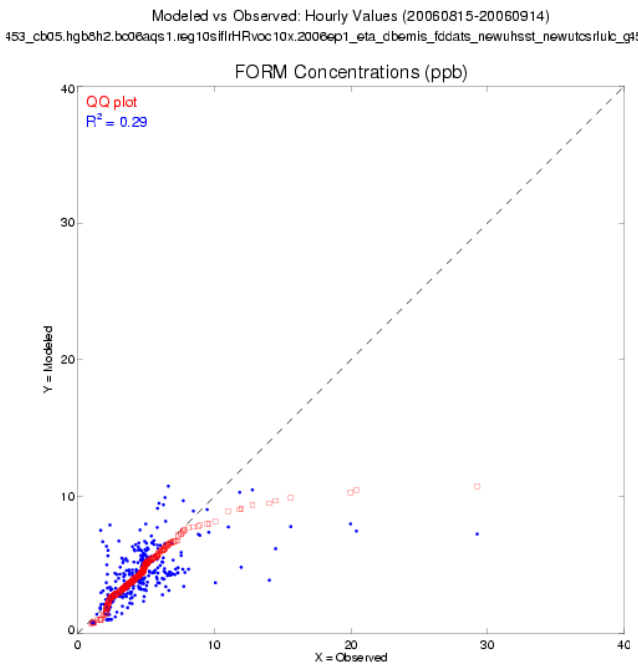


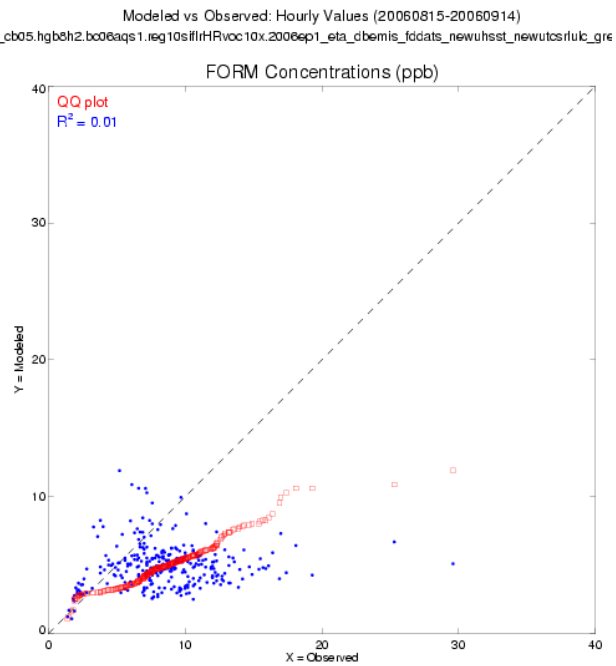
CAMx Formaldehyde Model Performance

10X Flare HRVOC Sensitivity

Moody Tower, AQS-1



Lynchburg Ferry, AQS-1



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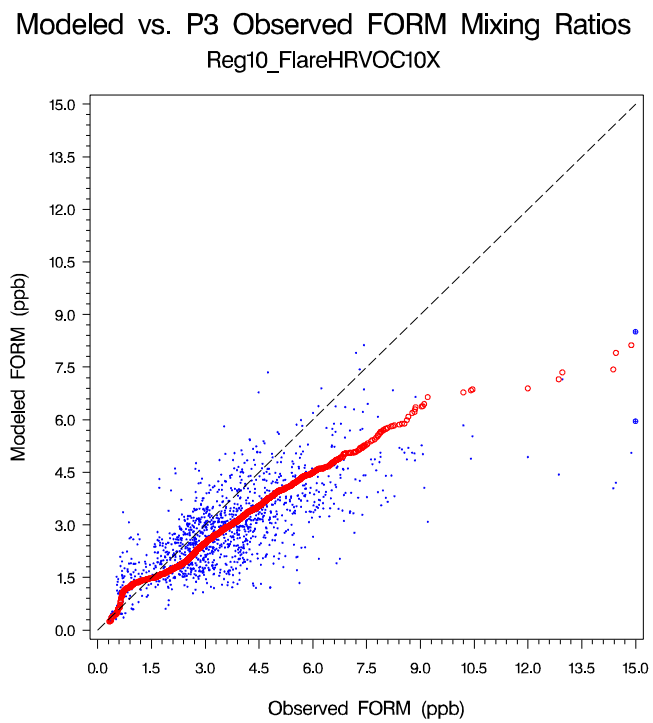
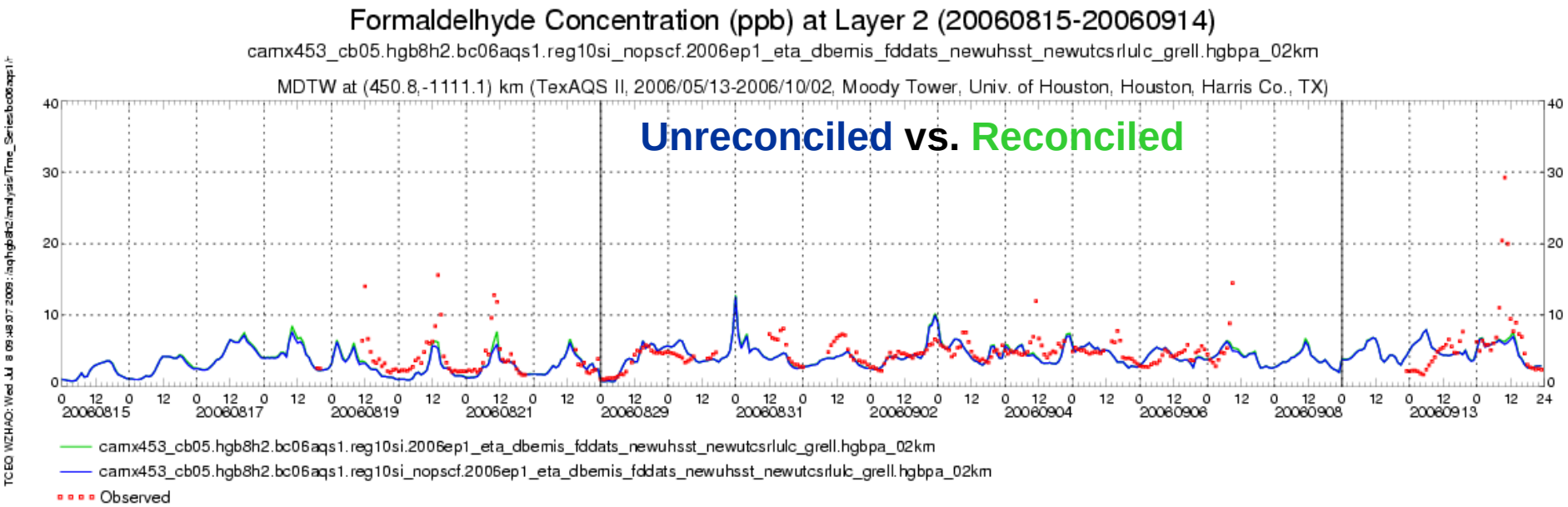
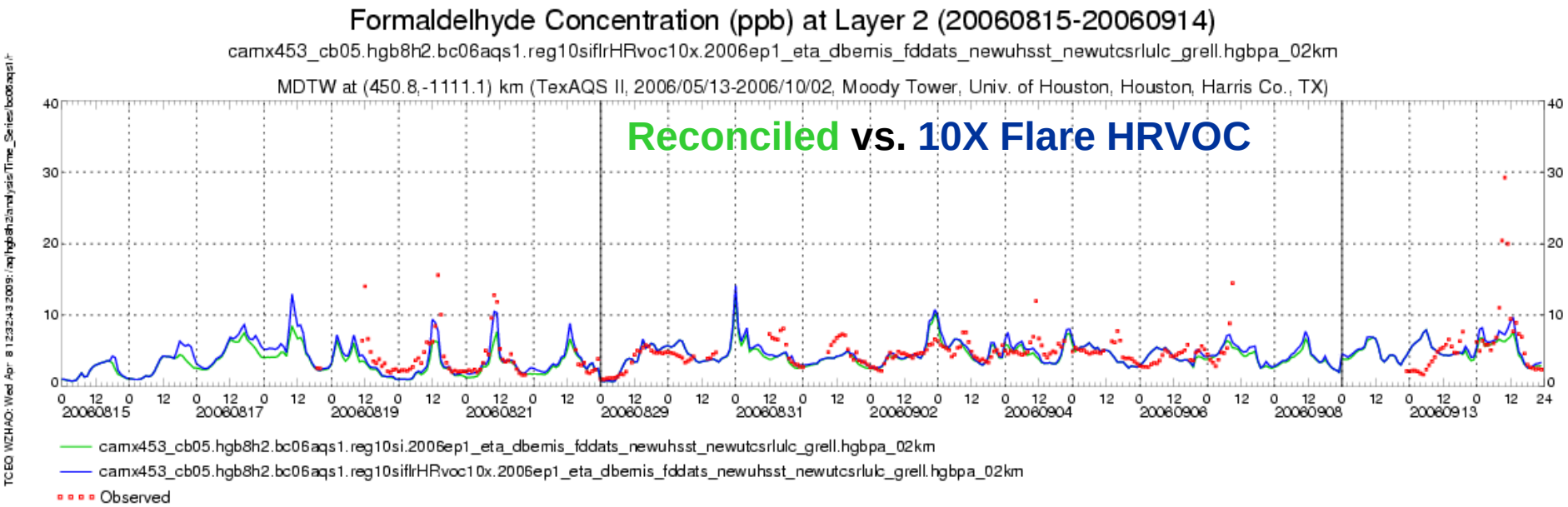


CAMx Formaldehyde Model Performance

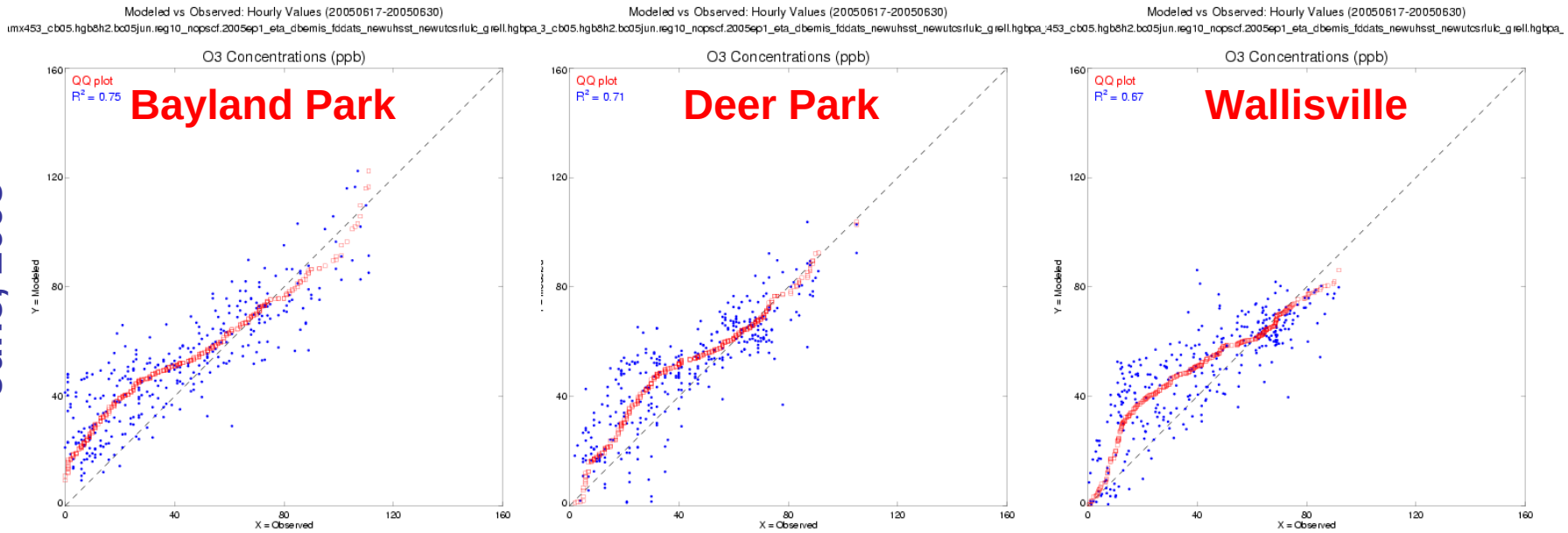




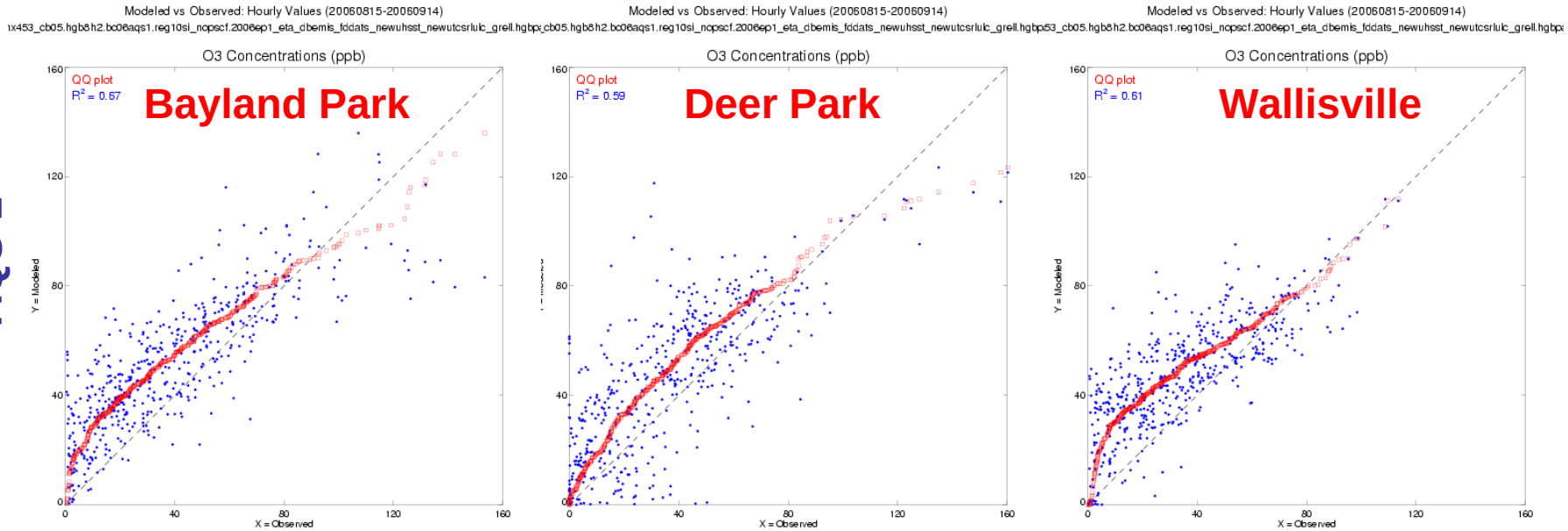
CAMx Ozone Model Performance

Unreconciled Emissions

June, 2005



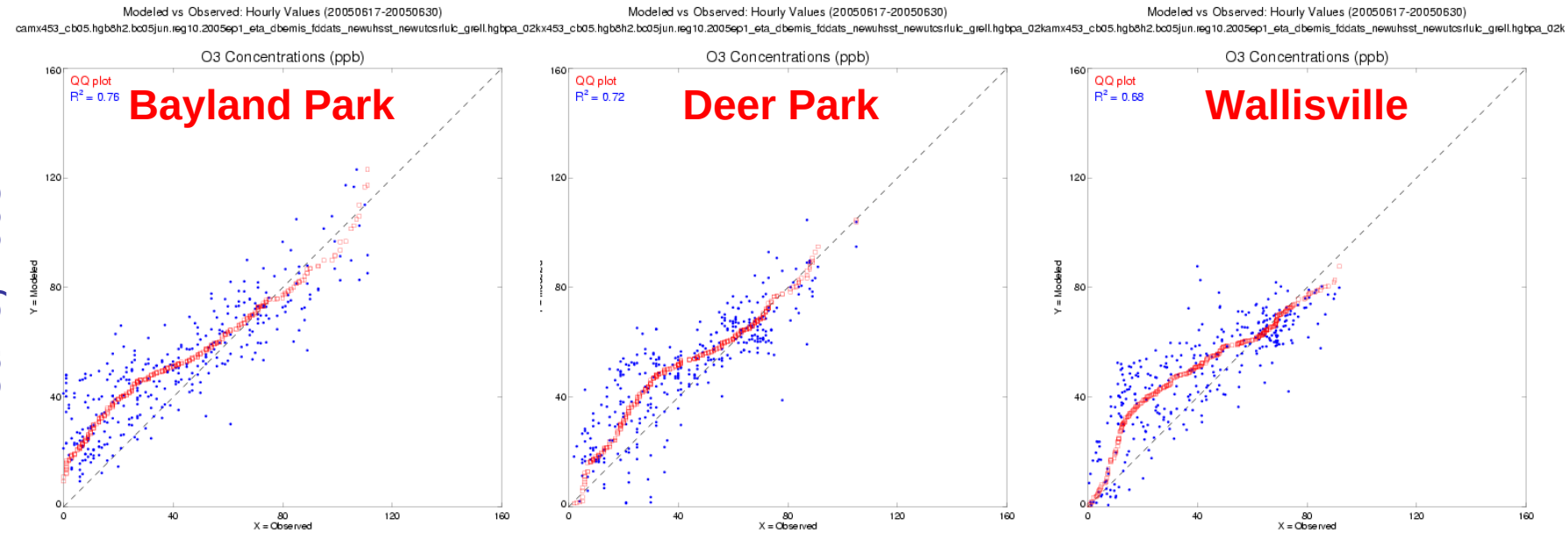
AQS-1



CAMx Ozone Model Performance

Reconciled Emissions

June, 2005



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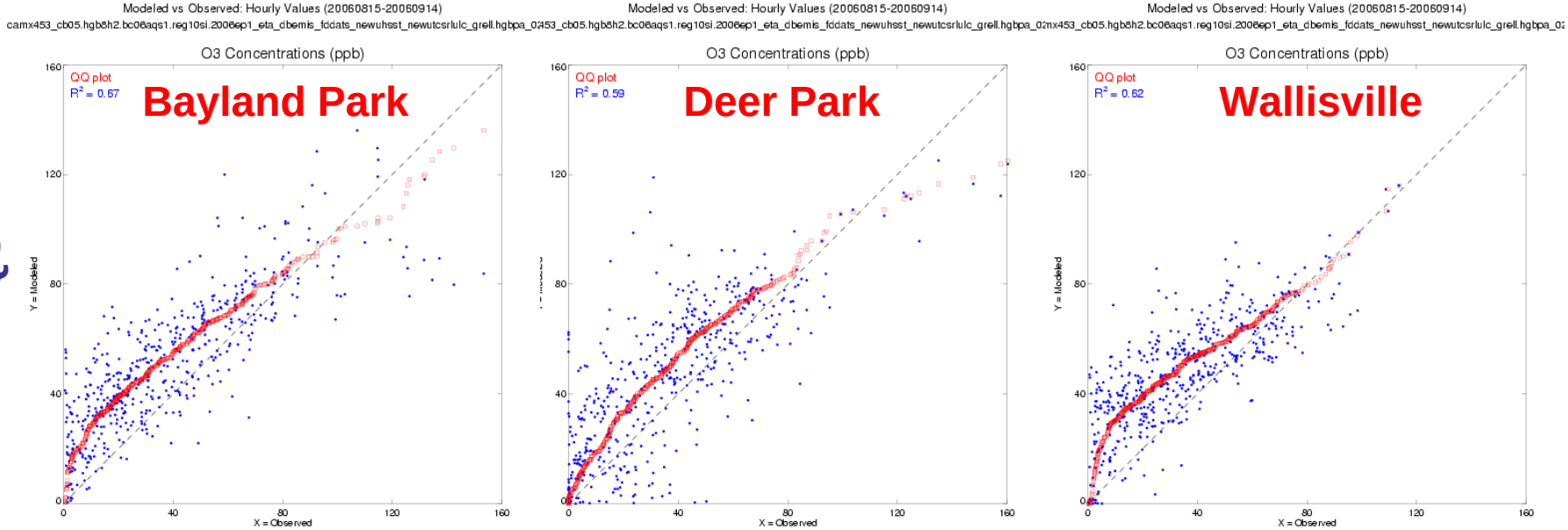
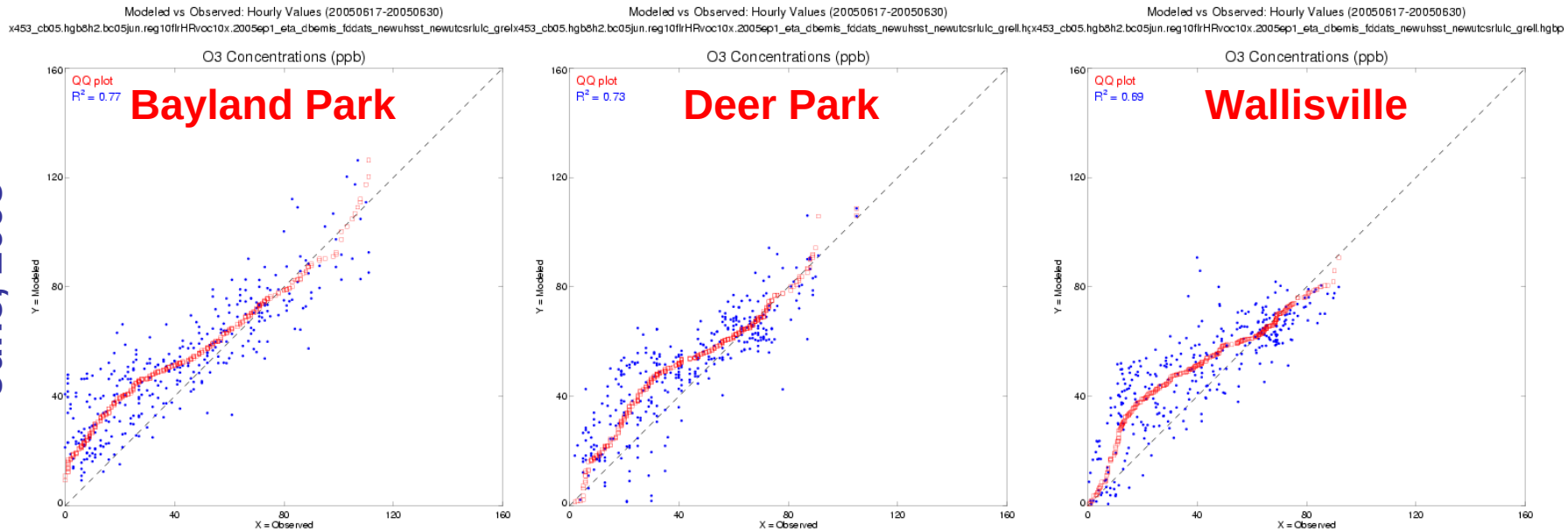


CAMx Ozone Model Performance

10X Flare HRVOC Sensitivity

June, 2005



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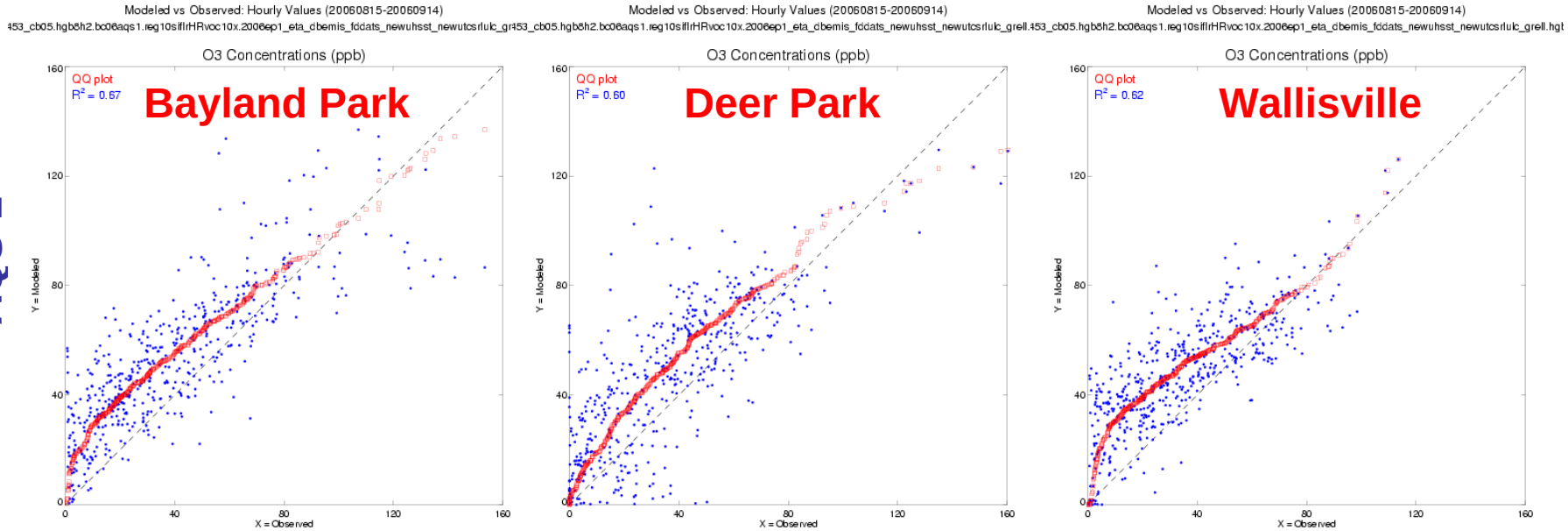
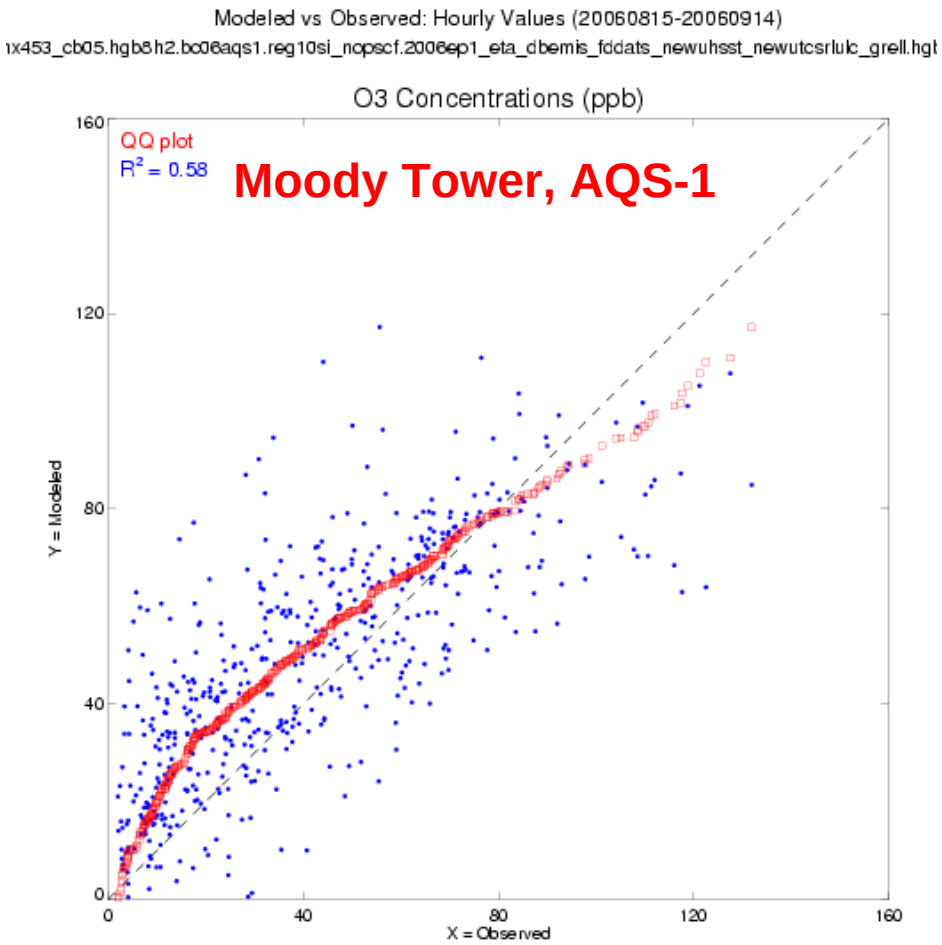
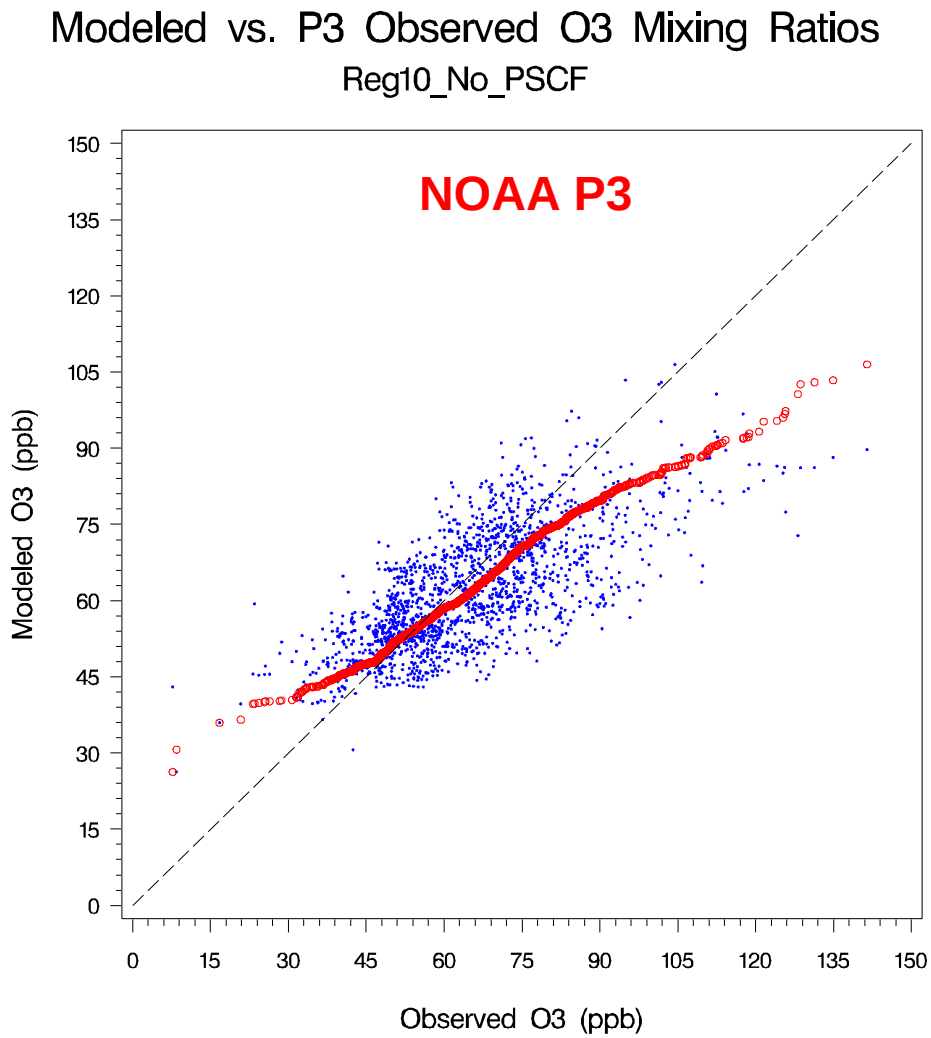


CAMx Ozone Model Performance

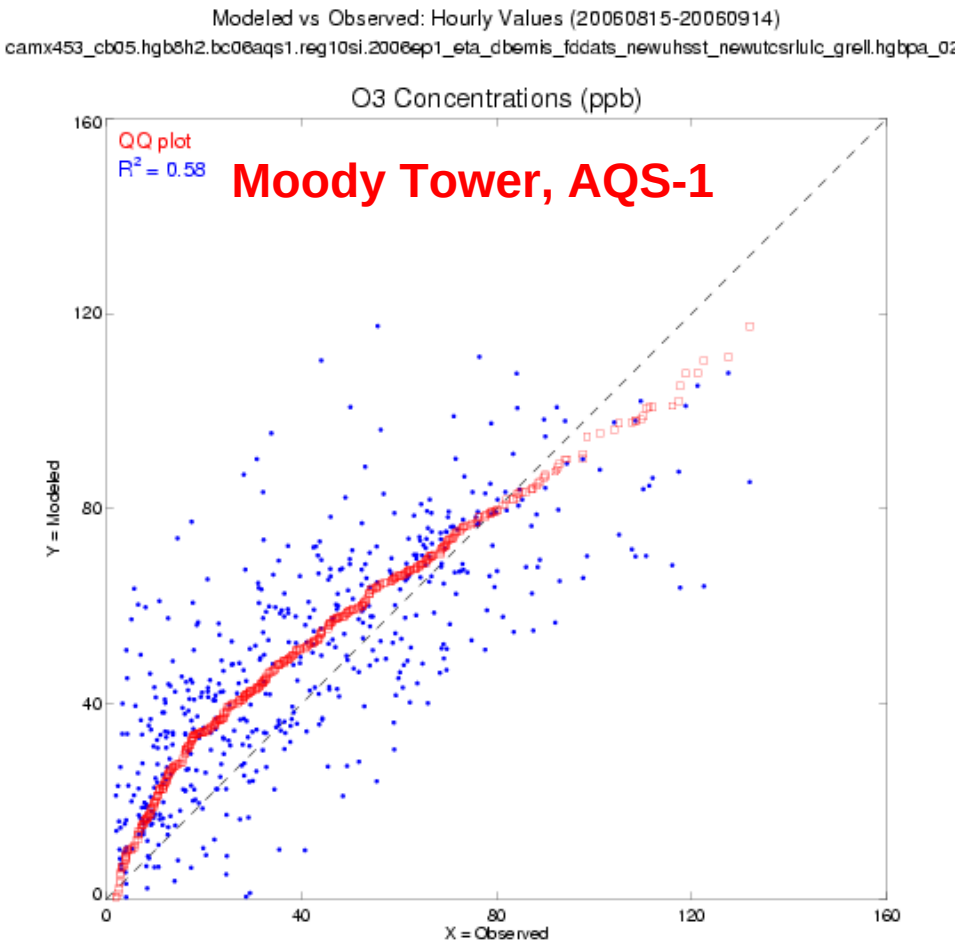
Unreconciled Emissions

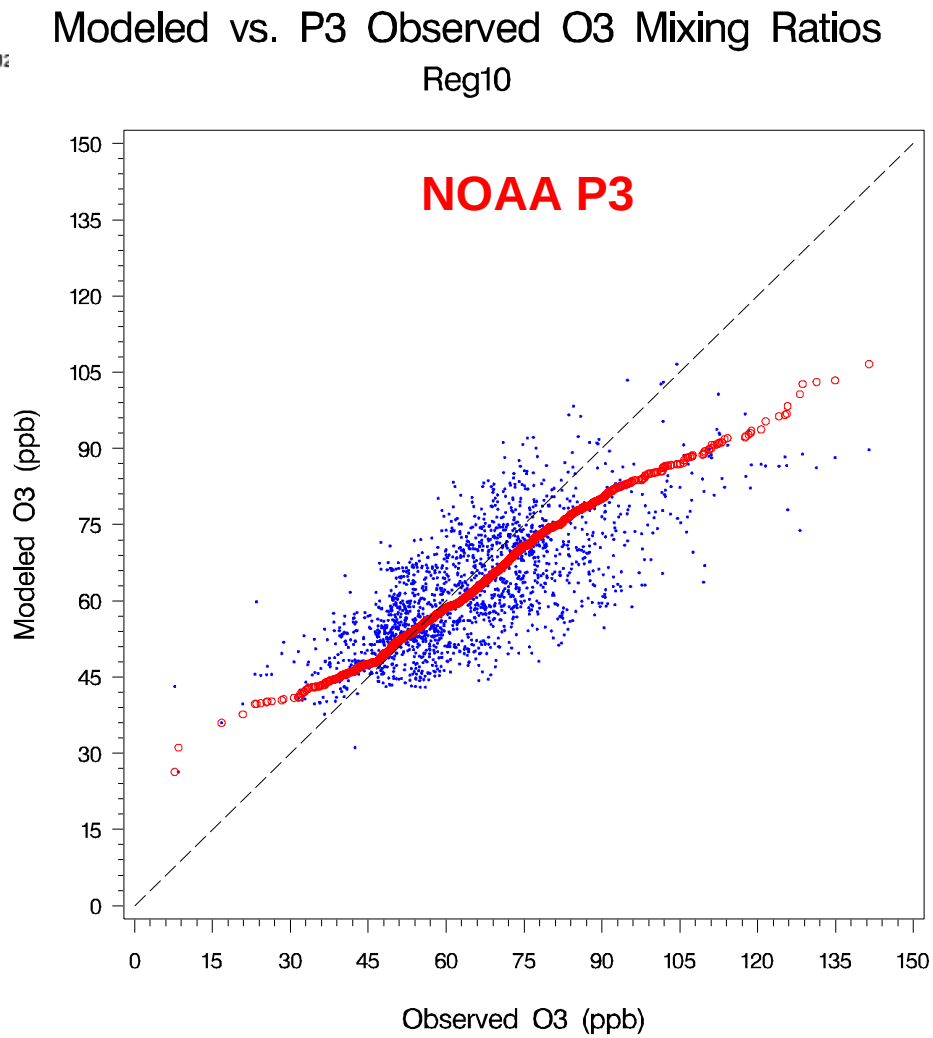




CAMx Ozone Model Performance

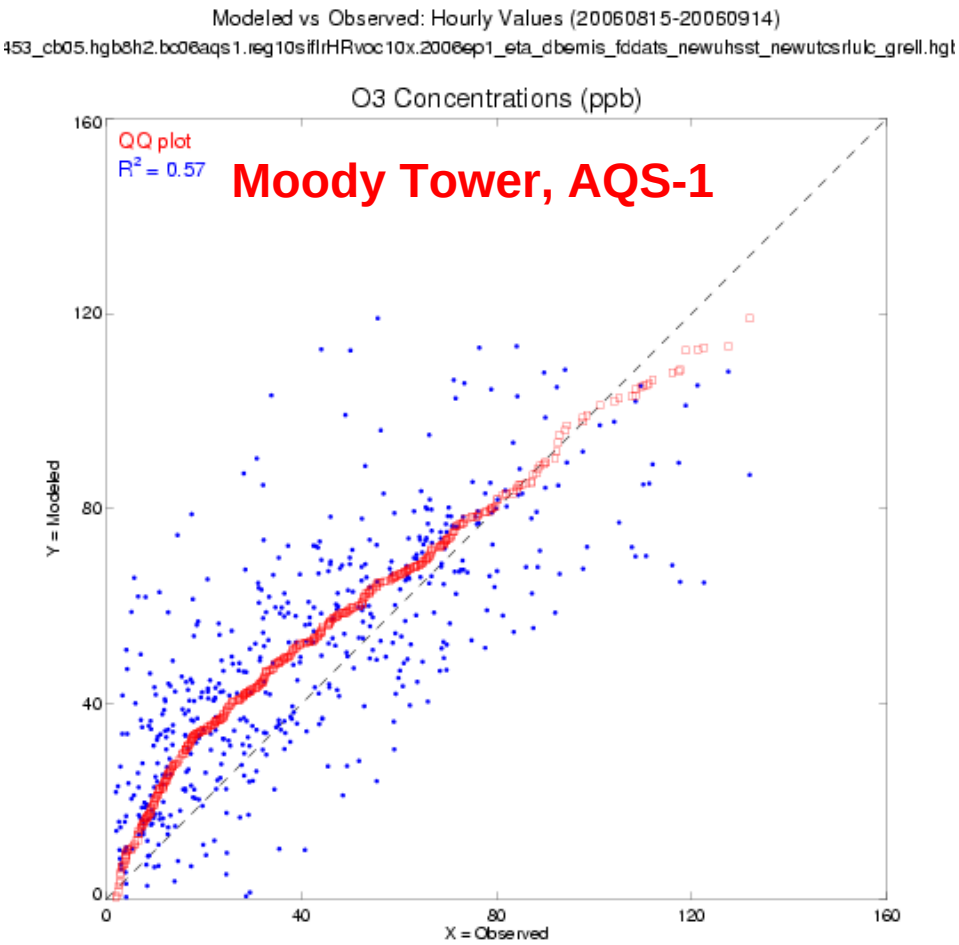
Reconciled Emissions

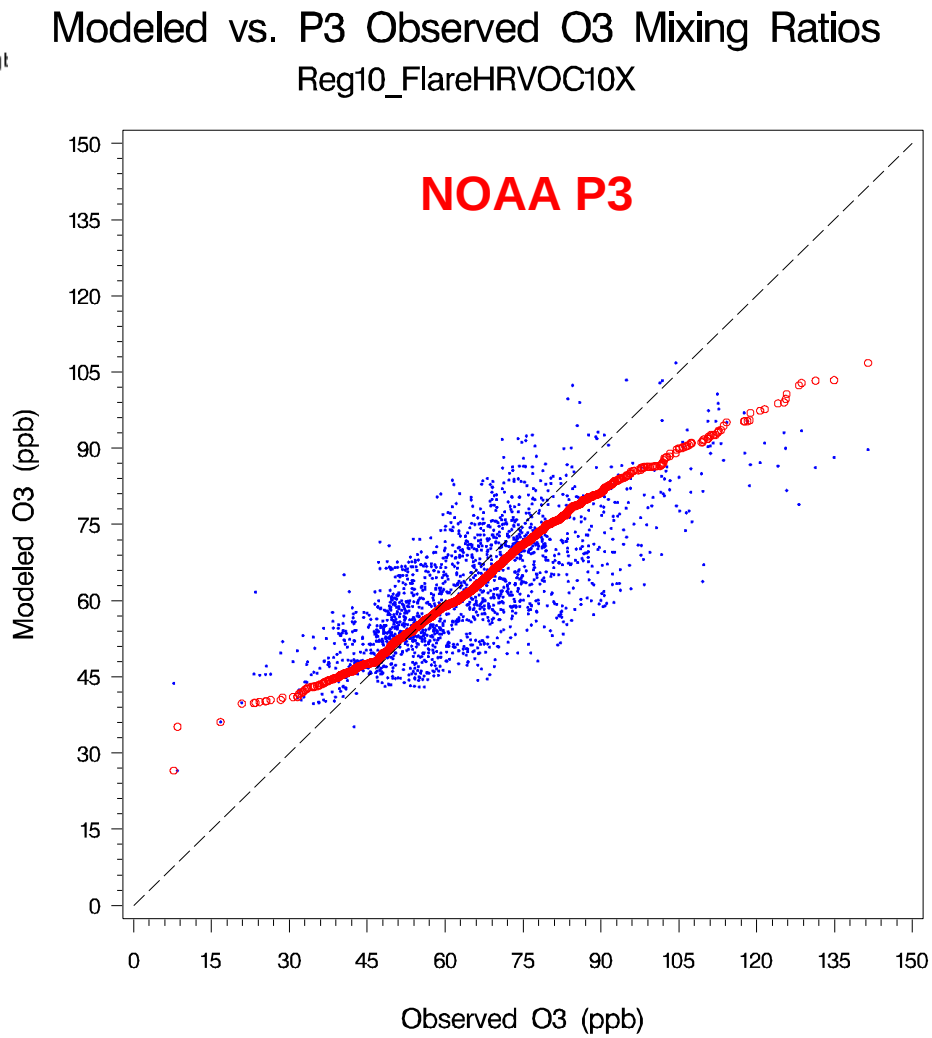




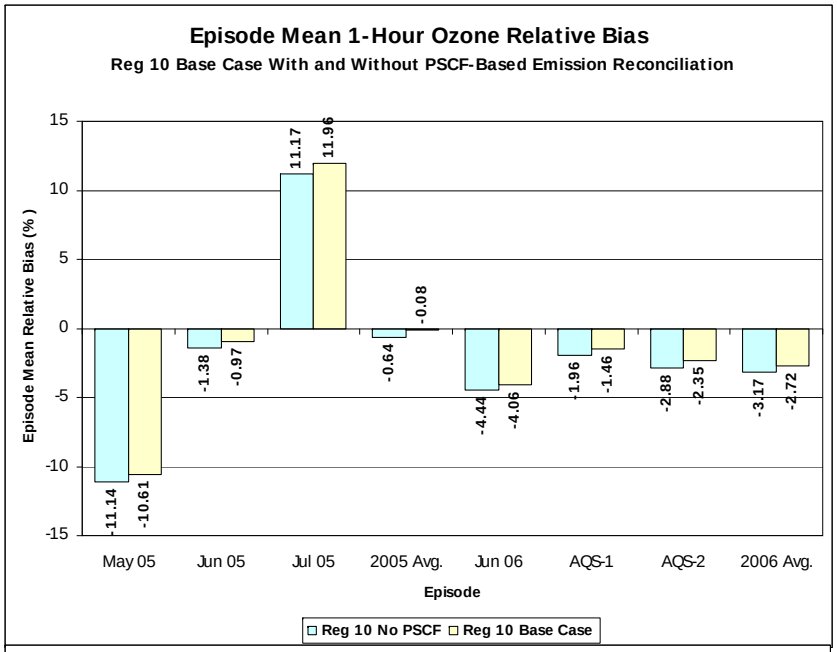
CAMx Ozone Model Performance

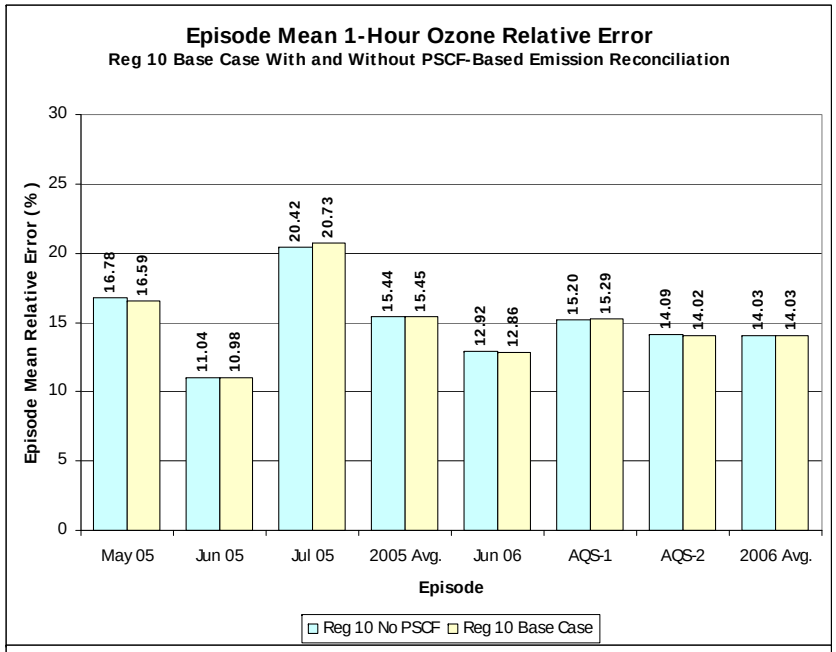
10X Flare HRVOC Sensitivity

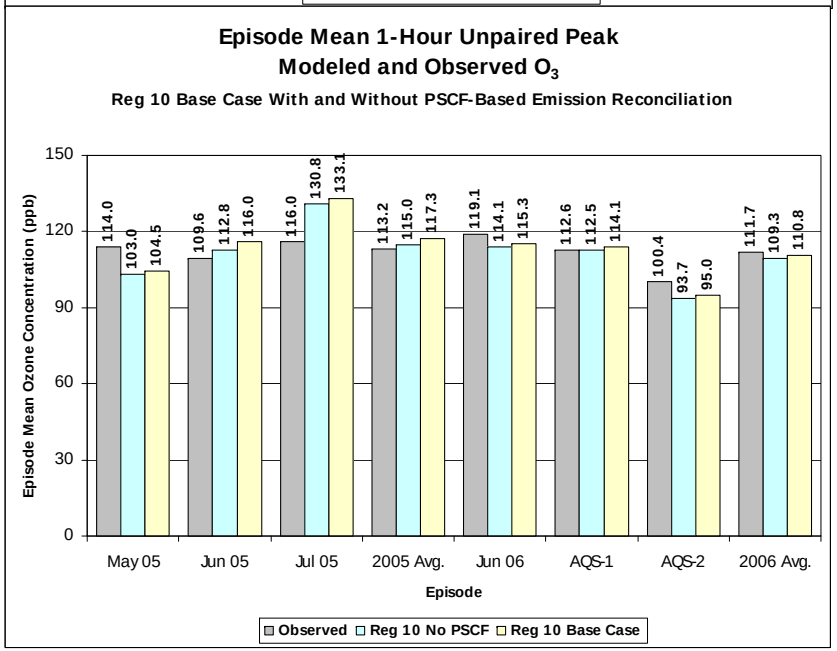


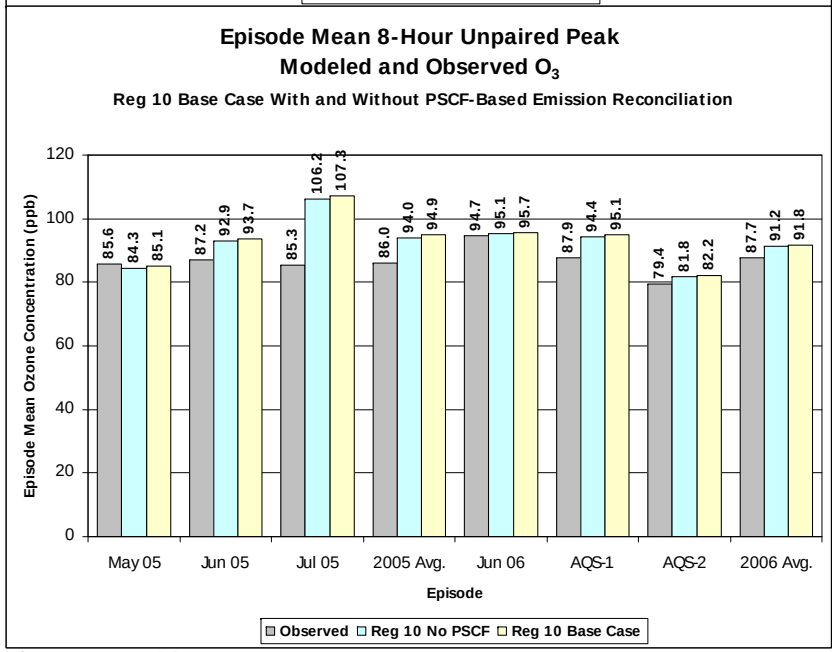


CAMx Ozone Model Performance Summary









Conclusions

- **PSCF-based emission reconciliation:**
  - **Improves the comparison between ISC-modeled HRVOC concentrations and observations.**
  - **Generally improves model performance at surface sites for OLE. Performance for ETH tends to improve for measured concentrations > 1 ppb. Slight improvement for IOLE.**
  - **Improves performance for P3-observed ETH, OLE, and IOLE, but large discrepancies remain.**
  - **Provides modest improvement for formaldehyde, and for ozone concentrations > about 75 ppb.**

Conclusions (Cont.)

- **Compared with the PSCF-based emission reconciliation, the 10X Flare HRVOC Sensitivity:**
  - **Improves performance for P3 observations of ETH, OLE, IOLE, FORM and O3**
  - **Shows better performance for surface FORM**
  - **In some cases improves ozone performance at the upper end of the concentration range, but also sometimes exacerbates over-prediction at lower concentrations**
  - **Causes significant over-predictions of ETH, OLE, and IOLE at surface sites**

Conclusions (Cont.)

- **Emissions reconciliation increases episode average one-hour daily peak ozone concentrations by 1.2 to 3.2 ppb.**

- **Emissions reconciliation increases episode average eight-hour daily peak ozone concentrations by 0.6 to 1.1 ppb.**

Issues

- **Why does the model still under-predict aircraft observations even after reconciliation?**
  - **Model may not be sufficiently mixing surface-level pollutants upwards**
  - **Additional emissions may need to be released above ground level (flares, cooling towers)**
- **Additional investigation is needed:**
  - **Parameterization of vertical mixing**
  - **Apply PSCF analysis to elevated sources**